Experimental Study Results on Corrosion Issues in Oxyfuel Combustion Process

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IEAGHG International Oxyfuel Combustion Research Network
1. Introduction

2. IHI’s Activities

3. Study results

4. Conclusions
1. Introduction
1. Introduction

Typical System flow

Coal Bunker

Mill

Air

ASU

N₂

O₂

Boiler

Flue gas treatment process

Dust Removal

Stack

Non-Condensable Gas

CO₂ Liquefier

CO₂ Tank

Treatment process & compressor

Cold Box

(CO₂, H₂O, SO₂…)

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1. Introduction

Corrosion issues in oxyfuel process

- **Low temperature corrosion**
  - High concentration of corrosive substances
  - With high concentration of moisture

- **CO2 Processing Unit**
  - Possibility of containing Hg in the gas
  - Corrosion by contact between aluminum base metal and Hg at heat exchanger

- **High temperature corrosion in the furnace**
  - Sulfidation at furnace wall in case of staging for low NOx combustion
  - Ash corrosion at SH/RH/Furnace wall
  - Higher concentration of CO2/SO2/H2O/etc. in the flue gas
2. IHI’s Activities
IHI’s activities for corrosion issues

1. High temperature corrosion of boiler tube
   (1) Estimation of corrosion environment & ash component / Combustion test & simulation
   (2) Lab test for corrosion of tube material / Lab-scale test
   (3) Corrosion test under the actual flue gas / Actual atmosphere

2. Low temperature corrosion
   (1) Confirmation of the SO2/SO3/H2O characteristics in boiler process / Combustion test

3. Hg corrosion at CO2 liquefaction process
   (1) Behavior of Hg at oxyfuel boiler process / Combustion test
   (2) Behavior of Hg at CO2 compression & purification process / Simulation
IHI’s activities for corrosion issues

1. High temperature corrosion of boiler tube
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   (2) **Lab test for corrosion of tube material** / Lab-scale test
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   (2) Behavior of Hg at CO2 compression & purification process / Simulation
3. Study Results

3.1 Pilot-scale combustion test
3.2 Lab-scale corrosion test
Objectives

➢ To obtain the **SO2/SO3/H2O characteristics**

➢ To compare and evaluate the **deposited ash** component between in air and in oxyfuel combustion process for ash corrosion test

➢ To compare and evaluate the behavior of **mercury (Hg) in flue gas and ash** between in air and in oxyfuel combustion
3.1 Pilot-scale combustion test

Combustion test facilities

Capacity: Max. 150kg/h (Coal) (1.2MW thermal)
Furnace: Vertical type
  I.D. 1.3m × L 7.5m
burner: IHI-TR burner
3.1 Pilot-scale combustion test

**SO2/H2O/SO3 characteristics**

3 types of Australian coals were tested and SO2, SO3 and H2O at oxyfuel with pre-mixing O2 were compared with them of air combustion.

*Good relationships between air and oxy were obtained.*

*SO2 and SO3 concentration are increased to be 3 times of them at air combustion*
3.1 Pilot-scale combustion test - Previous study for SO$_3$ behavior

**Previous study for SO$_3$ behavior**

- **SO$_3$ concentration is rapidly decreased at outlet of air heater**
- **SO$_3$ emission is below the detection limit at the stack inlet**
- **SO$_3$ is captured in ash deposit on the heat transfer surface of air heater and the filter of the bag filter**
- **This behavior is the same as flue gas in condition of air combustion**
- **Corrosive environment after bag filter outlet is the same as in air combustion**
3.1 Pilot-scale combustion test

Ash sampling in the furnace for ash corrosion test

Deposit ash on the probe was sampled near the burner throat and near the furnace exit during staging. Combustion gas was also sampled.
3.1 Pilot-scale combustion test

-Ash component of Coal A-

Deposit ash near burner throat

Deposit ash near furnace exit

- Oxyfuel ash -

Coal A: Australian bituminous coal
3.1 Pilot-scale combustion test

-Ash component of Coal B-

Deposit ash near burner throat

Deposit ash near furnace exit

Ash at AH hopper

Coal B: US sub-bituminous coal
*High moisture and high Ca content in ash
3.1 Pilot-scale combustion test
-Summary of ash component-

Summary

1. Sulfur in ash shows the tendency of increasing in oxyfuel condition.

2. Totally, there is not so much difference of ash component between in oxy- and in air-combustion.

3. These results will be reflected into the lab-scale ash corrosion test of boiler tube.
3.1 Pilot-scale combustion test -Oxyfuel Hg-

**Combustion condition**

<table>
<thead>
<tr>
<th>Combustion mode</th>
<th>Air</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC feed rate [kg/h]</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Total O₂ to the furnace [wet %, calc.]</td>
<td>(21.0)</td>
<td>27.0</td>
</tr>
<tr>
<td>Flue gas O₂ [dry %]</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Staging</td>
<td>Without staging</td>
<td></td>
</tr>
</tbody>
</table>

**Mercury Sampling from flue gas and ash**

- Gas sampling at Inlet and outlet of Air heater, inlet & outlet of Bag filter
- Analysis of Hg₀, Hg₂⁺, and Hg in dust

**Gas sampling**

- Ash sampling at the 7 hoppers of furnace bottom, gas cooler, air heater (4) and bag filter
- Analysis of carbon-in-ash and Hg

**Sampled ash**

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3.1 Pilot-scale combustion test
-Ash component of Coal B-

**Hg in flue gas**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Hg (μg/Nm³)</th>
<th>Gas sampling point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Hg₂⁺</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>Hg (mg/h)</th>
<th>Gas sampling point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg₀</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Hg₂⁺</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Dust</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>4</td>
</tr>
</tbody>
</table>

**Oxy**
Gas sampling point: 1. AH inlet(450 deg C)  2. AH outlet(200 deg C)  3. BF inlet(170 deg C)  4. BF outlet(120 deg C)

**Air**
3.1 Pilot-scale combustion test  
-Ash component of Coal B-  

**Hg in hopper ash**

- **Hg concentration**
- **Hg flow rate**

**Carbon-in-ash**

**Ash sampling point:**
1. Furnace bottom  
2. GC hopper  
3. AH No.1 hopper  
4. AH No.2 hopper  
5. AH No.3 hopper  
6. AH No.4 hopper  
7. BF hopper
Summary

1. Hg in flue gas of oxyfuel combustion is slightly higher than Hg in flue gas of air combustion. Most of the Hg at furnace outlet is Hg(0), and that at bag filter outlet is Hg(2+) in the flue gas. This result shows the same tendency between in oxy- and in air-combustion.

2. Hg is captured in ash at the bag filter.
Objectives

- Establishment of knowledge about corrosion in oxyfuel atmosphere
- Establishment of countermeasure against corrosion (Ash corrosion, Carburization)

Study items

- Evaluation of corrosion environments
- Study of high temperature corrosion in oxyfuel atmosphere and countermeasure against corrosion

Introduction of corrosion test results at oxidizing atmosphere
3.2 Lab-scale corrosion test

-Corrosion test-

Measurement of corrosion weight loss and cross-section observation of the coupon after 300hrs exposure

O₂-CO₂-H₂O-SO₂-bal.N₂ (Oxidizing atmosphere)

Temperature: 500 deg C
3.2 Lab-scale corrosion test

Alloys for Corrosion Test at 500 deg C

Chemical Compositions of Alloys Tested

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>A210-A1 (STB42)</td>
<td>0.32</td>
<td>0.35</td>
<td>0.3-0.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SA213-T2 (STBA20)</td>
<td>0.13</td>
<td>0.24</td>
<td>0.46</td>
<td>-</td>
<td>0.67</td>
<td>-</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SA213-T12 (STBA22)</td>
<td>0.12</td>
<td>0.35</td>
<td>0.46</td>
<td>-</td>
<td>0.94</td>
<td>-</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SA213-T22 (STBA24)</td>
<td>0.11</td>
<td>0.39</td>
<td>0.49</td>
<td>-</td>
<td>2.13</td>
<td>-</td>
<td>0.95</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SA213-T91 (Ka-STBA28)</td>
<td>0.09</td>
<td>0.36</td>
<td>0.42</td>
<td>-</td>
<td>8.61</td>
<td>0.07</td>
<td>0.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Super304H</td>
<td>0.10</td>
<td>0.18</td>
<td>0.77</td>
<td>2.9</td>
<td>18.4</td>
<td>9.3</td>
<td>-</td>
<td>0.43</td>
<td>0.1N</td>
</tr>
</tbody>
</table>

In Mass %
### Test Gas Composition

<table>
<thead>
<tr>
<th>Case</th>
<th>Mode</th>
<th>CO₂</th>
<th>SO₂</th>
<th>O₂</th>
<th>H₂O</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>ppm</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>#1</td>
<td>Oxyfuel</td>
<td>Bal.</td>
<td>-</td>
<td>4</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(66)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#2</td>
<td>Air</td>
<td>15</td>
<td>-</td>
<td>4</td>
<td>13</td>
<td>Bal.</td>
</tr>
<tr>
<td>#3</td>
<td>Oxyfuel</td>
<td>Bal.</td>
<td>2500</td>
<td>4</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(65.75)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>#4</td>
<td>Air</td>
<td>15</td>
<td>800</td>
<td>4</td>
<td>13</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Effect of High SO₂: Accelerated oxidation

Effect of High CO₂: Carburization
Gas Corrosion Test Results at 500 deg C

- Corrosion test -
3.2 Lab-scale corrosion test

Cross Sections of T2 Steel

*After 300hrs Gas Corrosion Test*

- #1 OxyFuel Without SO$_2$
- #2 Conventional Without SO$_2$
- #3 OxyFuel With SO$_2$
- #4 Conventional With SO$_2$
3.2 Lab-scale corrosion test

Cross Sections of Super304H
After 300hrs Gas Corrosion Test

- Corrosion test -

#1 OxyFuel Without SO$_2$

#2 Conventional Without SO$_2$

#3 OxyFuel With SO$_2$

#4 Conventional With SO$_2$
Cross Sections of Super304H (etched)

After 300hrs Gas Corrosion Test in Case #1 (Without SO₂ Condition)

#1 Oxyfuel  
#2 Conventional

In high CO₂ environment (Oxyfuel condition), carburization may occur more than conventional combustion environment.

But these corrosion rate were very low and comparable.
Conclusion of the test obtained by now.

The gas corrosion test results at 500degC showed

1. The corrosion rate of carbon steel and low alloy steels were comparable. The austenitic stainless steel showed low corrosion rate.

2. The higher CO$_2$ content in gas did not affect the gas corrosion rate of alloys. The existence of SO$_2$ accelerated the corrosion of T2 alloy.

3. In the high(66%) CO$_2$ environment, carbon steel did not show carburization. The austenitic stainless steel showed the possibility of carburization, but it did not affect to its corrosion rate. Further study would be required at higher temperature conditions.
4. Conclusions
Some studies on corrosion in oxyfuel combustion have been conducted in order to obtain the design parameters for the commercialization.

Further study on corrosion test (higher temperature corrosion of higher grade material, ash corrosion test) will be required.

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Thank you for your attention!!