The Laboratory Coal Ash Corrosion Test Results of Superheater Tube Materials in Oxyfuel Gas Conditions

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Purpose of this study

Effect of Oxyfuel combustion to the superheater tube corrosion:

Higher CO$_2$ : Carburization, Carbonate formation

SO$_x$ : Accelerate coal ash corrosion by formation of molten alkali iron tri-sulfate

\[
3(Na,K)_2SO_4 + Fe_2O_3 + 3SO_2 + 1.5O_2 = 2(Na,K)_3Fe(SO_4)_3
\]

The effect of gas compositions on the corrosion rate of superheater tube materials (stainless steels, Ni-based alloys) were investigated.
Coal ash corrosion test method

Steam Generator → Gas Mixer → Retort → Gas → Electric Furnace → Synthetic Coal Ash (40mg/cm²) → Exaust Gas

- T/P
- 34%Na₂SO₄ - 41%K₂SO₄ - 25%Fe₂O₃

Exposure time: 100hrs

After test evaluation:
- Corrosion weight loss of metals
- Cross sections by Optical Microscope.
### Test conditions

<table>
<thead>
<tr>
<th>Gas Composition (vol.%)</th>
<th>Test Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>SO₂</td>
</tr>
<tr>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>0.08</td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
</tr>
<tr>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td>66</td>
<td>0.08</td>
</tr>
<tr>
<td>66</td>
<td>0.25</td>
</tr>
</tbody>
</table>

#### Tested Materials

**Stainless Steels**: Alloy A (18Cr-9Ni-3Cu)  
Alloy B (18Cr-12Ni-Nb)  
Alloy C (25Cr-20Ni-Nb-N)

**Ni base alloys**: Alloy D (22Cr-12Co-9Mo-1Al-bal. Ni)  
Alloy E (20Cr-20Co-6Mo-2.3Ti-bal. Ni)
Maximum corrosion rate were observed at 923K.
At 1023K, Ni based alloy showed large corrosion rate than stainless steels.
CO$_2$ content increase (15% to 66%) did not affect on the ash corrosion rate.
Effect of gas composition on the corrosion at 923K

SO₂ content increase accelerated the corrosion of alloys. CO₂ content increase (15% to 66%) did not affect on the ash corrosion rates.
SO\textsubscript{2} content increase accelerated the corrosion of alloys.

CO\textsubscript{2} content increase (15\% to 66\%) did not affect on the ash corrosion rates.

Alloy C (25\%Cr) showed lower corrosion rate than other alloys.
Effect of gas composition on the ash corrosion at 1023K

The corrosion rates of stainless steels are small.

Ni-based alloys showed large corrosion rate in high SO$_2$ atmosphere.
Cross Sections of Alloy A After Corrosion Test (66%CO₂)

3rd Oxyfuel Combustion Conference

Corrosion morphologies of Alloy A (stainless steel):

In no SO₂ atmosphere: Corrosion were very slight
At 923K-973K in 0.25% SO₂: Severe general corrosion
At 923 - 973K in 0.08% SO₂: Localized corrosion

(localized formation of molten salt by reaction of salt and corrosion product)
At 1023K: General corrosion with small corrosion rate
Cross Sections of Alloy E After Corrosion Test (66% CO₂)

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Corrosion morphologies of Alloy E (Ni-based alloy)

In no SO₂ atmosphere: Corrosion were very slight

In 0.08% SO₂: Localized corrosion

In 0.25% SO₂: Severe general corrosion

Alloy E showed severe corrosion at 1023K.
Since alkali-iron-tri-sulfate $(\text{Na}_2\text{K})_3\text{Fe}$(SO$_4$)$_3$ is unstable at high temperature, the ash melts under low (923-973K) temperature and high SO$_2$ atmospher.
In the environment in which the synthetic ash melt, severe general corrosion were observed after 100hrs corrosion test.

In 0.08% SO₂ atmosphere, reaction of metal corrosion products and ash cause molten salt corrosion: Localized corrosion were observed after 100hrs.

Severe corrosion of alloy E at 1023K will be caused by other mechanism.
Effect of Mo in alloy on corrosion at 1023K

**Alloy D:** 22Cr-12Co-9Mo-1Al-bal.Ni
*Aloy E: 20Cr-20Co-6Mo-2.3Ti-bal.Ni*

**MoO$_3$** will form as corrosion product

10% of MoO$_3$ was added to the synthetic ash and exposed at 1023K in 0.25%SO$_2$ atmosphere

The formation of MoO$_3$ causes the formation of molten salt at 1023K, without formation of molten alkali iron tri-sulfate.
Effect of MoO$_3$ in ash on corrosion rates at 1023K

Alloy D: 22Cr-12Co-9Mo-1Al-bal.Ni
Alloy E: 20Cr-20Co-6Mo-2.3Ti-bal.Ni
Alloy F: 22Cr-1.5Al-10Fe-bal.Ni

Corrosion test of Alloy F (without Mo) was carried out with the synthetic ash (With and without MoO$_3$ addition) at 1023K in 66%CO$_2$-0.25%SO$_2$ gas

MoO$_3$ addition in the synthetic ash accelerates the corrosion of alloy F.

MoO$_3$ or Mo sulfate in the corrosion product reacts with the synthetic ash and accelerate the formation of molten salt.
Conclusions

- The difference of CO$_2$ content (66% vs 15%) in gas did not affect the ash corrosion rates of alloys.

- The SO$_2$ content increase accelerated the corrosion at 923K and at 973K.

- At 1023K, alkali iron tri-sulfate became unstable, therefore the corrosion rates of stainless steels became small. In the case of Mo containing Nickel based alloys, formation of MoO$_3$ cause the molten salt formation at 1023K and accelerate corrosion.

- The longer term (- 1000hrs.) laboratory corrosion test

- Tube material exposure in Callide Oxyfuel boiler are planned now
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