Abstract

The Petra Nova Project will be the world’s largest post combustion CO₂ capture plant on coal fired flue gas once it begins operation expected in the 4th Quarter of 2016. The CO₂ capture plant uses MHI’s KM CDR Process™ which has been in development by Mitsubishi Heavy Industries, Ltd. (MHI) in collaboration with the Kansai Electric Power Co., Inc. (KEPCO) since 1990 and has been refined through the application of lessons learned from other commercial plants and R&D projects. MHI continues to improve its technology by focusing on developing more efficient systems and reducing CO₂ capture costs. MHI demonstrated a 25 MW heat integration technology using (Mitsubishi Hitachi Power Systems Ltd.) MHPS’s High Efficiency System (HES) with Southern Company Services. The project resulted in significant heat recovery and improvements in pollutant capture performance in the electrostatic precipitator (ESP). MHI also evaluated the performance of a new, novel solvent at a 2 tpd pilot test plant in Japan. The pilot test results show lower steam consumption, solvent degradation, and solvent emissions than those of KS-1™ solvent. MHI plans to continue developing the new solvent until it is ready for commercial deployment. Through R&D and through the collection of lessons learned from commercial plants, MHI is working towards reducing the cost and the environmental footprint of CO₂ capture.

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1. Introduction

As part of the United Nations Framework Convention on Climate Change (UNFCCC), representatives from 197 countries adopted the Paris Agreement to combat climate change and invest in a low carbon future. The agreement will be enforced 30 days after 55 countries ratify the agreement and after 55% of the total global greenhouse gas emissions are accounted for by the ratifying countries. As of September 22, 2016, 60 countries including, China and the United States, have ratified the agreement marking one of two thresholds required for enforcement of the treaty. One of the major goals of the Paris Agreement is to maintain global temperature rise below 2°C above pre-industrial levels. As such, the Paris Agreement is expected to accelerate reductions in greenhouse gas emissions [1].

Widespread adoption of CO₂ Capture and Storage (CCS) is essential to achieving the goals set out by the Paris Agreement. Solvent-based absorption is a proven technology and is at the forefront of CCS technology commercialization. It is, however, generally recognized that one of the main challenges to widespread global adoption is cost reduction.

Mitsubishi Heavy Industries, Ltd. (MHI) has been developing its solvent-based technology since 1990 and continues to improve the process through lessons learned from commercial deployment and through R&D. Through these projects, MHI continuously works to reduce both the capital cost and the operational cost of CCS.

In this paper, MHI presents background information on its newest and largest project at NRG’s W. A. Parish Plant and on results from two R&D projects on heat integration and a new solvent.

2. Development of MHI’s CO₂ capture technology

MHI developed a high efficiency chemical solvent process called the KM CDR Process™ (Kansai Mitsubishi Carbon Dioxide Recovery Process) in collaboration with the Kansai Electric Power Co., Inc. (KEPCO).

Initially, MHI’s vision was to replace MEA with a superior solvent for CO₂ capture. This led to the development of a laboratory scale test program which evaluated more than 200 different solvents. MHI narrowed those solvents down to 20 and tested them at its first pilot plant at KEPCO’s Nanko Power Plant in 1991. The pilot plant has a 2 metric tons per day (tpd) CO₂ capacity and is capable of evaluating the CO₂ capture performance of various solvents. The pilot plant test program resulted in the joint development and commercialization of the proprietary KS-1™ solvent which is an advanced sterically hindered amine-based solvent. The development of KS-1™ is seen as a major technological breakthrough due to the significant number of advantages it offers over MEA. KS-1™ has exceptionally low corrosivity, high stability, and high CO₂ loading.

MHI continues to use the 2 tpd pilot plant to develop new solvents, new process scheme, and new equipment to reduce amine emissions and costs.

MHI has deployed 11 commercial CO₂ capture plants ranging in CO₂ capture capacity from 200 to 500 tpd. Most of these commercial plants capture CO₂ from natural gas-fired flue gas to enhance urea production for the chemical and fertilizer industries. MHI’s most recent plant built in Qatar captures CO₂ from natural gas-fired flue gas to enhance methanol production.

Understanding that one of the greatest challenges of our time is the reduction of CO₂ emissions from electricity generation, MHI has been tailoring its KM CDR Process™ to the unique challenges of coal-fired flue gas. In 2006, MHI completed several test programs on a test facility with a 10 tpd slip stream from the flue gas of a commercial 500MW coal fired power plant in Matsushima, Japan. Long term operation of this plant verified the impact of coal fired flue gas impurities on the KM CDR Process™ and allowed MHI to develop countermeasure technologies.

Along with Southern Company, Mitsubishi Heavy Industries America, Inc. (MHIA) demonstrated the viability of its technology on a 25 MW scale demo plant with a 500 tpd CO₂ capacity at Alabama Power’s Plant Barry. From 2011 to 2014, approximately 200,000 tons of CO₂ were captured and more than 100,000 tons of captured CO₂ were successfully injected into the Citronelle Dome as part of the Department of Energy (DOE) funded Southeast Regional Carbon Sequestration Partnership (SECARB) Phase-III “Anthropogenic Test”. Over the course of the
program, the demo plant has operated and generated invaluable information on the challenges of coal-fired post-combustion CO₂ capture. MHIA was able to successfully demonstrate key features of the technology including the stability of the KS-1™ solvent, amine emissions reduction, heat integration, and automatic load following control.

The combination of these experiences resulted in development of the world’s largest CO₂ capture and compression plant for a coal-fired boiler at NRG’s W. A. Parish Plant in Thompson, TX, southwest of Houston. The carbon capture plant, owned by Petra Nova Parish Holdings (a joint venture between NRG Energy and JX Nippon Oil & Gas Exploration), will process a 240 MW equivalent slipstream from a 650 MW coal-fired boiler. 4,776 tpd of CO₂ will be transported 130 km to the West Ranch Oil Field near the Gulf Coast. CO₂ injection is expected to increase oil production from 500 barrels per day (bpd) to 15,000 bpd.

In addition, MHI has started construction on its thirteenth plant in Japan and is scheduled to complete construction in October 2017. The plant will capture 283 tpd, and the captured CO₂ will be used in the liquefied carbonic acid gas production facilities. Fig. 1 shows the location of MHI’s 13 commercial projects and the large-scale demonstration project with Southern Company.

![Fig 1. Map of KM CDR Process™ commercial and large scale demonstration plants.](image)

### 3. Overview of the Petra Nova Project

Mitsubishi Heavy Industries America, Inc. (MHIA) and TIC (The Industrial Company) formed a consortium to design and build the 4,776 tpd CO₂ capture plant for Petra Nova in Thompson, Texas. Table 1 shows the basic overview of the plant, and Fig. 2 is an artist’s rendering of the W. A. Parish Plant with the CO₂ capture plant. Construction started in July 2014, and operation is expected to start in the 4th Quarter of 2016. The DOE is providing $190M in financial assistance through the Clean Coal Power Initiative (CCPI) which supports the growth, deployment and commercialization of CO₂ capture technologies.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
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<tbody>
<tr>
<td>Location</td>
<td>NRG W. A. Parish Power Plant in Thompsons, TX</td>
</tr>
<tr>
<td>Project Owner</td>
<td>Petra Nova, a partnership between NRG Energy, Inc. and JX Nippon Oil &amp; Gas Exploration Corporation</td>
</tr>
<tr>
<td>Flue Gas Source</td>
<td>240 MW slipstream off of 650MW coal-fired boiler flue gas</td>
</tr>
<tr>
<td>CO₂ Capture Capacity</td>
<td>4,776 TPD (240 MW equivalent)</td>
</tr>
<tr>
<td>CO₂ Capture Ratio</td>
<td>90%</td>
</tr>
<tr>
<td>Operation Start</td>
<td>Expected for 4th Quarter, 2016</td>
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The system has minimal tie in points with the existing plant and no parasitic energy loss. The steam and electricity required for the CO₂ capture plant are supplied from a separate gas turbine (GT) and heat recovery steam generator (HRSG). The GT was previously built to provide electricity during peak season while the HRSG was added to provide steam for the CO₂ capture plant. The CO₂ capture plant also requires a new cooling tower to supply cooling water. Fig. 3 shows the relationship between the existing plant and the CO₂ capture plant. The only tie-in to the existing plant is downstream of the FGD right before the stack.

4. Large scale CO₂ capture technology

MHI focuses its R&D on commercializing and promoting large scale CO₂ capture plants for CO₂ EOR and sequestration. A large part of this R&D has been dedicated to understanding how to increase the size of the process equipment to maintain optimum performance at commercial scales. Luckily, most of the equipment used at the CO₂ capture plants are commercially proven at commercial scales. The main difficulty in designing a large CO₂ capture plant is achieving proper gas and liquid distribution in the larger towers.
Uniform gas and liquid distribution are crucial to achieve desired CO₂ capture performance. MHI uses vapor distributors to uniformly distribute gas in the quencher, absorber, and regenerator. These distributors are validated by a computational flow dynamic (CFD) simulation study to ensure uniform distribution.

According to packing manufacturers, high performance packing is very sensitive to liquid distribution so extra care must be taken when developing liquid distributors. An added challenge for MHI is that while industry generally uses round towers, MHI decided to build its quencher and absorber as rectangular towers to simplify construction at the site. As such, MHI had to verify adequate liquid distribution in its rectangular towers. In 2008, MHI tested its liquid distributors at its test facility at Mihara Works. This test facility has a 400 MW eq absorber measuring 10.9m W x 5.4m L. MHI believes that it is the largest test facility in the world. MHI tested various distributor malfunctions to determine the effect on CO₂ capture performance. These malfunctions included installing the distributors at an angle and plugging half of the holes in the distributor. As to be expected, the mass transfer coefficient was affected by maldistribution of the liquid. The results of this test program and information from the manufacturer informed the final design and installment plan of the large distributors.

Based on the above, the 25 MW demo plant was confidently constructed with a rectangular quencher and a rectangular absorber. The CO₂ capture plant performed as expected and so MHI was able to focus on testing and refining other key features pertinent to commercialization. MHI applied these key features, proven at the 25 MW demo plant, to the Petra Nova Project. These features include:

- Amine emission reduction system
  - MHI was the first to discover that solvent emissions increased significantly with the presence of SO₃ mist [2]. As a countermeasure, a proprietary amine emission reduction system was tested at the demo plant and is included in the KM CDR Process™ for the Petra Nova Project.
- Solvent degradation reduction system
  - The Petra Nova Project was designed to reduce solvent degradation based on lessons learned from the demo plant and process calculations.
- Automatic load adjustment control system
  - MHI demonstrated the control system and achieved continuous stable operation at the demo plant. The system is applied at the Petra Nova Project to optimize operating conditions continuously.
- Amine purification system
  - Impurities introduced from the flue gas can degrade CO₂ capture performance. MHI successfully demonstrated a particulate control system and reclaiming process to maintain stable operation.
- Energy saving system
  - Multiple configurations and operating conditions were tested at the demo plant to reduce steam consumption. MHI took these lessons learned and properly optimized the process for the Petra Nova Project to achieve low utility consumption.

MHI’s extensive R&D, design, and operations experience gives MHI confidence that its technology can perform as designed at commercial power plant scales.

5. R&D update – Heat integration

5.1. Outline of HES Project

MHIA and Southern Company completed a 25-MW scale pilot demonstration of Mitsubishi Hitachi Power System (MHPS)’s High Efficiency System (HES) for a DOE project in 2015. The purpose was to evaluate the benefits of heat integration with the 25-MW scale CO₂ capture plant located at Plant Barry. The benefits demonstrated in this pilot include waste heat recovery and SO₃, mercury, and selenium removal improvements in the electrostatic precipitator (ESP). The HES recovered waste heat from the flue gas by incorporating a flue gas cooler downstream of the air pre-heater. Another heat exchanger, the CO₂ cooler, recovered heat from the CO₂ product stream downstream of the regenerator. This heat was applied to the boiler feed water, thereby reducing the
energy penalty for amine-based CO₂ capture plants. Reduced flue gas temperatures upstream of the ESP improves the removal performance of SO₃, PM, and toxic trace elements in the ESP such as selenium and mercury.

A block flow diagram of the 25-MW slip-stream demonstration test facilities, which was installed on Plant Barry Unit 5 (720 MW), is shown in Fig. 4.

Fig 4. Block flow diagram of the HES test facilities at Plant Barry.

5.2. Test results

The project evaluated the waste heat recovery performance of the HES’s flue gas cooler (FGC). Based on the pilot-scale results, MHI estimated 240-300 MMBTU/hr of heat recovery for a 550-MW base plant. MHI also confirmed that up to 65% of FGD makeup water could be reduced based on the calculation results from actual data. The HES also showed multi-pollutant removal performance as below:

- PM removal: > 99.5%
- SO₃ removal: < 0.05 ppm at ESP outlet
- Hg removal: > 85% w/o SO₃ injection, ~40% w/ SO₃ injection
- Se removal: > 98%

The improved removal performance positively impacts downstream systems. In a full-size plant, the FGD wastewater would have lower pollutant concentrations since less is coming into the system. The CO₂ capture plant would have lower amine emissions since less SO₃ is introduced with the flue gas.

The internals of the FGC were inspected before and after the operation (3-4 weeks without SO₃ injection and 3 weeks with SO₃ injection) and no significant corrosion was found on tube bundles and FGC internals. Sufficient ash loading effectively protected the tubes from sulfuric acid condensation. This supports the fact that carbon steel can be used for the construction material as opposed to a more expensive material such as stainless steel.

6. R&D update–New novel solvent

6.1. Initial screening

MHI computationally screened multiple solvents through a self-developed program based on MHI’s numerous operation data and solvent R&D knowledge. The program compared each new solvent being screened to KS-1™
and evaluated the amount of steam that would be consumed for each new solvent, the amount of amines that would be emitted, and the overall stability of the solvent [3].

After the computational screening, MHI performed laboratory scale tests to verify the actual performance and operability of the potential new solvent. As a result of the computational and laboratory screening, MHI has selected one candidate as its new and novel solvent to potentially replace KS-1™.

6.2. Pilot test unit

MHI and Kansai Electric Power Co., Inc. conducted a pilot scale test to evaluate the performance of the new solvent using the 2 tpd Nanko Pilot Test Plant in Japan. Table 2 shows the overview of the pilot test plant. The test used natural gas fired flue gas and mimic gas for coal-fired flue gas conditions to evaluate solvent performance on both types of gas. Since overall capture performance depends on the plant configuration and the utility condition, both KS-1™ and the new solvent were used in the test to compare performance under the same condition.

Table 2. Overview of Nanko Pilot Test Plant.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Nanko Power Plant in Osaka, Japan</td>
</tr>
<tr>
<td>Plant Owner</td>
<td>Kansai Electric Power Co., Inc.</td>
</tr>
<tr>
<td>Flue Gas Source</td>
<td>Slipstream off of NG boiler</td>
</tr>
<tr>
<td>CO₂ Capture Capacity</td>
<td>2 TPD (0.2 MW equivalent)</td>
</tr>
<tr>
<td>CO₂ Capture Ratio</td>
<td>90%</td>
</tr>
</tbody>
</table>

The main assessment points for this solvent screening project were steam consumption and solvent loss. Steam consumption determines the parasitic load required to run the CO₂ capture plant. A steam flow meter was used to measure steam consumption continuously. Solvent emissions from the top of the absorber could pose an environmental obstacle to technology adoption in locations where VOC emissions need to be kept to a minimum. During the test, gas samples were analyzed to compare solvent emissions between the new solvent and KS-1™. Solvent degradation should also be kept to a minimum to reduce reclaiming operations and to reduce the potential of solvent loss through reclaiming. Liquid samples were taken to monitor solvent degradation performance.
6.3. Test results

Table 3 shows the performance comparison between KS-1™ solvent and the new novel solvent. The new solvent performed better in terms of steam consumption, solvent degradation, and solvent emission. The new solvent required 5~10% less steam, decreased solvent degradation by almost half, and decreased solvent emissions by more than half when compared to KS-1™. The solvent circulation flow rate for the new solvent is higher than KS-1™ solvent. However, the difference in solvent rate only slightly increases electricity consumption, and the benefits of the new solvent are expected to outweigh this slight increase in electricity consumption.

<table>
<thead>
<tr>
<th>Performance</th>
<th>KS-1™</th>
<th>New Solvent</th>
</tr>
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<tbody>
<tr>
<td>Steam Consumption</td>
<td>1</td>
<td>0.92</td>
</tr>
<tr>
<td>Solvent Degradation</td>
<td>1</td>
<td>0.53</td>
</tr>
<tr>
<td>Solvent Emission</td>
<td>1</td>
<td>0.40</td>
</tr>
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</table>

The new solvent has proven to be a very promising successor to KS-1™ since it can potentially reduce the operational costs and the energy penalty of the power plant and reduce the environmental footprint of the CO₂ capture plant. For the next stage of solvent development, Southern Company Services, Inc. has applied for a new DOE-funded solvent demonstration program to test the new solvent at the 25 MW demo plant at Plant Barry. DOE awarded the Phase I of this study in October 2015. Basic design was conducted during this phase.

Acknowledgements

MHIA would like to acknowledge the DOE and Southern Company for their contribution to the HES project and Phase I of the solvent test at Plant Barry. We would also like to acknowledge our partners at AECOM who assisted in reporting and testing at the plant site for the HES project.

Finally, MHIA would like to acknowledge the DOE, NRG and JX for the international public-private partnership in the development of the sophisticated integrated project model that enabled the deployment of Petra Nova.

References