Development of the Highly Durable COS Hydrolysis Catalyst for IGCC Gas Clean-up System

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Photo: 250MW IGCC Demonstration Plant @Nakoso, Japan

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Outline

• Update of Nakoso Demonstration Plant
• MHI IGCC System
• MHI Gas Clean-up System
• Characteristic of MHI COS Hydrolysis Catalyst
• Results of Demonstration Test
250MW IGCC Demonstration Plant (Nakoso)

- **Gasifier**
- **HRSG**
- **GT / ST**
- **Gas Clean-Up**

**MHI**
- Single Point Responsibility (EPC Turn-Key Contract)
  - Power Plant Section
  - Chemical Section

**METI**
- Ministry of Economy, Trade and Industry
  - 30% Subsidy

**Clean Coal Power R&D Co., Ltd.**
- 70% Contribution
- Researchers

**Hokkaido EPCo.**
- Tohoku EPCo.
- Tokyo EPCo.
- Chubu EPCo.
- Kansai EPCo.
- Chugoku EPCo.
- Kyushu EPCo.
- J-Power
- CRIEPI

**Joint Project Agreement**
- Power Plant Section
- Chemical Section
2007 ~ 2010

- Project execution went on Schedule.
- Operation started Sep. 2007
  - 100% Load
  - 2,000hrs. Continuous Operation completed (2008)
- Various testing activities
  - Coal Change / Load Swing / Efficiency Improvement, etc.
  - 5,000hrs. Durability Test completed
  ⇒ Subsidy from METI ended

2011 ~

- Coal Change / Load Swing / Efficiency Improvement, etc.
- 18,000 hrs. Operation
## Targets & Achievement of Demo. Plant

<table>
<thead>
<tr>
<th>Performance</th>
<th>Targets</th>
<th>Achievements</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output</td>
<td>250MW</td>
<td>250MW</td>
<td></td>
</tr>
<tr>
<td>Efficiency (Net, LHV)</td>
<td>&gt; 42.0%</td>
<td>42.9%</td>
<td></td>
</tr>
<tr>
<td>Carbon Conversion</td>
<td>&gt; 99.9%</td>
<td>&gt; 99.9%</td>
<td></td>
</tr>
</tbody>
</table>

| Emission (@dry, 16%O<sub>2</sub>) | SOx      | < 8 ppm  | 1.0 ppm  |
|                                    | NOx      | < 5 ppm  | 3.4 ppm  |
|                                    | Dust     | < 4 mg/m³N | < 0.1 mg/m³N |

<table>
<thead>
<tr>
<th>Operational Flexibility</th>
<th>Coal tested</th>
<th>Bituminous Sub-bituminous</th>
<th>Chinese, PRB 3 Indonesian Subs Colombian, Russian</th>
<th>Continuously testing other coals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start-up Time</td>
<td>&lt; 18 hr</td>
<td>15 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minimum Load</td>
<td>50%</td>
<td>36%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ramping Rate</td>
<td>3%/min</td>
<td>3%/min</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Reliability</th>
<th>Long-term Continuous Operation</th>
<th>2,000 hr</th>
<th>2,238 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-term Reliability Run</td>
<td>5,000 hr</td>
<td>5,013 hr</td>
<td></td>
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</table>

- All of the demonstration targets have been achieved.
- Future plan focuses on the further improvement of operational flexibility.
MHI Supplied All the Key Components
Each Section of MHI

Gasification Section
- Gasifier

Combined Cycle Section
- Gas Turbine
- Steam Turbine

Gas Clean-up Section

Remove impurities and purify the raw syngas.

- Impurities: H₂S, COS, NH₃, HCl, HCN and etc.
- Impurities cause corrosion problem
- Use chemical wet scrubbing to purify (ex. MDEA)
COS hydrolysis reaction

COS + H₂O $\rightarrow$ H₂S + CO₂

( COS + H₂ $\rightarrow$ H₂S + CO )

COS can’t be removed with amine solvent, it needs to convert to H₂S with COS hydrolysis catalyst.

HCN + H₂O $\rightarrow$ NH₃ + CO

HCN hydrolysis reaction is also occurred at the same operating condition as COS hydrolysis catalyst.

* HCN : Deadly poison gas in gasification raw syngas
Characteristics of MHI catalyst

1. High durability against impurities in syngas
   High durability against halogen, COS hydrolysis catalyst fit in front of halogen removal system.

2. High COS hydrolysis performance at high temperature
   Reaction temperature: 300 ºC (572 ºF)

3. Low pressure drop and less plugging
   Honey-comb shaped module
Honey-comb shaped catalyst

Low pressure drop and less plugging

- Honey-comb shaped module
- Less plugging than pellet typed catalyst
- Many experiences of MHI SCR honey-comb shaped catalyst
History of the catalyst development

R&D has been carried out step by step to commercialize the new catalyst

Evaluation by MHI 24T/D Pilot Plant

Labo. Test @ Hiroshima R&D Center

Pilot Test (Honey-comb shaped) 24tpd

Demonstration Test 1,700tpd

Scale-up 3,600tpd

Commercial
History of the catalyst development

**Testing more than 18,000 hr at Demo. Plant**
- Changing the load of the plant
- Syngas from several types of coal

The demo. plant is now in operation and the catalyst test still continues

**MHI catalyst is ready to offer for commercial IGCC plant**

- **Pilot Test** (Honey-comb shaped)
  - 24tpd
- **Labo. Test** @ Hiroshima R&D Center
- **Demonstration Test**
  - 1,700tpd
- **Scale-up**
  - 3,600tpd

Evaluation by Nakoso Demo. Plant
Results of Demo. Test (~16,000hr) @Nakoso

Stable & High Performance
• The measured value is consistent with **prediction from rate equation**

• High COS hydrolysis **performance with 1~100 ppm halogen** in syngas

• **No replacement** of the catalyst from 2007~present

• Syngas from several types of coals have tested

• HCN Conversion : > 99%
Comparison of Gas Clean-up System

(a) Conventional system

- Syngas to GT
- COS Converter
- Washing Tower
- H₂S Absorber
- Re-heating
- Water wash (decrease temp.)
- Scrubber
- Removes dust and halogen

(b) MHI system

- Syngas to GT
- COS Converter
- Washing Tower
- H₂S Absorber
- Minimize heat loss
- 300°C 572°F
(a) Conventional (ex.)

Waste Water → Chemical → Ca and F removal → Ozone → Cyanide oxidation → Chemical → Heavy metals removal → Evaporation → Salt

(b) Use of MHI COS hydrolysis Catalyst

Waste Water → Chemical → Ca and F removal → No cyanides → Chemical → Heavy metals removal → Chemical → Evaporation → Steam → Salt

- Improve OPEX and CAPEX
- Safe process (no cyanides)
## Advantages of MHI Catalyst

<table>
<thead>
<tr>
<th></th>
<th>MHI</th>
<th>Other</th>
</tr>
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<tbody>
<tr>
<td>Process</td>
<td>◎ Simple</td>
<td>△ Complex</td>
</tr>
<tr>
<td>Pressure drop</td>
<td>◎ Honey-comb</td>
<td>△ Pellet</td>
</tr>
<tr>
<td>Waste water treatment</td>
<td>○ No cyanide</td>
<td>△</td>
</tr>
<tr>
<td>Plant efficiency</td>
<td>◎ Excellent</td>
<td>○ Good</td>
</tr>
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There are many advantages of MHI Catalyst
Conclusion

• Nakoso IGCC demo. plant is now in operation and all of the targets have been achieved

• COS hydrolysis performance is confirmed from 18,000 hrs demonstration test

• MHI designed gas clean-up system minimizes the energy loss and provides highest reliability

MHI offers COS Hydrolysis Catalyst based on our own technology.