Material research with focus of Vattenfalls oxyfuel pilot plant

3rd Oxyfuel Combustion Conference

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Overview

1. Introduction
2. Vattenfalls material tests at OxPP
3. Test panel analysis from the OxPP boiler
4. OxyCorr project
5. Conclusion
Introduction
### Measurements in dry gas after ESP

<table>
<thead>
<tr>
<th></th>
<th>CO₂ Vol%</th>
<th>O₂ Vol%</th>
<th>CO mg/Nm³</th>
<th>SO₂ mg/Nm³</th>
<th>NOₓ mg/Nm³</th>
<th>H₂O Vol. % in flue gas</th>
<th>Fly-ash SO₃ mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-firing</td>
<td>13</td>
<td>6</td>
<td>7</td>
<td>1600</td>
<td>300</td>
<td>8</td>
<td>46 + 9</td>
</tr>
<tr>
<td>Oxyfuel</td>
<td>95</td>
<td>6.8</td>
<td>2.5</td>
<td>7000</td>
<td>1600</td>
<td>30</td>
<td>77 + 18</td>
</tr>
</tbody>
</table>
Material tests at Vattenfalls 30MWth Oxyfuel Pilot Plant in Schwarze Pumpe
Purpose and Questions

- Super heater at 580°C, 650°C and 720°C
- Economisers, Water walls
- Low temperature corrosion (70 – 170°C)
- Analysis of deposits formed on super heaters (ash formation)
- ESP, FGD, FGC, recirculation duct, etc
- Identify differences between conventional coal firing and oxyfuel firing
- Different types of probes
- Various burner
- Variation of coal quality (moisture, sulphur content, particle size)
Materials, flue gas composition and fly ash

Materials:
Ferritic, Martensitic, Austenitic and Nickel-base alloys
Examples:
10CrMo910, 13CrMo44, 15Mo3, Super304H, T23, T92, X20, Inconel625, Alloy617, Alloy740, KanthalAPMT, 253MA 347HFG, Sanicro25, VM12, HR3C, AC66
... and so on

Flue gas measurements after ESP (wet) for Oxyfuel
• CO₂ ~ 65% and O₂ < 4 %
• SO₂ ~ 7000mg/m³ (Air ~ 1600mg/m³)
• H₂O ~ 27-29% (Air ~ 8%)
• CO < 200 mg/Nm³, NOₓ < 500 mg/Nm³
• SO₃ in fly ash
  - Air SO₃ 46 ± 9 (mg/kg)
  - Oxyfuel SO₃ 77 ± 18 (mg/kg)
• Otherwise ash composition is similar
• Corrosive species SO₂ and H₂O approx 4 times greater in oxyfuel.
Low temperature gradient probe

Corrosion probes after exposure in plant

SAF2101 at Level 12 (3rd Draft)

15Mo3 at Level 13 (3rd Draft)
Summary on material tests

- Deposit composition and corrosion attack on the high temperature components were similar in both oxyfuel and air firing mode.
- Indication of higher material wastage rate in OxyFuel
- The temperature range where low temperature components are susceptible to corrosion has increased due to oxyfuel firing probably due to increased susceptibility to SO3 dewpoint corrosion.
- There may be more ash deposition in the oxyfuel mode.

Additional observations with some materials
- Increased S-concentration in corrosion front
- Ni-based alloys may form non-protective NiO
- (Cu - containing alloys may form non-protective Cu-crystallites)
- Al-containing materials may form protective oxide (Al2O3) and is not getting carburised
- Super austenitic stainless steels (30%Fe, 30%Ni, 30%Cr) forms protective oxide
Test panel at OxPP
Wall material P235GH (1.0345) with joints made of S235JRG2 (1.0038)
4 part where send to Alstom, BAM, FZJ and VPC
Panel analysis

Air combustion: 3847.5 h
Oxyfuel combustion: 8789.0 h

Steam parameter: 235°C
30.7 bar

- thin irregular corrosion layer
- some corrosion at HAZ
- isolated corrosion craters at inside and outside
OxyCorr - High temperature corrosion test under lignite oxyfuel firing
OxyCorr Project 2009 - 2012

University of Stuttgart, Institute of Combustion and Power Plant Technology (IFK)  
Swerea KIMAB AB  
Outokumpu Stainless AB, Avesta Research Centre

Vattenfall Research & Development AB  
Alstom Power Systems GmbH, Stuttgart  
ENEL PRODUZIONE SpA, Area Tecnica Ricera

WP 1: Mechanistic study on material corrosion in an oxy-coal fired flue gas environment:  
- Material manufacture  
- Long-term hot/cold corrosion tests  
- Parametric study on Cl behaviour

WP 2: Deposit and material testing in technical scale test facilities:  
- Determination of corrosive species  
- FA and deposit  
- Condensate  
- Gas composition in hot and cold zones  
- Material exposures in hot and cold zones

WP 3: Impact of oxy-fuel process on the ash characteristics and its usability:  
- Role and impact of fly ash on deposit formation, material corrosion and ESP performance  
- Characterization of fly ashes according to utilisation requirements

WP 4: Evaluation and assessment of results - implications for full scale plants

IFKs KSVA (500 kWth)  
ENELs Fosper (5 MWth)
### Lignite used in test campaigns & Flue gas composition

LaTBK-S and LaTBK-SS lignite were used for material tests:
- Rich in sulfur and alumino-silicatic character.
- Higher volatile content at “waf” basis.
- different ash content

**FG composition, combustion chamber:**
0,3 MW with approx. 60 % recirculation rate

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>LaTBK</th>
<th>LaTBK-S</th>
<th>LaTBK-S+</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>% raw</td>
<td>9,8</td>
<td>10,15</td>
</tr>
<tr>
<td>Volatiles</td>
<td>% waf</td>
<td>57,39</td>
<td>56,98</td>
</tr>
<tr>
<td>Ash</td>
<td>% wf</td>
<td>5,57</td>
<td>18,64</td>
</tr>
<tr>
<td>Fixed C</td>
<td>% waf</td>
<td>42,61</td>
<td>43,02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>LaTBK</th>
<th>LaTBK-S</th>
<th>LaTBK-S+</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>% waf</td>
<td>66,45</td>
<td>67,99</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>% waf</td>
<td>4,75</td>
<td>5,33</td>
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<tr>
<td>N</td>
<td>% waf</td>
<td>0,66</td>
<td>0,73</td>
</tr>
<tr>
<td>S</td>
<td>% waf</td>
<td>0,56</td>
<td>2,31</td>
</tr>
<tr>
<td>O</td>
<td>% waf</td>
<td>27,58</td>
<td>23,65</td>
</tr>
<tr>
<td>Cl</td>
<td>% waf</td>
<td>---</td>
<td>&lt; 0,02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Main Elements</th>
<th>LaTBK</th>
<th>LaTBK-S</th>
<th>LaTBK-S+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>% wf</td>
<td>3,71</td>
<td>5,95</td>
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<tr>
<td>CaO</td>
<td>% wf</td>
<td>26,6</td>
<td>8,43</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>% wf</td>
<td>24,1</td>
<td>8,1</td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>% wf</td>
<td>0,63</td>
<td>0,98</td>
</tr>
<tr>
<td>MgO</td>
<td>% wf</td>
<td>8,65</td>
<td>2,4</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>% wf</td>
<td>0,13</td>
<td>0,19</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>% wf</td>
<td>0,01</td>
<td>0,08</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>% wf</td>
<td>12,5</td>
<td>48,7</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>% wf</td>
<td>0,15</td>
<td>0,44</td>
</tr>
<tr>
<td>SO\textsubscript{3}</td>
<td>% wf</td>
<td>18,3</td>
<td>9,34</td>
</tr>
</tbody>
</table>

### Heating Value

<table>
<thead>
<tr>
<th>Heating Value</th>
<th>LaTBK</th>
<th>LaTBK-S</th>
<th>LaTBK-S+</th>
</tr>
</thead>
<tbody>
<tr>
<td>HHV</td>
<td>J/g, raw</td>
<td>22,279</td>
<td>19,424</td>
</tr>
<tr>
<td>LHV</td>
<td>J/g, raw</td>
<td>21,163</td>
<td>18,078</td>
</tr>
</tbody>
</table>

LaTBK-S lignite_ Corrosive species in the FG ducts:
H\textsubscript{2}CO\textsubscript{3} = 60 mg/m\textsubscript{N}\textsuperscript{3}; SO\textsubscript{3} = 100 mg/m\textsubscript{N}\textsuperscript{3}
Test campaign conditions for material tests

Test 1 - Nov 2010:
72h exposure time
one probe 580 C material temperature exposed at 750 C flue gas temperature
one probe 650 C material temperature exposed at 1050 C flue gas temperature
one set of pre-exposed samples were further tested in a lab furnace at their respective material temperature

Test 2 - Nov 2011:
38h exposure at
two probes at 480 C material temperature exposed at 1200 C flue gas
HTC - Probe samples from Test 1

Direct analysis after Test 1 (72h exposure)

- F (310 650 C)
- P (304 650 C)
- C (304 580 C)
- B (T92 580 C)
- G (617 650 C)
- L (310 580 C)
- M (617 580 C)

Analysis after Test 1 (72h) and lab exposure (928h)

- A (T92 580 C)
- D (304 580 C)
- E (310 650 C)
- H (617 650 C)
- K (310 580 C)
- N (617 580 C)
- O (304 650 C)

(T92 - 580 C)

- A
- B

(304 - 580 C)

- C
- D

(310 - 650 C)

- E
- F

(617 - 650 C)

- G
- H

(Alloys - planned temperature)

- K
- L

- M
- N

- O
- P
304 at 580°C and 650°C

Test 1

Sample C (304 A580)

Sample P (304 A650)

Test 1 + Lab

Sample D (304, L580)

Sample O (304, L650)
304 - 580°C (Sample C and D)

Sample C - A580

Sample D - L580
304 - 650°C (Sample P and O)

Sample P - A650

Sample O - L650
• Corrosion as expected more for low alloyed steel T92 and less for high alloyed austenitics
• However it seems that alloy 617 could be susceptible to more attack.
• Steel with higher Cr content for 580C
• Stainless steels form protective oxide layer at 650 which appears to be affected by prolonged exposure
• Stainless steels more effective at 650 than 580