Biomass combustion and boiler corrosion: State of the art knowledge and solutions

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TUT energy seminar: bioenergy
Sonja Enestam
Contents

- Fuels and challenges
- Corrosion types in FB boilers
- Corrosion mechanisms
- Solutions
The trend: From coal and peat to biofuels and recycled fuels
The fuel dilemma

- **Fossil**
  - Hard coal

- **Wood biomass**
  - Northern wood
  - Pulp & Paper sludges
  - Wood pellets

- **Fast growing wood**
  - Willow
  - Eucalyptus

- **Agro biomass**
  - Straw
  - Sunflower hulls
  - Corn Stover
  - Miscanthus

- **Recycled fuels**
  - Packaging waste
  - Recycled wood
Fuel related challenges

- Fuel feeding
- Agglomeration
- Slagging & Fouling
- Corrosion
- Ash quality
- Emissions
The influence of corrosion on boiler technology and plant efficiency

- Final steam temperature and pressure → Efficiency
- Change of material → Price
- Fuel mixture Boiler availability → Economy
- Superheater placement → Design

S. Enestam
High temperature corrosion in bio- and waste combustion

Heavy metal induced corrosion of cooler heat exchanger surfaces such as primary superheater and furnace walls ➢ Waste combustion

Alkali chloride induced corrosion of the hottest superheaters ➢ Bio fuel and waste combustion

Caused by impurities in the fuel, typically:

- Potassium and chlorine in biofuels
- Potassium, sodium, heavy metals in combustion of waste derived fuels

The metal loss can be greatly increased by a combination of corrosion and erosion, e.g. in the second draft in a BFB boiler or in the furnace of a CFB boiler burning bio fuel or waste.
Corrosion management – the Valmet approach

Detailed understanding of the physical and chemical phenomena involved in the corrosion process enables smart solutions and optimized corrosion control.

Transportation of corrosive compounds to the tube surface

Furnace reactions, formation of corrosive compounds

The corrosivity of the environment surrounding heat exchanger tubes
- Flue gas temperature and composition
- Composition and corrosivity of fly ash and deposits

Corrosion mechanisms
Corrosion resistance of different steel grades

➢ State of the art knowledge achieved through long term corrosion research including cooperation with universities, research institutes, customers and steel suppliers worldwide

➢ Continuous development process in order to be able to provide the best solutions for our customers
The influence of fuel composition on corrosion

Corrosive environment
Low melting ash

Corrosion
Fouling
Slagging
Bed sintering
## Typical analyses of different types of fuels

*Elements influencing on corrosion*

<table>
<thead>
<tr>
<th></th>
<th>Peat</th>
<th>Wood chips</th>
<th>Bark</th>
<th>Demolition wood</th>
<th>SRF</th>
<th>AGRO Straw, Barley</th>
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<tbody>
<tr>
<td>S [mg/kg ds]</td>
<td>0.2</td>
<td>0.04</td>
<td>0.05</td>
<td>0.07</td>
<td>0.5</td>
<td>0.08</td>
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<tr>
<td>Cl [mg/kg ds]</td>
<td>0.04</td>
<td>0.01</td>
<td>0.07</td>
<td>0.07</td>
<td>0.7</td>
<td>0.3</td>
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<tr>
<td>Na [mg/kg ds]</td>
<td>580</td>
<td>160</td>
<td>380</td>
<td>850</td>
<td>7800</td>
<td>240</td>
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<tr>
<td>K [mg/kg ds]</td>
<td>850</td>
<td>850</td>
<td>1700</td>
<td>850</td>
<td>4800</td>
<td>12000</td>
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<tr>
<td>Pb [mg/kg ds]</td>
<td>8</td>
<td>&lt;5</td>
<td>10</td>
<td>150</td>
<td>50</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Zn [mg/kg ds]</td>
<td>30</td>
<td>35</td>
<td>1600</td>
<td>1800</td>
<td>400</td>
<td>35</td>
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</table>
Corrosion mechanism

1. Corrosive chlorides are formed in the combustion process
   - KCl in biomass combustion
   - KCl, NaCl, PbCl$_2$, ZnCl$_2$ in waste combustion

2. The corrosive chlorides condense on cooled heat exchanger surfaces
   - Corrosive deposits
   - Deposits with low melting points

3. The chlorine in the deposits react with the tube forming volatile metal chlorides, hence consuming the tube wall
Pb-induced corrosion

Corrosion probe, $T_{fg} \sim 800^\circ C$ and $T_{mat} \sim 360^\circ C$, low-alloy material

$K_2PbCl_4$

$KPb_2Cl_5$

<table>
<thead>
<tr>
<th>Analysis point</th>
<th>O [at-%]</th>
<th>Cl</th>
<th>K</th>
<th>Pb</th>
<th>Fe</th>
<th>Na</th>
<th>Ca</th>
<th>Si</th>
<th>Others</th>
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<tr>
<td>1</td>
<td>65.13</td>
<td>3.33</td>
<td>1.52</td>
<td>1.18</td>
<td>1.22</td>
<td>9.73</td>
<td>11.42</td>
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<tr>
<td>2</td>
<td>54.08</td>
<td>12.06</td>
<td>3.99</td>
<td>2.53</td>
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<td>2.94</td>
<td>2.64</td>
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<td>3</td>
<td>60.53</td>
<td>22.34</td>
<td>12.44</td>
<td>4.68</td>
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<td>4</td>
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</table>
Corrosion control

The corrosion rate is influenced by:

- The corrosivity of the environment
  - Flue gas temperature
  - Flue gas composition
  - Deposit composition

- Material temperature

- Material grade

The corrosion rate can be decreased by influencing on one or more of the above. However, efficient corrosion control requires understanding of the phenomena and mechanisms leading to corrosion.
Corrosion -> solutions

1. Superheater material and coatings
2. Steam temperature
3. Tube shields – most corrosive locations
4. Superheater location
5. Superheater design
6. Fuel mixture: Co-firing or additives
7. Gasification
Superheaters
## Typical boiler materials

<table>
<thead>
<tr>
<th>Grade</th>
<th>Category</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Others</th>
<th>Relative price&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Typical use (boiler part)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P265GH</td>
<td>Non-alloy</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>Eco, furnace, boiler bank</td>
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<tr>
<td>16Mo3</td>
<td>Low alloy</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>Furnace, boiler bank</td>
</tr>
<tr>
<td>13CrMo44</td>
<td>Low alloy</td>
<td>1</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>1.8</td>
<td>Superheaters</td>
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<tr>
<td>10CrMo9-10</td>
<td>Low alloy</td>
<td>2.25</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>2.3</td>
<td>Superheaters</td>
</tr>
<tr>
<td>X10CrMoVNb9-1</td>
<td>High alloy ferritic</td>
<td>9</td>
<td>1</td>
<td>-</td>
<td>V, Nb</td>
<td>5.4</td>
<td>Superheaters</td>
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<tr>
<td>AISI 347</td>
<td>Standard stainless steel</td>
<td>19</td>
<td>-</td>
<td>10</td>
<td>Nb</td>
<td>6.7</td>
<td>Superheaters</td>
</tr>
<tr>
<td>AISI 310 (Mod&lt;sup&gt;c&lt;/sup&gt;)</td>
<td>High Cr stainless steel</td>
<td>25</td>
<td>-</td>
<td>21</td>
<td>N, Nb</td>
<td>10.0</td>
<td>Superheaters</td>
</tr>
</tbody>
</table>

<sup>a</sup> May 2011  
<sup>c</sup> Modified with Nb
HYBEX boiler
Bubbling Fluidized Bed (BFB) technology

Kymin Voima,
Kuusankoski,
Finland

Steam  269 MW$_{th}$
107 kg/s
114 bar
541 °C

Fuels  Bark, forest residue,
       sludge, peat, gas, oil

Start-up  2002
HYBEX boiler
Bubbling Fluidized Bed (BFB) technology

Furnace:
• Width 12 m
• Depth 11 m
• Height 36 m

Furnace membrane tubes 26 km
Superheater tubes 35 km
Economizer tubes 15 km
Connection tubes 2 km
Weight of pressure parts 1600 ton
Furnace wall corrosion and overlay welding

Typical problem in boilers burning waste and waste wood

=> Low alloy base material overlay welded with Ni-based alloy

![Furnace wall corrosion and overlay welding](image-url)
Superheater location

Reduced concentration of gaseous, corrosive chloride in the vicinity of tube surfaces
Superheater design

Reduce probability of contact between tube surface and corrosive chlorides

Double tube superheater design

=> Reduced condensation of corrosive compounds

Target surface temperature is determined by the environment (fuels, flue gas temperature, steam temperature,...)

Surface temperature is achieved by controlling the tube heat transfer characteristics with additional, coaxial layers

Single tube design
Life length < 1 year

Double tube design
Life length > 3 years
Comparison of deposit compositions (XRF)
Ways to minimize corrosion
Modification of the combustion environment

• Additives
  ➢ Sulphur
  ➢ Aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$
  ➢ Ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$
  ➢ Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$

• Co-combustion
  ➢ Peat
  ➢ Coal
  ➢ Sludge
Corrosion management by sulphur addition

CorroStop Additives

- The sulphate eliminates alkali chlorides in the gas phase and attaches to superheater surfaces forming a protective coat and neutralize the effects of alkali chloride in the process.

- Sulfate decomposes at high temperature:
  \[ \text{Fe}_2(\text{SO}_4)_3 \rightarrow 2 \text{Fe}^{3+} + 3 \text{SO}_4^{2-} \]

- Alkali chloride reacts with sulfur trioxide or dioxide:
  \[ 2\text{MCl(g,c)} + \text{SO}_3(g) + \text{H}_2\text{O (g)} \rightarrow \text{M}_2\text{SO}_4(g,c) + 2 \text{HCl (g)} \]
  \[ 2\text{MCl(g,c)} + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O (g)} \rightarrow \text{M}_2\text{SO}_4(g,c) + 2 \text{HCl (g)} \]
  where \( M \) is Na or K.

Slow down corrosion of superheaters
Fuel mixture - additive

Valmet corrosion management

Corrored Analyzer

• On-line sampling and analysis of the corrosivity of the flue gas
• Provides information for fuel blend and additive control

CorroStop Additives

• CorroStop™ – liquid solution
  Aluminiumsulfate \( \text{Al}_2(\text{SO}_4)_3 \) or Ferric sulfate \( \text{Fe}_2(\text{SO}_4)_3 \)
  15-30 % liquid solutions
  Spraying through nozzles before superheaters

• CorroStop+™ – elementary sulphur
  Sulphur content > 95 %
  0,5 – 3,2 mm granulates
  Addition to fuel feeding screws
Gasification
Recycled waste gasification plant for Lahti Energia Oy

➔ Metso delivery: waste gasification process, gas boiler, flue gas cleaning system with auxiliary and automation systems

➔ 2 gasification lines: 50 MW of electricity and 90 MW of district heat

➔ High-efficiency (gas boiler 121 bar, 540 C) conversion of recycled waste to energy and reduction of fossil fuels

➔ Waste is turned into combustible gas, which is cooled, cleaned and combusted in a high-efficiency gas boiler to produce steam for a steam turbine
Fuel based CYMIC concepts

Fossil
- Coal
- Coal rejects
- Pet coke
- Portion of SRF

Bio/Multi
- Biomass
- Coal
- Portion of SRF

Recycled Wood

Solid Recovered Fuel (SRF)
- Multifuel

- 50–1200 MW<sub>th</sub>
- Max 565 °C
- 175 bar

- 50–900 MW<sub>th</sub>
- Max 565 °C
- 175 bar

- 50–250 MW<sub>th</sub>
- Max 540 °C
- 90 bar

- 50–200 MW<sub>th</sub>
- Max 480 °C / 70 bar
- 520 °C / 90 bar