Study of Hg and \( \text{SO}_3 \) Behavior in Flue Gas of Oxy-fuel Combustion System

September 14, 2011

Yoshiaki Mitsui, Noriyuki Imada and Hirofumi Kikkawa

Environmental Research Department
Kure Research Laboratory
Babcock-Hitachi K.K., JAPAN

Atsushi Katagawa
Kure Division, Babcock-Hitachi K.K., JAPAN
1. Subjects on AQCS for Oxy-fuel Combustion
2. Pilot Plant Test
3. Hg and SO$_3$ Behavior in Oxy-fuel Combustion
4. Conclusion
Subjects on AQCS for Oxy-fuel combustion

AQCS: Air Quality Control System

- keep SCR, DESP, FGD performance (NOx, SOx, Hg etc)
- reduce corrosive gas

Fuel-pipe
Gas Recirculation line
-reduce corrosive gas: SO3

CPU (CO2 Purification Unit)
-reduce corrosion potential (Hg, SO3, etc)

*DESP : Dry Electrostatic Precipitator
**WFGD : Wet Flue Gas Desulfurization

Babcock-Hitachi K.K.
Concept of Hitachi New AQCS

**Hitachi new AQCS for oxy-fuel combustion**

*TRAC™ (Triple Action Catalyst): Hitachi’s new Hg oxidation catalyst
*CER (Clean Energy Recuperator)
Pilot Plant Test
Appearance of Pilot Test Plant (1.5MWth)

- AQCS (Air Quality Control System)
- Combustion facility
- DESP
- CER
- SCR
- WFGD
- Oxygen Supply Unit
- Re-Circulation Line
- Control room
Schematic Diagram of Pilot Test Plant (1.5MWth)

- **O₂**: Oxygen
- **Burner**: Combustion area
- **Coal**: Input of coal
- **Heat Exchanger**: Heat exchange section
- **SCR reactor**: Selective Catalytic Reduction reactor
- **CER**: Clean Energy Recuperator
- **DESP**: Dry Electrostatic Precipitator
- **WFGD**: Wet Flue Gas Desulfurization
- **A~E**: Sampling points for mercury and sulfur trioxide (Hg and SO₃)
- **GRF**: Gas Recycling Facility
- **CPU**: Control Unit
- **BUF**: Bottom Ash and Fly Ash Collection Unit

**Definitions**
- **SCR**: Selective Catalytic Reduction
- **CER**: Clean Energy Recuperator
- **DESP**: Dry Electrostatic Precipitator
- **WFGD**: Wet Flue Gas Desulfurization
TRAC™ and Finned tube in CER

TRAC™
(Triple Action Catalyst)

- TRAC™ has a higher oxidation activity of elemental mercury while keeping a very low SO₂ to SO₃ conversion rate.

Finned tube in CER

- This structure of finned tube has been used without any troubles for many years in commercial plants in Japan.
## Coal Analysis

<table>
<thead>
<tr>
<th>Coal brand</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>3.7</td>
<td>2.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Volatiles (% dry)</td>
<td>36.3</td>
<td>19.0</td>
<td>38.8</td>
</tr>
<tr>
<td>Fixed Carbon (% dry)</td>
<td>49.7</td>
<td>33.0</td>
<td>50.8</td>
</tr>
<tr>
<td>Ash (% dry)</td>
<td>14.0</td>
<td>47.9</td>
<td>10.3</td>
</tr>
</tbody>
</table>

### Proximate analysis

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (% daf)</td>
</tr>
<tr>
<td>H (% daf)</td>
</tr>
<tr>
<td>O (% daf)</td>
</tr>
<tr>
<td>N (% daf)</td>
</tr>
<tr>
<td>S (% daf)</td>
</tr>
<tr>
<td>Hg (ppb, daf)</td>
</tr>
<tr>
<td>Cl (ppm, daf)</td>
</tr>
</tbody>
</table>

### Ash analysis

| CaO (% ash) | 14.7 | 3.01 | 6.18 |
## Gas composition at SCR inlet

<table>
<thead>
<tr>
<th>Coal Brand</th>
<th>Component</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exhaust gas amount (m³N/h)</td>
<td>1050</td>
<td>850</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td>CO₂ (% dry)</td>
<td>13.5</td>
<td>8</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>O₂ (% dry)</td>
<td>3.5</td>
<td>8</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>H₂O (%)</td>
<td>10 * Two times 31</td>
<td>14 * four times 40</td>
<td>10 * four times 30</td>
</tr>
<tr>
<td></td>
<td>SO₂ (ppm, dry)</td>
<td>170 → 350</td>
<td>1000 → 4000</td>
<td>2000 → 8000</td>
</tr>
<tr>
<td></td>
<td>SO₃ (ppm, dry)</td>
<td>7</td>
<td>29</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Hg (μg/m³N, dry)</td>
<td>4</td>
<td>7</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>HCl (ppm, dry)</td>
<td>26</td>
<td>54</td>
<td>35</td>
</tr>
</tbody>
</table>

At DESP inlet temperature: 90°C (194°F)
Hg and SO$_3$ Behavior in Oxy-fuel Combustion
Hg behavior of oxy-fuel combustion with coal A

(a) Without CER (DESP inlet temp 160℃ (320°F))  (b) With CER (DESP inlet temp 90℃ (194°F))

- Hg removal across DESP increased from 77% to 92% by decreasing DESP inlet temperature from 160℃ to 90℃
Relationship between Hg removal and Hg Conc.

- The amount of Hg re-circulated to the furnace was decreased as Hg was removed by the DESP.
Effect of HCl on Hg oxidation across the SCR

Hg oxidation across SCR (%) vs. HCl concentration at SCR inlet

- Hg oxidation across SCR increased with HCl conc. in both air and oxy comb.
- Original chlorine content of coal was high enough to oxidize Hg efficiently

Coal A | Coal B
---|---
Air comb. | ○ | □
Oxy comb. | ● | ■

Oxy-fuel comb. SCR inlet temp. 380°C (716°F)
Effect of flue gas temperature on Hg removal across DESP

- CER system was very effective in removing Hg

### Table

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Coal A</th>
<th>Coal B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area of ash</td>
<td>m²/g</td>
<td>8.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### Graph

- Flue gas temperature at DESP inlet (°C)
  - Oxy-fuel comb.
  - SCR inlet temp.
  - 380°C (716°F)
  - CER range

- Graph showing Hg removal across DESP (%) with flue gas temperatures ranging from 0 to 200 °C (32 °F to 392 °F) for Coal A and Coal B.
SO₃ Behavior of Oxy-fuel Combustion of Coal B

- SO₃ conc. at DESP outlet decreased to less than 1ppm by using CER.

**Oxy-fuel comb.**
- SCR inlet temp.: 380°C (716°F)

**Carbon Steel**
- Temp.: 90°C (194°F)
- Moisture: 30%

**Target**
- SCR in
- CER in
- DESP in
- DESP out

<table>
<thead>
<tr>
<th>Coal</th>
<th>Without CER (DESP 160°C=320°F)</th>
<th>With CER (DESP 90°C=194°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Coal C**: higher S, lower ash

**Burner**
- **O₂**
- **Coal**
4. Conclusion

(a) Hg concentration at the SCR inlet for oxy-fuel combustion was higher than that for air combustion due to the re-circulation of flue gas containing Hg.

(b) The sum of Hg$^{++}$ and Hg(p) at the SCR outlet was 92% of the total Hg under oxy-fuel combustion condition.

(c) Both Hg and SO$_3$ removal increased across the DESP as the gas temperature at the DESP inlet was reduced by a CER. SO$_3$ concentration at DESP outlet decreased to less than 1ppm. Therefore, corrosion of the equipment and ducts of oxy-fuel combustion system can be prevented.
This study was partly carried out under the contract with New Energy and Industrial Technology Development Organization (NEDO) of Japan for fiscal years 2007-2010.