There is now a growing demand for coal, which provides countries throughout the world with a cheap, stable and abundant fuel source. The problem, from an environmental perspective, is that the combustion of coal produces large concentration of CO₂ which is the most abundant greenhouse gas contributing to global warming. Therefore, we and many scientists believe that CO₂ capture and sequestration (CCS) from coal-fired power plants will be an essential countermeasure against global warming in the future. Working in collaboration with Kansai Electric Power Co., Inc. (KEPCO), Mitsubishi Heavy Industries, Ltd. (MHI) has developed an outstanding technology – KM-CDR process to recover CO₂ from the flue gas of natural-gas-fired boilers and is now applying the technology at a commercial scale in several countries. However to be truly effective at reducing global CO₂ emission we must apply this technology to the coal-fired boilers. In recognition of this important fact MHI constructed a 10 ton/day demonstration plant at a coal-fired power station in Matsushima, Japan along with funding received from the Research Institute of Innovative Technology for the Earth (RITE) and in cooperation with Electric Power Development Co., Ltd. (J-POWER). MHI has recently completed 4,000 hours of demonstration operation at this site and this document seeks to provide a summary of those achievements.

1. Introduction
The prices of petroleum and natural gas are being pushed up by the concern that the supplies of these resources will run short in the near future. On the contrary, coal is relatively cheap and stably available over the long term. In fact, many analysts believe that coal-fired power generation is expected to become the main method of thermal power generation in the future.

There is an obvious problem, however, as coal-fired power plants release abundant CO₂. Thus, CCS for coal-fired power plants are essential countermeasure against global warming.

Working in collaboration with KEPCO, MHI has developed KM-CDR process to recovery CO₂ from the flue gas of natural-gas-fired boilers and gas turbines with high energy-saving performance (see Fig. 1). MHI has commercial delivery records which include facilities utilizing CO₂ for chemical processing and general use products (dry ice, etc.). One of these CO₂ recovery plants has been in operation since 1999 at a urea production facility in Malaysia and has achieved consistently high levels of performance (see Fig. 2).
The flue gas of coal-fired boilers includes SOx, dust, and other impurities not normally present in natural gas. Through the cooperation of RITE and J-POWER, MHI constructed a CO2 recovery demonstration plant which incorporated countermeasures capable of effectively removing these impurities prior to induction in the CO2 recovery plant. Demonstration by continuous operation commenced in July 2006. In this article we report on the results of this demonstration test and describe our approach moving forward in the future.

2. The need for CO2 recovery in coal-fired power stations

To continue using fossil energies for thermal power generation effectively in the coming years, we need to consider the options of both natural gas and coal. It is expected that petroleum will be used as a secondary fuel for thermal power generation to respond to peak demand. Large reserves of natural gas exist in Russia and the Middle East. However the production of natural gas is now forecasted to peak about 10 years following the peak in petroleum. With the recent dramatic rises in the price of natural gas, the ratio of fuel coal for electric power generation will continue to increase well into the future.

Gas-producing countries are expected to apply natural gas combined cycle (NGCC) to their newer thermal power stations, while other countries are expected to apply coal-fired power generation.

When we consider the countermeasures against global warming, we know that CCS will be essential as long as we continue to utilize fossil fuels. Research on CCS has made good progress in recent years, and there are now calls for concrete implementation. Thermal power stations account for about one-third of CO2 emissions worldwide and are concentrated sources of CO2 release. These stations are therefore extremely attractive sites for CCS implementation.

MHI has been developing CO2 recovery technology from the flue gases of power stations aiming an effective use of CO2 and a countermeasure against global warming. MHI commercialized the technology for application in boilers and furnaces that fire natural gas (a relatively clean flue gas). Our next aim is to commercialize this technology for application in coal-fired power stations, and thus we have commenced a demonstration test.

3. Technical considerations of CO2 recovery from coal-fired flue gas streams

The flue gas of coal-fired boilers contains SOx, NOx, dust and other impurities. For this reason it is critically important to develop this technology to achieve the following tasks:

(1) Confirming long-term operation
To monitor the operation of the CO2 recovery plant for a long period to confirm whether stable operation is possible with the assumed pretreatment equipment and to identify factors that hinder stable operation.

(2) Understanding the influences of dust
i. Understanding the capture efficiency
   Dust accumulation may lead to scaling of the equipment, plugging of strainers, and other undesirable impact. Equipment designs therefore need to significantly accommodate the potential impacts of dust accumulation. Successful design work requires accurate knowledge on the amounts of dust accumulated and the efficiency with which dust is captured in the various systems.
   ii. Understanding the influence on solvent
   Dust accumulation in the solvent may lead to an increased foaming tendency of the solvent. If the foaming tendency increases, the flooding (Note 1) occurs more readily in the regenerator and absorber, hindering stable operation of CO2 recovery plant. Therefore it becomes necessary to firstly confirm the interaction between the amount of dust in the solvent, the foaming tendency, and flooding phenomenon. We then design equipment and implement operational control strategies in response.
   Note 1: The rising gas restrains the descent of a flowing liquid in a packed column.
   iii. Understanding the influences on the equipment
   Dust in the liquid is known to scale and plug equipment and potentially reduce heat transfer efficiency. It thus becomes necessary to understand the influences of dust on the equipment, and to design the equipment and control the operation in response to those influences.

(3) Understanding the influences of SOx
i. Removal ratio in the flue gas desulphurization section
   SOx promotes the degradation of solvent. A flue gas desulphurization section using caustic soda is therefore installed to reduce the concentration of the SOx introduced into the absorber. It thus becomes necessary to confirm the removal ratio of SOx, in order to verify the desulphurization efficiency in the flue gas desulphurization section.
   ii. Understanding the influence on solvent
   The gas that passes through the flue gas desulphurization section may contain trace amounts of SOx. This trace level SOx may then accumulate in the solvent to produce heat-stable salts (Note 2). The behavior of these heat-stable salts therefore needs to be confirmed.
   Note 2: Compounds of acid and alkali that resist disassociation by steam heating.

(4) Understanding the influences of NOx
NOx influences the degradation of the solvent. It thus becomes necessary to identify the sections where NOx is absorbed in a CO2 recovery plant and to assess the amounts absorbed.
(5) Understanding the influences of chlorine and fluorine
The accumulation of chlorine and fluorine may lead to corrosion of the equipment. When selecting the materials for the equipment, it is important to identify the sections where chlorine and fluorine accumulate in a CO₂ recovery plant and to assess the amounts accumulated.

(6) Understanding solvent loss
The cost of solvent accounts for a large portion of the operation cost, next to that of steam. Therefore minimizing solvent loss is very important and accordingly, the solvent loss need be confirmed.

4. Demonstration test results
4.1 Outline of plant
Using a subsidy (subsidy of 50% cost share) under the "Technology Development Program to Promote the Achievement of the Kyoto Protocol" by RITE, and through cooperation of J-POWER, MHI was able to successfully construct the demonstration test plant at an existing coal-fired thermal power station in Matsushima. The test plant specifications and flow diagram are shown in Table 1 and Fig. 3, respectively.

4.2 Measurement methods and test results
(1) Monitoring of operational status
(a) Measurement methods
Input data relating to flow rates, temperatures, pressures, etc. into a computer model in time sequence, to characterize the operational status of the CO₂ recovery plant. Confirm the CO₂ purity by gas measurement.

(b) Test results
The installation of pretreatment equipment enabled stable operation over a long period (4,000 h) with no unexpected problems. Evaluations from the viewpoint of performance are shown below.

i. Efficiency and capacity of CO₂ recovery
Fig. 4 demonstrates the time sequence data of the CO₂ recovery efficiency calculated from the values indicated by CO₂ densitometers at the absorber inlet and outlet and the amount of CO₂ recovery measured using flow meters.

Performance values equivalent to or higher than the planned values could be obtained over the demonstration period (4,000 hours) for both the CO₂ recovery efficiency and CO₂ recovery capacity.

ii. Specific heat consumption required for CO₂ recovery
The most effective way to reduce plant operation costs is to minimize the steam consumption of the CO₂ recovery plant, the largest contributor to the operation cost. We calculated the specific heat consumption required for CO₂ recovery from the steam consumption and the CO₂ recovery capacity during this test, as shown below.

- Actual achievement of specific heat consumption required for CO₂ Recovery: 730 – 820 kcal/kg-CO₂

Though the design approach for the absorber and regenerator is almost the same as that for the natural-gas-fired boiler, the performance was superior to what was expected in terms of the specific heat consumption required for CO₂ recovery. Moreover, regarding the specific heat consumption required for CO₂ recovery, we expect to achieve a further reduction of about 15% by applying a new process (Note 3) (jointly developed by KEPCO and MHI) to the CO₂ regeneration process.

Note 3: Energy-saving process in the CO₂ regenerator using heat recovery from the solvent and steam condensate.

Table 1 Specifications of CO₂ recovery demonstration plant

<table>
<thead>
<tr>
<th>Items</th>
<th>Parameters (planned values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installation location</td>
<td>Within Matsushima Thermal Power Station owned and operated by J-POWER</td>
</tr>
<tr>
<td>Flue gas source</td>
<td>Flue gas coal-fired boiler</td>
</tr>
<tr>
<td>Amount of flue gas to be treated</td>
<td>1750 m³/h</td>
</tr>
<tr>
<td>CO₂ recovery efficiency</td>
<td>90%</td>
</tr>
<tr>
<td>CO₂ recovery capacity</td>
<td>Planned value: 9.5 ton/day (Max. 10 ton/day)</td>
</tr>
<tr>
<td>CO₂ concentration</td>
<td>14.1v%</td>
</tr>
<tr>
<td>Other impurities</td>
<td>Dust, SOₓ, NOₓ, etc.</td>
</tr>
<tr>
<td>Solvent</td>
<td>KS-1 solvent</td>
</tr>
</tbody>
</table>

![Flow diagram of CO₂ recovery demonstration plant](image)

![Movement of the CO₂ recovery efficiency and CO₂ recovery capacity](image)
iii. Purity of the recovered CO₂

Table 2 compares the commercial CO₂ recovery plant for the natural-gas-fired boiler and the new coal-fired demonstration CO₂ recovery plant.

The result shows that KM-CDR process achieved a high-purity equivalent compared to that of the natural-gas-fired boiler for the coal-fired boiler.

Table 2 Recovered CO₂ purity

<table>
<thead>
<tr>
<th>Actual performance of commercial plant with a natural-gas-fired boiler</th>
<th>Actual performance of this demonstration plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9 % or more</td>
<td>99.9 % or more</td>
</tr>
</tbody>
</table>

(2) Understanding the influences of dust

i. Understanding the capture efficiency

(a) Measurement methods

Clarify the amounts of dust accumulated and capture efficiencies in the respective sections of the CO₂ recovery plant by measuring the dust concentrations in both the gas and liquid. Table 3 shows the areas where the amounts of accumulated dust and capture efficiencies are assessed and the measurement items used for the assessment.

Table 3 Items measured for the quantification of the dust capture efficiency

<table>
<thead>
<tr>
<th>Sections where the amount of accumulated dust and capture efficiency are assessed</th>
<th>Measurement items</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Flue gas cooler system</td>
<td>• Dust concentration at the inlet of the flue gas cooler</td>
</tr>
<tr>
<td></td>
<td>• Dust concentration at the outlet of the flue gas cooler</td>
</tr>
<tr>
<td></td>
<td>• Dust concentration in the waste water of the flue gas cooler</td>
</tr>
<tr>
<td>2. Solvent system</td>
<td>• Dust concentration in gas at the outlet of the absorber</td>
</tr>
<tr>
<td></td>
<td>• Dust concentration in the solvent</td>
</tr>
<tr>
<td></td>
<td>• Dust concentration in the solvent before and after the filter (*1)</td>
</tr>
</tbody>
</table>

*1: Installed in the solvent circulation line

(b) Test results

The dust from the coal-fired boiler flue gas accumulated in the solvent and did not cause flooding during this demonstration test. The amount of dust in the solvent and the respective foaming tendency had no interaction with either the absorber pressure loss or the regenerator pressure loss.

ii. Influence on equipment

(a) Measurement methods

Monitor the operational status of the equipment affected by dust, as shown in Table 4, to understand the influences of dust on the equipment.

Table 4 Items monitored for understanding the influences of dust on the equipment components

<table>
<thead>
<tr>
<th>Equipment component</th>
<th>Monitoring items</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Flue gas cooler</td>
<td>• Pressure loss of tower</td>
</tr>
<tr>
<td>Absorber</td>
<td></td>
</tr>
<tr>
<td>2. Heat exchanger</td>
<td>• Heat transfer coefficient</td>
</tr>
</tbody>
</table>

(b) Test results

- Flue gas cooler pressure loss and absorber pressure loss

Figs. 5 and 6 show the time sequence data of the pressure losses in the flue gas cooler and absorber. There was no tendency for increased pressure loss even after an elapse of 4,000 hours of operation. The result revealed that the plugging of packing material and demisters can be prevented by the pretreatment method applied on this occasion.

Fig. 5 Movement of pressure loss of the flue gas cooler

Fig. 6 Movement of the pressure loss of absorber
Heat transfer coefficient of the heat exchanger

The heat transfer coefficient decreased in the heat exchanger using cooling water after the elapse of so many hours of operation. This was explained, however, by the scaling of material in the cooling water to the heat transfer surface of the heat exchanger. We believe that the problem can be solved by implementing appropriate water treatment. No significant decreases of the heat transfer coefficient were found in the heat exchanger operated without the use of cooling water.

(3) Understanding the influences of SOx
i. Removal ratio in the flue gas desulphurization section
(a) Measurement methods
   Determine the SOx removal ratio in the flue gas desulphurization section by measuring the SOx concentration in the flue gas at the inlet of the flue gas cooler and in the flue gas at the outlet.
(b) Test results
   The SOx removal ratio in the flue gas desulphurization section was 98% or higher.
ii. Influence on solvent
(a) Measurement methods
   Measure the concentration of the heat-stable salts in the solvent.
(b) Test results
   Though almost all of the SOx at the outlet of the flue gas cooler was absorbed by the solvent and became heat-stable salts, the amounts produced could be maintained at a low level by installing a flue gas desulphurization section. Thus, the performance of the solvent could be consistent with that of the natural-gas-fired boiler.

(4) Understanding the influences of NOx
i. Absorption ratio
(a) Test methods
   Determine the NOx absorption ratio in the flue gas cooler and absorber by measuring the NOx concentrations in the gas at the inlet and outlet of the flue gas cooler and in the gas at the outlet of the absorber.
(b) Test results
   The flue gas cooler absorbed almost none of the NOx in the flue gas. The absorber absorbed about 1 - 3% of the NOx.

(5) Understanding the influences of chlorine and fluorine
i. Amounts accumulated
(a) Test methods
   Measure the concentrations of chlorine and fluorine in the waste water of the flue gas cooler and in the solvent.
(b) Test results
   The tests confirmed that no chlorine or fluorine was detected in the flue gas or solvent, and that chlorine and fluorine were deeply removed upstream of the CO2 recovery plant (by the existing flue gas desulphurization system and other pretreatment equipment).

(6) Confirmation of solvent loss
i. Amount of solvent loss
(a) Test methods
   Determine the amount of solvent loss through analysis of the solvent, etc.
(b) Test results
   The solvent loss measured was close to the expected value. In this test we could assess the solvent loss quantitatively from the coal-fired boiler flue gas. We will apply the test result to actual projects in the future.

4.3 Outcome of the test results

We demonstrated that the impurities from the coal-fired boilers can be treated by installing a flue gas cooler with deep flue gas desulphurization and flue gas water washing functions as a pretreatment process. We also confirmed that CO2 can be stably absorbed and regenerated by these pretreatments and filters. The following concrete results were achieved:

(1) Demonstration operation for 4,000 hours and a CO2 recovery performance equivalent to or better than the expected performance.
(2) Data on the de-dust capacity of the pretreatment equipment and the behavior of the dust in the solvent system.
(3) Data on the absorption ratios of SOx and NOx in the respective sections, and their respective behaviors.
(4) Quantitative data on the solvent loss.

5. Approach for the future

MHI ultimately aims to provide customers with highly reliable commercial plants (of about 5,000 ton-CO2/day) at low cost. To achieve this, we need to verify not only the issues from the viewpoint of the chemical and equipment processes, but also the realization of larger-capacity plants as hardware in the future.

6. Conclusion

The demonstration operation of 4,000 hours was achieved at a coal-fired power station in Matsushima. We clarified the behaviors of dust, SOx, and NOx in the equipment systems and how these components influence the solvent. Accordingly, we have been able to achieve almost all of our targets of our tests to verify the influences of impurities contained in the flue gas produced from coal-fired power stations. In conclusion, we confirmed that KM-CDR process can be applied to the flue gas of coal-fired boilers through the implementation of appropriate pretreatment facilities. Having achieved the aforementioned, it is now technically feasible to apply this process in middle-class plants (with a capacity of several hundred up to a thousand tons-CO2/day).
Studies on CO2 recovery from coal-fired power stations have been actively commencing in recent years in efforts to realize countermeasures against global warming mainly in Europe and the United States and also in Japan. We are confident that MHI’s technology can take leading role in these efforts.

We would like to take this opportunity to express our most sincere gratitude to J-POWER for their full cooperation and support during the demonstration testing period.

References