Post-Combustion Carbon Capture from Flue Gas

June 4 2015
1. MHI Overview

2. Carbon Capture's Role in Reducing Carbon Emissions

3. MHI’s Carbon Capture Technologies
1. MHI Overview
MITSUBISHI Group

“Mitsubishi” means “Three Diamonds”

Mitsubishi Group is the largest Japanese conglomerate, which shares the Mitsubishi brand, trademark and legacy since 1870.

Companies of Mitsubishi Group:

Mitsubishi Heavy Industries (MHI)
Mitsubishi Corporation
The Bank of Mitsubishi-Tokyo UFJ
Tokyo Marin & Nichido Fire Insurance
Mitsubishi Motors (MMC)
Mitsubishi Electric (MELCO)
Nikon
Kirin Brewery, etc.
Total 29 core companies and those group companies
Delivering Comprehensive Solutions - Smart Community

Contribution to realize a Low-Carbon Society with the Integrated solutions of technologies.
“With these hands, we build”

https://www.youtube.com/watch?feature=player_detailpage&v=UZ-5qX1la00
2. Carbon Capture's Role in Reducing Carbon Emissions
Climate Change since 1850

(a) Globally averaged combined land and ocean surface temperature anomaly

Figure SPM.1 (a)
Annually and globally averaged combined land and ocean surface temperature anomalies relative to the average over the period 1986 to 2005. Colours indicate different data sets.

(b) Globally averaged sea level change

Figure SPM.1 (b)
Annually and globally averaged sea level change relative to the average over the period 1986 to 2005 in the longest running dataset. Colours indicate different data sets. All datasets are aligned to have the same value in 1993, the first year of satellite altimetry data (red). Where assessed, uncertainties are indicated by coloured shading.

Atmospheric CO₂ at the Mauna Loa Observatory
(Data from NOAA-ESRL)

Anthropogenic GHG emissions have continued to increase over 1970 to 2010, and CO₂ emission from fossil fuel combustion and industrial processes contribute about 78% of total emissions.

Carbon Capture from Industrial sources is very important to mitigate Global warming!!
Post-Combustion Carbon Capture (PCC)
# Carbon Capture system

## Post Combustion

- **Boiler**
- **EP DeSOx**
- **CO₂ Capture**
- **Solvent**
- **CO₂**

Inputs:
- **Air**
- **Coal**

Processes:
- **Air separation**
- **EP DeSOx**

## Oxy-Fuel Combustion

- **Boiler**
- **EP DeSOx**
- **Air separation**
- **Cooling**
- **H₂O**
- **CO₂**

Inputs:
- **Air**
- **O₂**
- **Coal**

Processes:
- **Air separation**
- **EP DeSOx**
- **Cooling**

## Pre Combustion

- **Gasification**
- **IGCC**
- **Reformer**
- **Gas cleanup**
- **Pressurized CO₂**
- **CO₂ Capture**
- **Solvent**
- **CO₂**

Inputs:
- **Air**
- **Coal**

Processes:
- **Gasification**
- **Reformer**
- **Gas cleanup**
- **Pressurized CO₂**
Post-combustion Capture from Coal-fired Boiler

(A) SCR
Selective Catalytic NOx Removal

(B) EP
Electrostatic Precipitator

(C) FGD
Flue Gas Desulfurization

(D) CO2 Capture

Clean Flue Gas

Stack

CO2 Capture

CO2 Compressor

De-NOx Catalyst
(Honeycomb Structure)
Case-1: LP steam extraction case
Steam System for Power Plant and CO₂ Capture (2/3)

Case-2: MP steam extraction case

BFP Turbine → CO₂ Capture (PCC) → Condenser → LP-1 Turbine → LP-2 Turbine → HP-IP Turbine → Deaerator → Boiler Feed Water Pump

Boiler Feed Water Pump → Regenerator Condenser (Option) → Deaerator → Boiler Feed Water Pump
Case-3: New Natural Gas Turbine

Existing steam system

Gas turbine + HRSG

Steam

Condensate

CO$_2$ Capture (PCC)
Energy Performance (Typical)

Calculation basis
- Subcritical Pulverized Coal Boiler
- CO₂ recovery 90% (LP steam extraction case without heat integration)

![Graph showing energy performance comparison between BASE and with PCC.](chart.png)

NETL, Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity, 2013, 1 – 5p
What is CO$_2$-EOR?
CO₂ Enhanced Oil Recovery (EOR) (1/2)

Facts about CO₂ EOR

Supercritical (fluid state) CO₂ is easily dissolved in crude oil under reservoir conditions.

This state increases flow-ability of crude oil to the production wells and enhances production.

Crude oil recovery ratio can be increased significantly by means of CO₂-EOR.
CO₂ Enhanced Oil Recovery (EOR) (2/2)

CO₂ Injection and Recycling System in EOR

Thermal Power Plant → CO₂ Capture → CO₂ Compression & Dehydration → CO₂ Injection Well → CO₂ Recycle Plant

Compression & Dehydration

Associated Gas → Separator → CO₂ → Natural Gas

NGL

Production Well → Tank → Crude Oil

Cap Rock

Oil Reservoir

Gas

CO₂

Crude Oil

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Canada – Weyburn CO₂ EOR Project

CO₂ Source: North Dakota Coal Gasification Plant
CO₂ Injection: 5000 T/D from Autumn 2001
EOR Start: 5,400 BBL/D incremental increase to crude oil recovery since 2002
In 2006, incremental crude oil recovery exceeded 10,000 BBL/D
CO₂ EOR the USA (Most CO₂ Sources are from Natural CO₂ Gas Reservoirs)

~3,000 Miles of CO₂ Pipe in U.S. Today…350,000 for Natural Gas.
As a global leader in industrial and infrastructure manufacturing, Mitsubishi Heavy Industries is creating commercially viable technology for capturing carbon emissions from coal-fired plants, while enhancing domestic oil production.

3. MHI’s Carbon Capture Technologies
Outline

1. History of R&D activity
2. Commercial experience
3. Carbon capture for coal-fired boiler
1. History of R&D activity

- Development of Proprietary amine
- High energy efficient process
- Patents
R&D, Pilot Plant and Engineering Head Quarters in Japan

MHI CO₂ Capture & FGD R&D Center
Hiroshima Pilot Plant
Hiroshima Bench Plant

1:1 scale test plant in Mihara
(400 MW equivalent)

10 tpd Matsushima pilot for testing coal fired flue gas (2006 ~ 2008)

Nanko 2 metric T/D (ton per day)
Natural Gas Fired CO₂ Capture Pilot Plant

Yokohama Engineering Head Quarters
<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>Started R&amp;D activities with Kansai Electric Power Company (KEPCO)</td>
</tr>
<tr>
<td>1991</td>
<td>Started a 2 ton per day pilot plant at KEPCO’s Nanko Power station</td>
</tr>
<tr>
<td>1994</td>
<td>Development of proprietary hindered amine solvent “KS-1®” and “KM CDR Process®” with KEPCO</td>
</tr>
<tr>
<td>1999</td>
<td>First commercial plant in Malaysia (200 ton per day, to enhance urea synthesis from the CO₂ recovered from a reformer flue gas)</td>
</tr>
<tr>
<td>2002</td>
<td>Started a pilot test for coal-fired power plant at MHI’s Hiroshima R&amp;D center</td>
</tr>
<tr>
<td>2003</td>
<td>High energy efficiency - Development of proprietary energy efficient process “Improved KM CDR Process“</td>
</tr>
<tr>
<td>2008</td>
<td>First commercial plant in Middle east (400 ton per day) which “Improved KM CDR Process“ applied</td>
</tr>
<tr>
<td>2011</td>
<td>World’s first - Started 500 ton per day fully integrated CCS demonstration plant with Southern Company for a coal-fired power plant at Alabama Power's James M. Barry Electric Generating Plant</td>
</tr>
<tr>
<td>2014</td>
<td>World’s Largest - Received an order for a PCC plant of 4,776 ton per day for EOR mainly promoted by NRG Energy Inc. and JX Nippon Oil &amp; Gas Exploration Corporation</td>
</tr>
</tbody>
</table>
Advanced CO₂ Capture Process – MHI’s Own Technology

1. CO₂ is recovered from the flue gas by contacting with KS-1™ solvent.
2. CO₂ is stripped from KS-1™ solvent in the Regenerator.
3. CO₂-rich solution is pumped into the upper section of the stripper.
4. The flue gas is cooled to a process desired temperature.
5. The flue gas is fed into the bottom section of the absorber and passed upward through the packing material inside the tower.
Solvent Comparison KS-1® V MEA

Amine Reaction Mechanism

- Mono-ethanol Amine (MEA)
  \[ 2 \text{R-NH}_2 + \text{CO}_2 \rightleftharpoons \text{R-NH}_3^+ + \text{R-NH-COO}^- \]

- Sterically Hindered Amine (KS-1)
  \[ 2 \text{R-NH}_2 + \text{CO}_2 \rightleftharpoons \text{R-NH}_3^+ + \text{R-NH-COO}^- \]

# Key feature is main KS-1 reaction mechanism requires only 1 mole of KS-1 to react with 1 mole of CO2 and H2O

Solubility of CO2 in KS-1 and MEA Solution

Corrosion Test Result

(Unit: mils per year)

<table>
<thead>
<tr>
<th></th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA</td>
<td>93.0</td>
<td>76.4</td>
</tr>
<tr>
<td>MEA + inhibitor</td>
<td>9.5</td>
<td>8.3</td>
</tr>
<tr>
<td>KS-1</td>
<td>3.1</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Test condition: 130 °C, in the presence of O2

Less corrosion
Improved KM CDR Process

Nanko Test Result

R&D start with KEPCO
Pilot start
First Commercial plant
400 TPD commercial plant
Improved KM CDR [PHASE I ]

500 TPD demonstration
Improved KM CDR [PHASE II ]

MEA 30 wt%
KS-1 development
Improved KM CDR [PHASE I ]
Improved KM CDR [PHASE II ]
Improved KM CDR [PHASE III ]
Improved KM CDR [PHASE IV ]

Energy Consumption

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MHI’s worldwide granted and pending patents
In the US: 82 granted, 78 pending (as of Nov. 2014)
2. MHI’s Commercial Experience

- General Use
- Chemical Use
- EOR / CCS
1. General Use

Beverages, Dry ice, Supercritical food application, Welding and etc.

2. Chemical usage of CO₂

■ Urea Synthesis

Natural gas | Urea | Extra H₂
---|---|---
CH₄ + H₂O + N₂ | CO(NH₂)₂ + H₂
3H₂ + N₂ + CO₂ | CO(NH₂)₂ + H₂O

■ Methanol Synthesis

Natural gas | Methanol | Extra H₂
---|---|---
CH₄ + H₂O | CH₃OH + H₂
3H₂ + CO₂ | CH₃OH + H₂O

3. CO₂ EOR (CCS)

- Supercritical CO₂ is easily dissolved in crude oil under reservoir conditions
- This state increases flow-ability of crude oil to the production wells and enhances production
MHI is a world leading LARGE-SCALE post combustion CO₂ capture technology licensor, with 11 commercial plants in operation.

Total operation hours = 620,000 hrs (As of April 2015)
MHI Commercial Experience for General Use

Client : “A” Chemical Company
Location : Kurosaki, Japan
Capacity : 283 T/D (Max 330 T/D)
Feed Gas : Fuel Oil / LNG fired Boiler
Process : KM CDR Process®
Solvent : KS-1® Solvent
Use of CO₂ : General Use
Start Up : October, 2005
MHI Scope : EPC & License Package
Increase of Urea Production

To install the flue gas CO₂ recovery unit can realize to maximize urea synthesis by balancing ammonia and CO₂.

- Maximize Urea Production
- Minimum Reconstruction
- Reduced CO₂ Emissions
MHI Commercial Experience for Urea Production

- **1999**: 210 t/d Malaysia
- **2006**: 450 t/d India
- **2006**: 450 t/d India
- **2006**: CO₂ Recovery (CDR) Plant – IFFCO Aonla Unit (India)
- **2006**: CO₂ Recovery (CDR) Plant – IFFCO Phulpur Unit (India)
- **2009**: 450 t/d India
- **2009**: 450 t/d Bahrain
- **2010**: 400 t/d UAE
- **2010**: 240 t/d Vietnam
- **2011**: 340 t/d Pakistan
- **2012**: 450 t/d India
Increase of Methanol Production

Case-1: CO2 Recovery - CO2 Injection at Reformer Inlet

1. NG → REFORMER → COMPRESSION → SYNTHESIS → DISTILLATION → MeOH
2. FLUE GAS → CO2 RECOVERY

Case-2: CO2 Recovery – CO2 Injection at Reformer Outlet before Compression

1. NG → REFORMER → COMPRESSION → SYNTHESIS → DISTILLATION → MeOH
2. FLUE GAS → CO2 RECOVERY
MHI Commercial Experience for Methanol Production

- World’s largest plant for Methanol application
- Captured CO₂ is utilized to boost Methanol production

Client : Qatar Fuel Additives Co. Ltd. (QAFAC)

Location : Mesaieed, Qatar

Capacity : 500 T/D

Feed Gas : Methanol Plant Reformer

Start Up : July, 2014

MHI’s Scope : Licenser + EPC

Methanol Production Flow with CO₂ Recovery Plant

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3. MHI’s Carbon Capture for Coal-fired Boiler
   - 500 tpd Demonstration Plant
   - 4776 tpd Commercial Plant for EOR
500 tpd Demonstration Plant
FULLY INTEGRATED carbon capture & storage project with CO₂ storage, by SECARB and Owner, in a saline formation at a nearby oil field

- Location: Alabama Power, James M. Barry Electric Generating Plant
- Partners: Southern Company, MHI & EPRI
- Flue Gas Source: Pulverized Coal Fired Boiler
- CO₂ Capacity: 500 Metric Ton / Day
- Process: KM-CDR Improved Process
- Solvent: KS-1® solvent
- Start Up: June 3, 2011
- Status: 100% load since June 22, 2011
  CO₂ injection started on August 20, 2012
Demonstration Plant Overview

CO₂ Absorber

Regenerator

CO₂ Compressor

Inlet Gas from FGD
Construction Progress Photos
Construction Progress Photos
Summary of Test Results

1. Long term operation test
2. Automatic operation control system
3. Amine emission reduction system
4. Online amine analyzer
### 1. Operation Status

<table>
<thead>
<tr>
<th>Items</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Operation Time</td>
<td>12,400 hrs *</td>
</tr>
<tr>
<td>Total Amount of Captured CO₂</td>
<td>230,100 metric tons *</td>
</tr>
<tr>
<td>Total Amount of Stored CO₂</td>
<td>115,500 metric tons *</td>
</tr>
</tbody>
</table>

(* As of August 31, 2014)
1. CO₂ Quality

- CO₂ purity is more than 99.9% and impurities concentrations are low.
- Moisture concentration in CO₂ was 200~400 ppm.
- CO₂ quality was satisfied with the criteria of CO₂ pipeline and injection site.

<table>
<thead>
<tr>
<th>Carbon Dioxide (CO₂) Analysis Performed by Denbury</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Purity [vol%]</td>
<td>99.9+</td>
</tr>
<tr>
<td>Hydrogen (H₂) [ppm vol]</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Oxygen (O₂) + Argon (Ar) [ppm vol]</td>
<td>38</td>
</tr>
<tr>
<td>Nitrogen (N₂) [ppm vol]</td>
<td>210</td>
</tr>
<tr>
<td>Carbon Monoxide (CO) [ppm vol]</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Ammonia (NH₃) [ppm vol]</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Nitrogen Oxides (NOₓ) [ppm vol]</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Phosphine (PH₃) [ppm vol]</td>
<td>&lt;0.25</td>
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<tr>
<td>Total Hydrocarbons [ppm vol as CH₄]</td>
<td>8.1</td>
</tr>
<tr>
<td>Methane (CH₄) [ppm vol]</td>
<td>0.3</td>
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<tr>
<td>Total Non-Methane Hydrocarbons [ppm vol as CH₄]</td>
<td>7.7</td>
</tr>
<tr>
<td>Acetaldehyde [ppm vol]</td>
<td>7.9</td>
</tr>
<tr>
<td>Aromatic Hydrocarbons [ppb vol]</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Total Sulfur Compounds [ppm vol]</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
2. Automatic operation control system

- Power plant load and the flue gas condition changes frequently.
- **The automatic operation control system is to maximize the efficiency of Carbon capture.**

![Graph showing power plant load and carbon capture load over time.](image)

: Automatic control depending on a boiler load, the flue gas condition and CO₂ demand
2. Test result of automatic operation

Confirmed
- Load change at 5% per minute without any adverse effect
- Automatically and continuously optimization

Very Stable!!

Manual operation

Automatic operation control system
3. Amine Emission from Absorber

**Amine Emission**

- Amine vapor
  - Evaporated amine from the CO$_2$ absorption section

- Amine mist
  - Entrained mists/droplets or Aerosols generated by amine and CO$_2$ reaction, etc

  - High sensitivity to SO$_3$ in flue gas
3. Pilot test Result - $SO_3$ influence on Amine emission

- CO$_2$ recovery testing from simulated flue gas at Hiroshima R&D center, MEA solvent
- Down stream of CO$_2$ absorber, white smoke was raised by SO$_3$ contained in the gas

<table>
<thead>
<tr>
<th>SO$_3$</th>
<th>0ppm</th>
<th>3ppm</th>
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<tbody>
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<td>Quencher</td>
<td><img src="image1.jpg" alt="Image" /></td>
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<td>Outlet</td>
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<td><img src="image4.jpg" alt="Image" /></td>
</tr>
<tr>
<td>Absorber</td>
<td><img src="image5.jpg" alt="Image" /></td>
<td><img src="image6.jpg" alt="Image" /></td>
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<tr>
<td>Washing</td>
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<td>Section</td>
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<tr>
<td>Outlet</td>
<td><img src="image11.jpg" alt="Image" /></td>
<td><img src="image12.jpg" alt="Image" /></td>
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</table>
3. Amine Emission Evaluation

- Amine emissions increased significantly with a small amount of SO₃.
  → It will cause the solvent consumption significantly.
- MHI’s amine emission reduction system decreases amine emission down to less than 1/10 of the emissions of the conventional system.
- The system is effective to maintain the low solvent consumption.

---

**Fig. Relationship between SO₃ conc. and solvent emission**

**Fig. Absorber top**

Low SO₃ in the gas

High SO₃ in the gas
MHI developed a proprietary online analyzer to monitor the **process conditions** and amine emissions.

The online analyzer improved **plant operability and controllability**.

**Fig. Online Amine Analyzer**

**Fig. Periodic Results of CO₂ Concentration Trends in KS-1® Solvent**
4,776 tpd Commercial Plant for EOR
MH1’s Scale up for Coal-fired CO2 Capture

From pilot to full scale

Pilot
1 TPD Scale

Small Scale Demonstration
500 TPD

Large Scale Demonstration
500 TPD

Full Scale
5,000 TPD

Know-how and Lesson learned from 11 commercial plants

Co2 Recovery (CDR) Plant – IFFCO Phulpur Unit (India)

Co2 Recovery (CDR) Plant – IFFCO Aonla Unit (India)

Simulator (CFD etc.)

Large Scale experience for FGD
- Large amount of flue gas
- More than 200 commercial plants
World’s largest CO₂ capture plant from an existing coal-fired power plant

- **Project Owner:** NRG Energy Inc. and JX Nippon Oil & Gas Exploration Corporation
- **Location:** NRG WA Parish Power Plant near Houston, TX.
- **Flue gas source:** 240MW slipstream from existing 650MW coal-fired boiler
- **Plant Capacity:** 4,776 metric ton/day
- **CO₂ recovery ratio:** 90%
- **CO₂ Use:** Enhanced Oil Recovery (EOR)
- **Injection Site:** West Ranch oilfield in Jackson County, TX
- **Operation Start:** 4th Quarter, 2016

*Artist Rendering*
WA Parish CO₂ EOR Overall System

Coal fired boiler

Flue gas → CO₂ Capture

CO₂ Compression & dehydration

Supercritical CO₂ → Oil field

Pipe line

Oil production

Electric power selling

Gas Turbine

Natural gas

Flue gas → Heat Recovery Steam Generation (HRSG)

Steam

Electric power generating

Selling

Electric power selling
Captured and compressed CO₂ from W.A. Parish Power Plant will be delivered by 80 mile CO₂ pipeline to the West Ranch oil field.

1.4 million metric tons of greenhouse gas will be annually injected into the West Ranch formation.

It is expected that oil production will be enhanced from 500 barrels/day to approx. 15,000 barrels/day.
Project Progress

Key Progress

- Signed EPC contract, Issued LNTP: Mar 2014
- Issued Final Notice to Proceed (FNTP): Jul 2014
- Construction start: Sep 2014

- Foundation work almost completed
- Structure work on going
- Operation Start: 4th Quarter, 2016

Site Photo (2015/5/12)
MHI’s Technology for Future

MHI’s Carbon Capture Technology

EPC Experience for Large Scale

Optimization Cost System

CO₂ ppm

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Thank you.