Fireside corrosion under oxyfuel combustion conditions

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• Background

• Experience from pilot plants

• Fireside corrosion lab testing

• Conclusions
Problem statement

• Fireside corrosion risk evaluation when introducing oxy-fuel firing in comparison to air-firing
  – Three scenarios to compare as gas composition is changing for different recycling schemes:
    • Air: Baseline
    • Oxy with recirculation w/o cleaning: $SO_X$ & Cl-contents increase by a factor of 3-4
    • Oxy with recirculation w/ cleaning (FGD): $SO_X$ & Cl-contents are slightly higher level to air-firing

• Fireside corrosion risk evaluation for hottest sections
  – In Ultra Supercritical (USC) boilers for retrofit applications for standard materials: martensitic steels, austenitic steels
  – in Advanced Ultra Supercritical (A-USC) for new plants: use of Ni-base alloys with or without coatings at hottest location
Approach: Corrosion risk evaluation

- Understanding of gas and coal ash compositions in the different operation schemes from pilot plants
- Thermodynamic modelling of gas and ash to determine lab testing conditions
- Lab testing to gain understanding of fireside corrosion mechanisms

⇒ Detailed corrosion risk evaluation for A-USC and USC boilers
Basis for evaluation: facilities

- Measurement of flue gas and ash composition has been made on mainly two pilot plants in air and oxy-mode:
  - Boiler Simulation Facility (BSF), Windsor, CT, 15MW$_{th}$:
    - Subbituminous coal (PRB), Low S Bituminous coal, High S Illinois Bituminous coal, North Dakota Lignite, Schwarze Pumpe Lignite
    - With and without cleaning in flue gas recirculation loop
  - ‘Schwarze Pumpe’, Germany, 30MW$_{th}$:
    - German Lignite:
      - No cleaning in recirculation loop
Gas compositions

- Detailed measurement of gas compositions at BSF for different conditions, air vs. oxy for different coal:
  - $\text{SO}_2$ to $\text{SO}_3$ conversion rate is comparable for air and oxy-firing [1, 2]
  - Absolute $\text{SO}_X$-content in flue gas was higher in oxy-fuel firing as the flue gas recirculation stream is not cleaned [1, 2]
  - $\text{SO}_2$ to $\text{SO}_3$ conversion rate seems to be influenced mainly by residence time and not by the absolute $\text{SO}_X$-level in the flue gas
- CO levels:
  - Increased for sub-bituminous coal & Lignite in oxy-mode
  - Comparable between air- & oxy-firing for bituminous coal
  - $\text{NO}_X$ (lb/ Mbtu or kg/ MWh) is lower in oxy-firing than air [1]

Thermodynamic modeling of the gas composition

SO₂ / SO₃-content for North Dakota Lignite

- Modelled gas composition matches well the values from BSF in oxy and air-firing

<table>
<thead>
<tr>
<th>Gas composition at 1000°C</th>
<th>#83A Air-firing</th>
<th>#98A Oxy-firing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BSF</td>
<td>Model</td>
</tr>
<tr>
<td>O₂</td>
<td>2.74</td>
<td>2.77</td>
</tr>
<tr>
<td>CO₂</td>
<td>14.86</td>
<td>14.78</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.34</td>
<td>11.85</td>
</tr>
<tr>
<td>N₂</td>
<td>71.97</td>
<td>70.05</td>
</tr>
<tr>
<td>SOₓ (Total)</td>
<td>0.087</td>
<td>0.084</td>
</tr>
</tbody>
</table>

- Modelled SO₂ / SO₃-conversion predicts to high SO₃-contents
  - Measured SO₃-content in all tests was below 3% of total SOₓ
  - SO₂→SO₃ conversion is kinetically hindered
  - Measured SO₃-content corresponds to the equilibrium content in the temperature range 950-1050°C
Ash composition in pilot plants

- Ash measurement from 15MWth oxy-pilot (BSF) with North Dakota lignite: no S capture in recirculation loop

- Ash samples from 30MWth Schwarze Pumpe with German (Lausatian) lignite from air- and oxy-firing: show comparable X-ray diffraction spectrum (= mineral composition)

Ash composition similar with higher \( \text{SO}_3 \)-content when no S is captured in recirculation loop
Basis for evaluation: Ash composition (Air vs. Oxy)

- General conclusions on ash composition in pilot plants (BSF & Schwarze Pumpe):
  - Ash in general similar between oxy & air
    - SO$_3$-content in ash is higher in oxy due to higher SO$_X$-content in flue gas of a factor ~3
    - No increased C-content in ash in oxy-mode
    - No detection of carbonates in ash

- Measurements from BSF on North Dakota Lignite were used to validate thermodynamic model of ash composition
Ash composition: Air vs. Oxy-firing

Thermodynamic model of ash composition

• Thermodynamic modelling for ash composition done for North Dakota Lignite
  – Model of ash composition is possible
  – Ash model confirmed by pilot plant operation:
    • Ash in general similar between oxy & air
    • $\text{SO}_3$-content in ash depending on $\text{SO}_x$-content in gas, hence recirculation scheme
  – Ash model will be extended to other ashes
Fireside corrosion testing at Alstom

• Samples:
  – Cut tube sections
  – Surface finish as received
  – Lower 2/3 of sample coated with ash

• Ash applied as slurry (addition of Methyl Cellulose) with a brush
  – Synthetic ashes:
    • Mixed in lab
    • 2.5wt% C as Charcoal was added to the ash
    • Ashes from pilots

• Gases:
  – No catalyst used for $\text{SO}_2 / \text{SO}_3$-equilibrium
  – $\text{SO}_x$ introduced as $\text{SO}_2$ in gas mixture

Total Metal Loss
= Metal recession + internal attack
Testing for German Lignite (I)

Alstom testing series w/ fly ash (2008-2010) [3, 4]

- 3 ashes from 0.5MW_th (IFK Stuttgart, low S & high S Lignite) & 3MW_th (Enel, Hard coal) pilots
- Effect of ash composition is small for 9% Cr steels
- Only slight difference between high S and low S at 580 C
- Small tendency for lower attack after 1000h for low S (0.08%) vs. high S (0.21%)
- High Cr Austenitics show low metal wastages at 580 C & 650 C

[4] work was performed in the frame of the OxyCorr Project, partly funded by the RFCS Research Program of the European Commission (RFCR-CT-2009-00005)
Testing for German Lignite (II)

Alstom internal testing series w/ synthetic ash (2008-10)

- 600 C & 700 C up to 4 month of testing w/ high SO\(_3\)-content in ash
- Only high Cr (21-25%) austenitic steels exhibit good corrosion resistance
- Ni-base alloys show high corrosion attack for high S-conditions (localised and / or along grain boundaries) [5, 6]

- Same tendency at 700 C

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Gas: 32% H\(_2\)O, 1.9% O\(_2\) 0.45%SO\(_2\), CO\(_2\) Bal.

CCA617, 700°C, 3066h
Alloy 740, 700 C, 3066h

Sulphides
Oxides
Alstom testing series w/ synthetic ash (2010-13) partially funded by DOE

- Goal: Separation of parameters: oxy vs. air, S-level, HCl-level, ash composition
  - At 650 °C: slightly higher attack in oxy-firing than air-firing for same S- and Cl-content
  - Higher alloyed materials (austenitic steels & Ni-base) showed only small corrosion attack, hence no discrimination possible after 3000h
- Low SO₃-content in ash & Low SO₂-content in gas

Air: 10% H₂O, 3.0% O₂ 0.2%SO₂, 0.02 Cl, CO₂ 15%, N₂ 71.3%
Oxy: 25% H₂O, 3.6% O₂ 0.2%SO₂, 0.02 Cl, CO₂ 64%, N₂ 7.6%

Ferritic steels: slightly higher attack for oxy- than air-firing
Testing for US Eastern Coal (I)

Alstom testing series w/ synthetic ash (2010-13) partially funded by DOE

- Testing done for US eastern coal: to separate parameters, e.g. oxy vs. air, S-level, HCl-level, ash composition
  - 600 °C: significant less corrosion attack than at 650 °C
  - Effect of temperature seems to be have a stronger effect than differences in CO₂, H₂O- levels (oxy vs. air)

Medium S, low Cl:
- 10% H₂O, 3.0% O₂, 0.2%SO₂, 0.01 Cl, 15% CO₂, 71.3% N₂

Low S, high Cl:
- 10% H₂O, 3.6% O₂, 0.08%SO₂, 0.03 Cl, 15% CO₂, 71.3%, N₂

Level of corrosive elements flue gas (S, Cl) seems to be crucial
Corrosion probes from ‘Schwarze Pumpe’

- Corrosion probes from air & oxy-firing of German Lignite
- Localised corrosion on high-alloyed steel & Ni-base (650 C, Oxyfuel):
  - Non-uniform attack
  - Some pits close to ash deposits
  - S- Phases in the corrosion pit close to metal interface
- T92 showed more uniform corrosion at 580 & 650 C
Conclusions: Air vs. oxy

• Good understanding of ash & gas composition in air- and oxy-fuel firing
  - SO$_2$/SO$_3$-conversion rate is comparable for both conditions
  - Ash composition similar: can have an increased SO$_3$-content, if flue gas recirculation is without cleaning in oxy-mode

• S- and Cl-content as well as the Alkali-content is crucial for corrosion rate

• Only a few experiments are available to compare air vs. oxy (w/ cleaning) vs. oxy (w/o cleaning) for the same coal

• Oxy w/o cleaning: severe increased metal wastage expected

• Oxy w/ cleaning: slightly higher attack than for air-firing expected

Oxy w/ cleaning in recirculation loop is preferred scheme to stay within experience range
Conclusions (USC vs. A-USC)

- Ni-base alloys show a tendency for localised corrosion and attack along grain boundaries
  - Effect enhanced for high S-conditions: sulfidation along grain boundaries (617) & in the grains (740)
  - Alloy 740 exhibits grain boundary attack also by oxidation
- Detailed oxidation model might be required (steam-side) for estimation of metal wastage
- Fireside corrosion database (lab & steam loop) is small for higher temperatures (T>650°C) and longer times (>3'000h) for both, air- and oxy-firing
Next steps

• Detailed investigation of Barry steam loop starting Autumn 2014 for high-alloyed materials at higher temperatures (T= 1200-1500 F / 650-815 C, Steam) expected to reach >15’000h
  – Investigation of corrosion morphology and products
  – Better understanding of mechanism over temperature (bell-shaped curve, temperature with maximum corrosion attack)
  – Comparison to lab-generated testing results with respect to
    • Materials ranking of corrosion resistance
    • Corrosion morphology / products

• Long term operation and evaluation of material performance in large-scale plant (e.g. USC-boiler in White Rose 426MWₑ) will be collected to confirm lab / pilot plant results
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