Corrosion behaviour at advanced steam parameters in a biomass (co-) fired powerplant

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Dipl.-Ing., M.Eng. Eva Miller
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• Motivation
• Corrosion monitoring and theory
• Measurement campaign at PP Rodenhuize/Belgium:
  Max Green
• Measurement campaign at PP Fusina/Italy
• Overall Conclusions
Motivation

In order to reduce CO$_2$ emissions, save the natural sources and increase efficiency of coal-fired power plants investigations are on:

- Biomass (co-) combustion
- higher steam temperature
- „Super“ materials for heat exchangers

**Aim IFK:**
Detection of corrosion mechanisms of typical and new designed super heater materials at advanced steam temperatures
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Corrosion monitoring: equipment

- The used corrosion probes were developed and built at IFK.
- Temperature control for the samples up to 750°C.
- The temperatures are recorded continuously by data acquisition.
- Possibility to fix a variable number of sample rings of different material.
- Possibility to change the samples during measurement campaigns on-site.
- Exposure times are variable from a few hours up to several weeks.
- Sample rings are of established outer diameters.
Main corrosion mechanism

\[
M(s) + 1 \text{Cl}_2(\text{g}) \rightarrow M\text{Cl}_2(\text{s})
\]
\[
M(s) + 2\text{HCl}(\text{g}) \rightarrow M\text{Cl}_2(\text{g}) + \text{H}_2(\text{g})
\]

Under the depositions on the superheater pipes depletion of oxygen by oxygen wasting reactions is possible. In oxygen poor areas ferric oxides and chlorine are building ferric chlorides. At temperatures that are high enough (>400°C) ferric chlorides evaporate partially, diffuse through the deposit and become oxidized to ferric oxide by higher oxygen partial pressures. Elemental chlorine (\text{Cl}_2) comprises. This chlorine diffuses back to the metal surface, where it reacts again with the iron of the pipe material (figure 1 and 2)

[ Nielsen et al.; 1999]
Main corrosion mechanism

- To prevent Cl-corrosion:
- Sulfation: Transformation of alkali chlorides into sulfate salts (in gasphase oder or at particles):

  \[ 2\text{NaCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl} \]
  \[ 2\text{KCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCl} \]

- Sulfur provides as a corrosion regulating element
- Access of S reduces formation of KCl in the flue gas

Mechanisms of high temperature corrosion [Karl, 2006]
To identify the existing corrosion mechanisms SEM-EDX is the method of choice.

1. To get an overview of the materials the rings were cut dry into cross sections and embedded in a SEM adequate round form.
2. To complete the preparation all corrosion samples were grinded and polished with for each material appropriate abrasive papers and polishing cloths.
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Measurements Rodenhuize Max Green

• 100% wood combustion
## Fuel compositions

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Milled wood Pellets [%]</th>
<th>Parameter @ 550°C</th>
<th>Milled wood pellets [dry %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>4.90</td>
<td>Al₂O₃</td>
<td>5.6</td>
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<tr>
<td>Parameter</td>
<td>[dry %]</td>
<td>CaO</td>
<td>23.1</td>
</tr>
<tr>
<td>Ash</td>
<td>0.66</td>
<td>Fe₂O₃</td>
<td>3.06</td>
</tr>
<tr>
<td>Volatiles</td>
<td>81.0</td>
<td>K₂O</td>
<td>7.03</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>18.4</td>
<td>MgO</td>
<td>5.45</td>
</tr>
<tr>
<td>C</td>
<td>50.4</td>
<td>Na₂O</td>
<td>2.15</td>
</tr>
<tr>
<td>H&lt;sub&gt;fuel&lt;/sub&gt;</td>
<td>4.55</td>
<td>P₂O₅</td>
<td>1.83</td>
</tr>
<tr>
<td>N</td>
<td>n.d. &lt; 0.3</td>
<td>SiO₂</td>
<td>31.6</td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
<td>TiO₂</td>
<td>0.37</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt; 0.01</td>
<td>SO₃</td>
<td>0.43</td>
</tr>
<tr>
<td>LHV</td>
<td>18484 [kJ/kg]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Used materials - composition

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr [%]</th>
<th>Ni [%]</th>
<th>Fe [%]</th>
<th>Others [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>low</td>
<td>low</td>
<td>&gt;90</td>
<td>C, Mn, Cu</td>
</tr>
<tr>
<td>Ni-base</td>
<td>&gt;20</td>
<td>&gt;50</td>
<td>low</td>
<td>Mo, Si, Mn, Co, Al, Ti</td>
</tr>
</tbody>
</table>

→ **Ferrite**: a standard material designed for superheaters up to 500-550°C

→ **Ni-base**: has a high-temperature strength and oxidation resistance, also excellent resistance to a wide range of corrosive environment
Rodenhuize measurement campaign 2012
Max Green

Power Plant Rodenhuize

Measurement point **corrosion probe**
Super heater area
Exposure time: 90h
Flue gas 1100-1200°C

inside boiler
(general picture)

convective area
corrosion studies

burner area
Gas measurement

43 m

19 m

russels

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IFK - Temperature controlled corrosion probe
Results Rodenhuize Max Green

Corrosion probe: @ 42 meters, ~ 92 hours
Max Green - Ferrite – 550°C - 90h - windward

KCl-border
Fe-Oxide
(ca. 30 µm)

O, Ca, Si

100µm

semiquantitative SEM-EDX analyses
Max Green - Ferrite – 550°C - 90h - side

4 Fe-oxide
6 KCl

O, Ca, K, Si

Semiquantitative SEM-EDX analyses

300μm
Max Green – Ni-base – 660°C - 90h - side

semiquantitative SEM-EDX analyses

O, K, Ca

Cr-Oxide

Ni-Oxide
Max Green – Ni-base – 660°C - 90h - windward

molten

10 µm

Cl Ca
K Mg
Ni Cr Co Si
100% wood combustion

- Ferrite:
  - nice Oxide scale, about 30 µm
  - Loose particles
  - KCl-particles at material surface

- Ni-base:
  - Typical two layer oxide scale: below – Ni-oxide; above – Cr-oxide
  - Deposition: molten areas
  - K and Cl homogeneous distributed in deposition
Conclusions - Rodenhuize Max Green

• Both the Ni-based and the ferritic materials show Cl in the deposits at different temperatures
• Ongoing damaging of material or decrease of material thickness can be detected with longterm tests with some hundred hours in the wood fired boiler
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Measurement Fusina

5% RDF-Combustion
95% coal
Fusina measurement campaign

Measurement point corrosion probe
Super heater area
Exposure time: 72h
Flue gas 880°C
## Fusina - Used materials, composition

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cr [%]</th>
<th>Ni [%]</th>
<th>Fe [%]</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP347H</td>
<td>18.17</td>
<td>11.76</td>
<td>rest</td>
<td>Si=0.5; Mn=1.64; Nb+Ta=0.88</td>
</tr>
<tr>
<td>Super 304H</td>
<td>18.27</td>
<td>8.96</td>
<td>rest</td>
<td>Si=0.2; Mn=0.73; Cu=3.20; Nb=0.46</td>
</tr>
</tbody>
</table>

### Diagram

- **TP347H (535°C)**
- **Super304H (585°C)**
- **Super304H (660°C)**
Fusina – TP347H – 535°C - 72h - windward

- No damage/attack visible
- No chlorine detected
- No oxide scale builted

70µm
Fusina – Super 304H – 585°C - 72h – windward
Fusina – Super 304H – 660°C - 72h – windward

Little cracks visible
No chlorine detected
little oxide scale builded

Windward

535°C

660°C

Fe-/Cr- oxide
Conclusions Fusina

- Co-combustion up to 5%th shows no Cl in deposits an no Cl-corrosion at Super heater
- Loose, single particles on corrosion probe → slagging problems rather little
- Si-Al particles on all samples detected at all temperatures (due to alumina-silicatic coal)
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Overall conclusions

Increasing steam temperatures at (Co-) Combustion of biomass or fuels with high content of biomass is possible, if:

- new materials or base materials with coating that are designed for higher resistance against corrosion are used
- The common and typical ferritic materials are not useful no or not enough homogenous protecting oxide scale

For protecting the superheater materials it's important:
- to have a constant firing system and avoid fluctuating temperatures
- to get a primary protecting oxide layer before Biomass (co-)combustion with high S- and Cl-contents
- Additivs (solid/liquid) for catching alkalis to prevent KCl or NaCl or to support sulphation
- At advanced steam temperatures alkali getter without S is to prefer, because of possible S-corrosion at temperatures >600°C → e.g. Al-Si rich minerals
Literature

- Karl J. (2006). Dezentrale Energiesysteme, Oldenbourg Verlag
- Sorell G. The Role of Chlorine in High Temperature Corrosion in Waste to Energy Plants; Materials at High Temperatures, Volume 14, Number 3, 1997