4th Meeting of the Oxy-Corrosion Working Group

Joint Workshops of the Oxy-Cap UK Programme & IEAGHG Oxy-Corrosion Working Group
Imperial College London
London, UK
17th-19th June 2014
Past OCC events and workshops
OCC1, Cottbus 2009

Anders Hjörnhede
Melanie Montgomery
Martin Bjurman
Alexander Gerhardt
Nicklas Folkesson (Chalmers University)

Corrosion rate?
- Carburization
- Heat transfer
- Recirculation of corrosive species
- More corrosive flue gas and condensation
Analysis of Carbide content (ESMA) and Carbide growth indicated an uptake of carbon.

Sulfur activity

Carbon activity

Carburization in low Carbon activity gases

David Young, University of New South Wales, Australia, meanwhile is clearly demonstrated and explained.
Sulfur versus Chlorine or Sulfur and Chlorine

High Sulfur and high Chlorine content causes higher corrosion rate at a fixed temperature.
**Oxyfuel flue gas versus air combustion flue gas**

- **Waterwall**: 399, 468, 538 °C
- **Superheater**: 538, 593, 649 °C
- **Low H₂O content**

### Project Preliminary Findings and Schedule

- **Lab Testing for 3200 ppmv wet Oxy Bulk SO₂ Completed**
- **Oxy Corrosion Varied with Material, Deposit, and Temperature**
  - Oxy Corrosion Rates Typically No Worse / Often Less Than Air-Fired
  - Conventional Weld Overlays Can Protect Against Oxy Atmospheres
  - Metallographic Analyses of Coupons Revealed No Carburization
- **Lab Results May Be Consistent with Coal-Fired Pilot Plant Data**
  - Vattenfall Schwartze Pumpe 30 MWt and Univ of Utah 1 MWt Tests
- **Final Report to be Issued End of December 2011**

### OCC2

A. Robertson et al.

Similar the results in the ifk,ENEL, Swerea/KIMAB project where comparable low H₂O content was used.

### Corrosion Test Gas Compositions (Vol%)
## Can we compare laboratory test conditions?

<table>
<thead>
<tr>
<th></th>
<th>Coupon Test (ISO)</th>
<th>Corrosion Probe Tube experiments</th>
<th>Laboratory Tube experiments</th>
<th>Dual corrosion test</th>
<th>Super Heater Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Temperature control</strong></td>
<td>++</td>
<td>0</td>
<td>+</td>
<td>++</td>
<td>0</td>
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<tr>
<td></td>
<td></td>
<td>Depends on heat transfer between test ring and support.</td>
<td></td>
<td></td>
<td>Heat transfer determines temperature distribution</td>
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<tr>
<td><strong>Gas flow control</strong></td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>++</td>
<td>-</td>
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<tr>
<td></td>
<td></td>
<td>Surface gas flow variable</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td><strong>Constant gas composition</strong></td>
<td>++</td>
<td>0</td>
<td>++</td>
<td>++</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>If flow is high enough</td>
<td>Depend on fuel and gas mixture</td>
<td></td>
<td></td>
<td>Depend on fuel and gas mixture</td>
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<tr>
<td><strong>Chemical condition at deposit- metal (oxide) interface</strong></td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<tr>
<td></td>
<td>Slow change depending on deposit reaction rate</td>
<td>Fluctuating with fuel and gas. Loss of deposit.</td>
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<tr>
<td><strong>Deposit composition</strong></td>
<td>0</td>
<td>++</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>Changes with time</td>
<td>Depend of fuel but permanent renewed</td>
<td>Changes with time</td>
<td>Changes with time</td>
<td>Depend on fuel but permanent renewed</td>
</tr>
<tr>
<td><strong>Deposit phases</strong></td>
<td>++</td>
<td>0</td>
<td>++</td>
<td>++</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Depend on fuel</td>
<td></td>
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<td>Depend on fuel</td>
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</tbody>
</table>
Variety of test conditions

- Most experiments have different gas composition or deposit composition or both.
- Gas flow rate is different
- Temperatures cover equivalent intervals
- Microstructure is not defined before experiment (Annealing procedure, interface or boundary density, precipitation distribution (Carbides).
- Surface preparation is not monitored (Roughness, surface deformation)
- J. Oakey OCC3: Wide variations are often found between labs carrying out tests to the same specifications – reflecting the difficulty in managing the test variables and in our understanding of the mechanism.
What do we believe we know?
( The remarks of J.Oakey, OCC3. included)

• For one coal blend or coal the deposits in air firing and Oxyfuel are basically identical in phases occurring. Mass relations shift towards Sulfats.
• Maximum corrosion rate depending on metal matrix phase occurs between 500 and 700 °C (bell shape rate graph)
• Increasing S content, increasing Cl content and increasing H₂O content increase corrosion rate.
• NaSO₄, NaCl, KCl, KSO₄ might become responsible for hot corrosion depending on coal or biomass addition.
• CO₂ can penetrate a Cr₂O₃-scale
• Carburization needs a special thermodynamic window and seems to be more expressed when the H₂O content exceeds 20% and the CO₂ content exceeds 60 %. The carburization rate is high in martensitic steels.
• Lower corrosion rates were observed for materials with higher Cr-content, austenitic structure.
• Ni-based alloys or Alumina-former should be better than Cr-Oxide-former.
The presentations will cover the aspects

- Requirements and material selection
  - Colin Davis, E.ON; Bettina Bordenet, Alstom
- Plant Experience
  - Steve Kung, B&W
- Comparability
  - John Oakey, Cranefield University
- New Materials
  - Jeffry Hawk, US DOE NETL
- Understanding
  - Joe Quadakkers, FZJ; Manoj Peneru, IFK; Bruce Pint, ORNL; Bettina Bordenet, Alstom, Axel Kranzmann, BAM; Nigel Simms, Cranefield University.
What is the most serious hurdle?

- acid ocean
- CO₂ impact path
- ash mountains
- sulfur desert
- Material jungle

Oxyfuel