Coal-ash Corrosion of Alloys for Combustion Power Plants

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Rationale for Advanced Combustion Systems

- Global warming
- CO$_2$ generation
- Acid rain
- New source performance standards
- Environmental compliance -- Toxins
- Plant economics

Plants with higher thermal efficiency and lower impact on environment are needed
Efficiency vs. CO$_2$ Emissions

CO$_2$ emissions per MWh of electricity produced from coal at various efficiency levels:

- **Emissions**
- **Coal used**

Coal consumed / MWh = 1 / (efficiency x CV)
CO$_2$ emissions in t / MWh = 1 / (efficiency x 44 / 12 x %C in fuel x 1 / CV)
CV = 7.4 MWh / t of coal
Coal = 70% carbon
## Comparison of Selected Coal Utilization Technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Unit size (Mwe)</th>
<th>Net efficiency (%)</th>
<th>Capital cost (US $/Kw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subcritical PC</td>
<td>50-1000</td>
<td>36-38</td>
<td>950-1300</td>
</tr>
<tr>
<td>Supercritical PC</td>
<td>50-1000</td>
<td>40-46</td>
<td>950-1600</td>
</tr>
<tr>
<td>PFBC</td>
<td>70-350</td>
<td>42-45</td>
<td>1000-1500</td>
</tr>
<tr>
<td>IGCC</td>
<td>100-320</td>
<td>43-45</td>
<td>1500-1600</td>
</tr>
</tbody>
</table>
Efficiency and Emissions for Coal-fired Boiler Technologies

<table>
<thead>
<tr>
<th></th>
<th>CO₂ (Million tons/y)</th>
<th>NOₓ (1000 tons/y)</th>
<th>SO₂ (1000 tons/y)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>5.3</td>
<td>8</td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Supercritical</td>
<td>4.9</td>
<td>7</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Ultrasupercritical</td>
<td>4.45</td>
<td>7</td>
<td></td>
<td>45</td>
</tr>
</tbody>
</table>
Pulverized Coal-Fired Boilers

Goal is to develop advanced steam cycles

Current:  16.5-24 MPa (2,400-3,500 psig), 540°C (1000°F) steam

Near-Term Goal:  34.5 MPa (5,000 psig), 650°C steam

Long-Term Goal:  34.5 MPa (5,000 psig), 760°C steam

Waterwall corrosion:  Formation of pyrosulfates, trisulfates
Superheater corrosion:  Formation of alkali-iron trisulfates
                      Alkali sulfates/alkali chlorides induced corrosion
                      Loss of mechanical properties
Alloy Development

• High temperature creep strength
  - solution strengthening W, Mo
  - precipitation strengthening VN, Nb(C,N), etc.
  - stable long-term strength (Cu addition in ferritics)

• Weldability

• Toughness

• Corrosion resistance (T, design life, fireside environment)
Program Objectives

• Evaluate fireside corrosion performance of metallic materials in coal-ash environments typical of advanced steam cycle systems

• Evaluate the role of alkali sulfates in the corrosion process

• Evaluate the role of alkali chloride in the corrosion process

• Establish the relative corrosion performance of off-the-shelf and experimental alloys

• Perform comparative corrosion tests on candidate materials by exposures in coal-burning combustion test facility at NETL, Pittsburgh
Laboratory Test Details

- Key variables: temperature, time, alloy composition, deposit composition
- Materials: ferritics, austenitics, claddings
- Gas: 1 vol.% SO$_2$ in air (catalyzed)
- Test temperatures: 575, 650, 725, and 800°C
- Test times: 336 to 1868 h
- Specimen evaluation: weight change, scanning electron microscopy, energy dispersive X-ray analysis, X-ray diffraction
Deposit chemistry

(a) $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3 = 1:1:1$

(b) $\text{Na}_2\text{SO}_4 : \text{K}_2\text{SO}_4 = 1:1$

(c) $\text{NaCl}$

Ash 1: 90 wt.% (a) + 10 wt.% (b)

Ash 2: 85 wt.% (a) + 10 wt.% (b) + 5 wt.% (c)

Ash 3: 89 wt.% (a) + 10 wt.% (b) + 1 wt.% (c)
Alloy Selection for Corrosion Tests

- **Solid-solution/precipitation hardening alloys**
  - 800HT, 310SS, 617, 671, 625, X, 556, 253MA, 214, 188

- **Oxide-dispersion-strengthened alloy**
  - MA 956

- **Intermetallic alloy**
  - FAL

- **Ni-base alloys**: 617, 671, 625, 214, X
- **Fe-base alloys**: 800HT, 310SS, 253MA, 556, MA956, FAL
- **Co-base alloy**: 188
Corrosion Test Facility

- Air
- \( \text{SO}_2 \)
- Flow Control
- Platinized Ceramic Catalyst
- Alumina Retort Tube
- Alumina Tray with Specimens covered in Ash Mixture
- Alumina Tray Thermocouple Well
- Viton Seal Gasket
- Stainless Steel Flange Seal Assembly
- Furnace
- Alumina
- Retort Tube
- with Specimens
- covered in Ash Mixture
## Fe-base Alloys Selected for Corrosion Tests

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Fe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCM12A</td>
<td>0.10</td>
<td>12</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
<td>Bal</td>
<td>W 2.0, V 0.2, Nb 0.05, Cu 0.9, N 0.05</td>
</tr>
<tr>
<td>Super 304H</td>
<td>0.10</td>
<td>18</td>
<td>9</td>
<td>1.0</td>
<td>0.3</td>
<td>-</td>
<td>Bal</td>
<td>Nb 0.45, Cu 3.0, N 0.09</td>
</tr>
<tr>
<td>347HFG</td>
<td>0.08</td>
<td>18</td>
<td>11</td>
<td>2.0</td>
<td>1.0</td>
<td>-</td>
<td>Bal</td>
<td>Nb + Ta = 10 x C min</td>
</tr>
<tr>
<td>HR3C</td>
<td>0.06</td>
<td>25</td>
<td>20</td>
<td>1.2</td>
<td>0.4</td>
<td>-</td>
<td>Bal</td>
<td>Nb 0.45, N 0.2</td>
</tr>
<tr>
<td>310TaN</td>
<td>0.05</td>
<td>25</td>
<td>20</td>
<td>1.0</td>
<td>0.2</td>
<td>-</td>
<td>Bal</td>
<td>Ta 1.5, N 0.2</td>
</tr>
<tr>
<td>NF709</td>
<td>0.07</td>
<td>20</td>
<td>25</td>
<td>1.0</td>
<td>0.6</td>
<td>1.5</td>
<td>Bal</td>
<td>Ti 0.6, Nb 0.2, N 0.18, B 0.004</td>
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<tr>
<td>SAVE 25</td>
<td>0.10</td>
<td>23</td>
<td>18</td>
<td>1.0</td>
<td>0.4</td>
<td>-</td>
<td>Bal</td>
<td>Nb 0.45, W 1.5, Cu 3.0, N 0.2</td>
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<tr>
<td>Modified 800</td>
<td>0.10</td>
<td>20</td>
<td>30</td>
<td>1.5</td>
<td>0.2</td>
<td>1.5</td>
<td>Bal</td>
<td>Ti 0.25, Nb 0.25, V 0.05, N 0.03, B 0.004</td>
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<tr>
<td>HR120</td>
<td>0.05</td>
<td>25</td>
<td>37</td>
<td>0.7</td>
<td>0.6</td>
<td>2.5</td>
<td>Bal</td>
<td>Co 3, W 2.5, N 0.2, Cu 0.18, B 0.004, Al 0.1, Nb 0.7</td>
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</tbody>
</table>

### 671 clad/800H

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>Fe</th>
<th>Other</th>
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<tr>
<td>671</td>
<td>0.05</td>
<td>48</td>
<td>Bal</td>
<td>0.02</td>
<td>0.2</td>
<td>-</td>
<td>0.2</td>
<td>Ti 0.4</td>
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<tr>
<td>800</td>
<td>0.05</td>
<td>21</td>
<td>32</td>
<td>0.5</td>
<td>0.2</td>
<td>-</td>
<td>Bal</td>
<td>Ti 0.4, Al 0.4</td>
</tr>
</tbody>
</table>
## Ni-base Alloys Selected for Corrosion Tests

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Mo</th>
<th>Al</th>
<th>Fe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>15.4</td>
<td>Bal</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>9.7</td>
<td>-</td>
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<tr>
<td>601</td>
<td>21.9</td>
<td>Bal</td>
<td>0.2</td>
<td>0.1</td>
<td>1.4</td>
<td>14.5</td>
<td>Ti 0.3, Nb 0.1</td>
</tr>
<tr>
<td>690</td>
<td>27.2</td>
<td>Bal</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>10.2</td>
<td>Ti 0.3</td>
</tr>
<tr>
<td>617</td>
<td>21.6</td>
<td>53.6</td>
<td>0.1</td>
<td>9.5</td>
<td>1.2</td>
<td>0.9</td>
<td>Co 12.5, Ti 0.3</td>
</tr>
<tr>
<td>625</td>
<td>21.5</td>
<td>Bal</td>
<td>0.3</td>
<td>9.0</td>
<td>0.2</td>
<td>2.5</td>
<td>Nb 3.7, Ti 0.2</td>
</tr>
<tr>
<td>602CA</td>
<td>25.1</td>
<td>Bal</td>
<td>0.1</td>
<td>-</td>
<td>2.3</td>
<td>9.3</td>
<td>Ti 0.13, Zr 0.19, Y 0.09</td>
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<tr>
<td>214</td>
<td>15.9</td>
<td>Bal</td>
<td>0.1</td>
<td>0.5</td>
<td>3.7</td>
<td>2.5</td>
<td>Zr 0.01, Y 0.006</td>
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<tr>
<td>230</td>
<td>21.7</td>
<td>Bal</td>
<td>0.4</td>
<td>1.4</td>
<td>0.3</td>
<td>1.2</td>
<td>W 14, La 0.015</td>
</tr>
<tr>
<td>45TM</td>
<td>27.4</td>
<td>46.4</td>
<td>2.7</td>
<td>-</td>
<td>-</td>
<td>26.7</td>
<td>RE 0.07</td>
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<tr>
<td>HR 160</td>
<td>28.0</td>
<td>Bal</td>
<td>2.8</td>
<td>0.1</td>
<td>0.2</td>
<td>4.0</td>
<td>Co 30.0</td>
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<tr>
<td>693</td>
<td>28.9</td>
<td>Bal</td>
<td>0.04</td>
<td>0.13</td>
<td>3.3</td>
<td>5.9</td>
<td>Ti 0.4, Nb 0.7, Zr 0.03</td>
</tr>
</tbody>
</table>
Corrosion Loss in Coal Ash + Alkali Sulfate

- Weight loss (mg·cm\(^{-2}\)) in 1000 h
- Test temperature (°C)

Presented in 2002 conference
Corrosion Loss in Coal Ash + Alkali Sulfate + NaCl

Weight loss (mg·cm$^{-2}$) in 1000 h

Test temperature (°C)

Presented in 2002 conference
Examples of weight loss data

- **HCM12A, 725°C, Ash 1**
  
  Weight loss (mg/mm²) = 0.00086 x time (h)

- **Modified 800, 725°C, Ash 1**
  
  Weight loss (mg/mm²) = 0.026 x time (h)

- **NF709, 650°C, Ash 3**
  
  Weight loss (mg/mm²) = 8.5 x 10^{-5} x time (h)

- **HR3C, 650°C, Ash 3**
  
  Weight loss (mg/mm²) = -4.4 x 10^{-5} x time (h)
Effect of NaCl on Corrosion

5%NaCl
Presented in 2002 conference
Effect of Deposit Chemistry on Corrosion of Fe-base Alloys

650°C

Scaling + Penetration rate (mm/y)

- Ash+10% alkali sulfates
- Ash+10% alkali sulfates+1% NaCl
- Ash+10% alkali sulfates+5% NaCl

Alloys:
- HCM12A
- 347HFG
- HR3C
- 310TaN
- NF709
- SAVE25
- Modified 800H
- HR120
- 800H
Effect of Deposit Chemistry on Corrosion of Ni-base Alloys

- 650°C
  - Ash+10% alkali sulfates
  - Ash+10% alkali sulfates+1% NaCl

Scaling+ Penetration rate (mm/y)
Comparison of Corrosion Rates for Fe- and Ni-base Alloys

650°C

Ash+10% alkali sulfates
Ash+10% alkali sulfates+1% NaCl

Scaling+ Penetration rate (mm/y)

HCM12A
347HFG
HR3C
310TaN
NF709
SAVE25
Modified 800H
HR120
800H

650°C

Ash+10% alkali sulfates
Ash+10% alkali sulfates+1% NaCl

Scaling+ Penetration rate (mm/y)

HCM12A
347HFG
HR3C
310TaN
NF709
SAVE25
Modified 800H
HR120
800H

650°C

Ash+10% alkali sulfates
Ash+10% alkali sulfates+1% NaCl

Scaling+ Penetration rate (mm/y)

HCM12A
347HFG
HR3C
310TaN
NF709
SAVE25
Modified 800H
HR120
800H

650°C

Ash+10% alkali sulfates
Ash+10% alkali sulfates+1% NaCl

Scaling+ Penetration rate (mm/y)

HCM12A
347HFG
HR3C
310TaN
NF709
SAVE25
Modified 800H
HR120
800H
X-ray Diffraction Data

Ash 1

Ash 3
Cross section of a typical specimen before exposure
668 h exposure at 650°C in ash + sulfates

Presented in 2002 Conference
900 h at 650°C in ash + sulfates + 1% NaCl
Alloy MA956, 900 h, 650°C
Ash + sulfates+ 1% NaCl
Alloy 625, 1680 h, 650°C
Ash + sulfates
Alloy 602CA, 1680 h, 650°C
Ash + sulfates
Alloy 230, 1680 h, 650°C
Ash + sulfates + 1% NaCl
Alloy 230, 1680 h, 650°C
Ash + sulfates
Alloy 45TM, 1680 h, 650°C
Ash + sulfates
Alloy 45TM, 1680 h, 650°C
Ash + sulfates + 1% NaCl
ash + sulfates

ash + sulfates + 1% NaCl

Alloy 693, 1680 h, 650°C
Deposit: Ash + sulfates
Deposit: Ash + sulfate + 1% NaCl

601, ash 3, 650°C, 1680 h
Hot Corrosion of Ni-Cr Alloys
Hot Corrosion of Ni-Cr-Al Alloys
Before exposure

After exposure

1500-1600°F (≈ 815-870°C)
Summary

- Fireside corrosion is a major issue in selection of materials for advanced steam cycles
- We have conducted studies at ANL to evaluate the corrosion performance of several Fe- and Ni-base alloys
- The laboratory tests simulated the combustion atmosphere and three deposit chemistries which included ash constituents, alkali sulfates, and two levels of NaCl
- Corrosion rates exhibited a bell shaped curve (for Fe base alloys) with peak rates around 725°C, and the rate itself is dependent on the alloy chemistry
- Several Fe-base alloys showed acceptable rates in the sulfate containing coal-ash environment; but, NaCl in the deposit led to catastrophic corrosion at 650 and 800°C
Summary (continued)

• Ni-base alloys, tested for 1680 h at 650°C, showed a substantial local attack in the form of pits and associated sulfidation of the alloy. This form of attack is well established and is known as “low temperature hot corrosion” or Type II hot corrosion (in gas turbine terminology)

• Need to establish the maximum levels for alkali sulfates and alkali chlorides in combustion environment (and their relationship to coal feedstock) for acceptable corrosion

• Additional tests are in progress with Ni-base alloys at ANL and in NETL combustor to evaluate their corrosion performance

• The combination of adequate creep strength and fireside and steamside corrosion resistance is still a challenge in materials development for advanced steam cycles