

CO₂ Capture Technology for Mitigating Global Warming and Climate Change



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CO₂ Capture and Sequestration (CCS) is an essential global warming solution as long as we continue to use fossil fuels. This report includes the features and latest experiences of the CO₂ recovery technologies of Mitsubishi Heavy Industries, Ltd. (MHI). We outline our approaches to the mitigation of global warming through the development of CO₂ recovery technology for coal-fired power plants, which are large sources of CO₂ emissions. Our proposed direction in the development of future technologies is also highlighted.

1. Introduction

As humans continue to rely on fossil fuels such as oil and coal, CO₂ will inevitably be generated, resulting in an increase of global warming. Research and development of CO₂ reduction technologies have been active since the 1990s, and many technologies, including energy-saving methods, the effective use of renewable energy, and CO₂ absorption through forestation, have been examined. Despite these approaches, CO₂ in the atmosphere has continued to rise, and a shift to a low carbon society is becoming mandatory. However, such a shift may be very difficult for industries and individuals that have depended on fossil fuels since the Industrial Revolution.

Based on this increasing need to reduce CO₂ emissions, technologies for CO₂ Capture and Sequestration (CCS hereafter) have been accelerated as one of several global warming solutions since around 2000.

2. Outline of CCS

The IPCC Special Report on Carbon Dioxide Capture and Storage (2005) indicated that more than 7,500 large stationary sources in the world emit >0.1 Mt CO₂/y. Most of these sources are located in North America (37%), followed by Asia (24%; mainly China, Japan, and India), and the EU (14%). Asia emits 5.6 Gt CO₂/y, accounting for 41% of the total volume, followed by North America 2.69 Gt CO₂/y (20%), and the EU 1.75 Gt CO₂/y (13%). **Table 1** presents these original stationary energy sources as well as their CO₂ emission volumes per year.

Large stationary emission sources can be broadly classified into those relating to fossil fuels and those relating to biomass; however, the latter group constitutes less than 1% of the total emissions. Power sectors (coal, gas, oil) account for 78% of total emissions from stationary CO₂ sources. **Table 2** presents CO₂ emission volumes for each sector and each fuel source. Based on the fuel used in power sectors, 76% CO₂ originates from coal-fired power plants, followed by plants fueled by gas and oil. When considering all industry sectors, coal-fired power plants account for about 60% of total CO₂ emissions from global stationary sources.

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Table 1 Large CO₂ stationary sources worldwide

Process	Number of sources	Emissions (Mt-CO ₂ /y)
Fossil fuel		
Power (coal, gas, oil, etc.)	4,942	10,539
Cement production	1,175	932
Oil refinery	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas process	N/A	50
Others	90	33
Biomass		
Bioethanol and bioenergy	303	91
Total	7,887	13,466

Source: IPCC 2005 Special Report: Carbon Dioxide Capture and Storage

Table 2 Global CO₂ emission volumes for each industrial sector and fuel

Process	CO ₂ volume in exhaust gas (%)	Number of emission sources	Emission volume (Mt CO ₂)	% of total emission (%)	Cumulative total CO ₂ emission (%)	Average emission/source (Mt CO ₂ per source)
CO₂ from fossil fuels or minerals						
Power						
Coal	12 - 15	2,025	7,984	59.69	59.69	3.94
Natural gas	3	985	759	5.68	65.37	0.77
Natural gas	7 - 10	743	752	5.62	70.99	1.01
Fuel oil	8	515	654	4.89	75.88	1.27
Fuel oil	3	593	326	2.43	78.31	0.55
Other fuel ^a	NA	79	61	0.45	78.77	0.77
Hydrogen	NA	2	3	0.02	78.79	1.27
Natural-gas sweetening						
	NA ^b	NA	50 ^c	0.37	79.16	
Cement production						
	20	1,175	932	6.97	86.13	0.79
Refineries						
	3 - 13	638	798	5.97	92.09	1.25
Iron and steel industry						
Integrated steel mills	15	180	630 ^d	4.71	96.81	3.50
Other processes ^d	NA	89	16	0.12	96.92	0.17
Petrochemical industry						
Ethylene	12	240	258	1.93	98.85	1.08
Ammonia: process	100	194	113	0.84	99.70	0.58
Ammonia: fuel combustion	8	19	5	0.04	99.73	0.26
Ethylene oxide	100	17	3	0.02	99.75	0.15
Other sources						
	NA	90	33	0.25	100.00	0.37
Total		7,584	13,375	100		1.76
CO₂ from biomass						
Bioenergy ^e	3 - 8	213	73			0.34
Fermentation	100	90	17.6			0.2

a Other gas, other oil, digester gas, landfill gas.

b A relatively small fraction of these sources has a high concentration of CO₂. (In Canada, only two plants out of a total of 24 have high CO₂ concentrations.)c Based on an estimate that about half of the annual worldwide natural-gas production contains CO₂ at concentrations of about 4% mol.d These values originate from different databases. A top-down approach estimated higher global CO₂ emissions, i.e., >1Gt CO₂.

e For North America and Brazil only. All numbers are for 2003, except for power generation from biomass and waste in North America, which is for 2000.

Source: IPCC 2005 Special Report: Carbon Dioxide Capture and Storage

Because coal is more abundant and cheaper than oil and natural gas, coal use will increase more rapidly, resulting in a larger contribution to total CO₂ emissions. Thus, reduction of CO₂ emissions from coal-fired power plants is a crucial global warming solution, and MHI has worked to realize the practical use of CO₂ recovery technology for coal-fired power plants.

A conceptual diagram of CCS is presented in **Figure 1**.

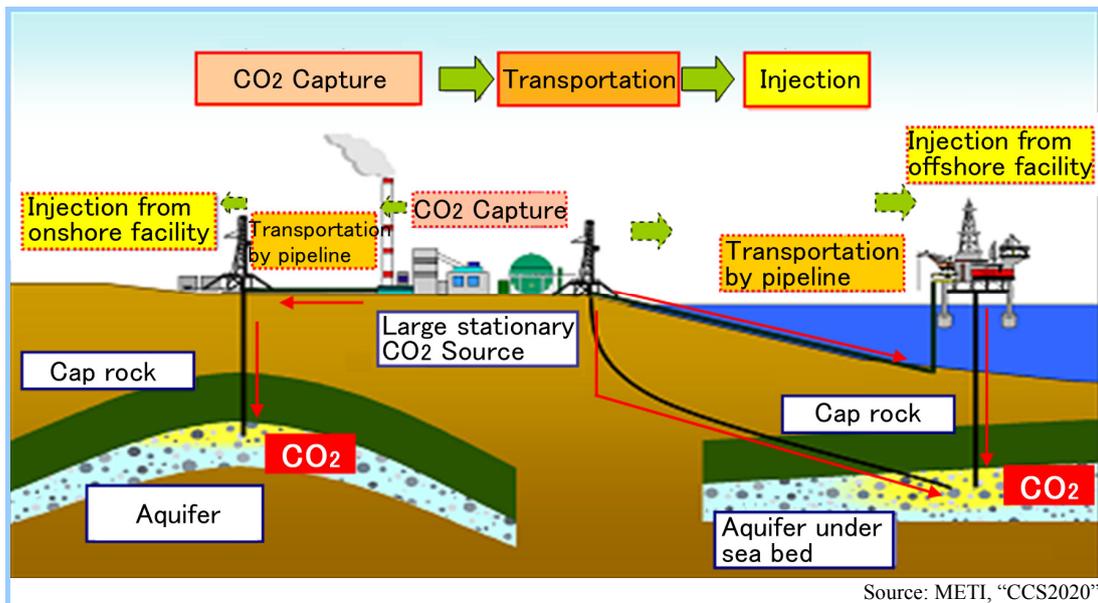


Figure 1 Conceptual diagram of geological CO₂ sequestration

CCS is a method used to separate and capture CO₂ from large emission sources such as power plants and to then transport the CO₂ through pipelines to onshore or offshore deep underground aquifers for geological storage. As the human population continues to consume fossil fuels (oil, gas, and coal), CO₂ emission reduction may be difficult without CCS. Figure 2 presents various CO₂ geological storage options. CO₂ can be stored in oil fields (EOR), coal-bed methane, depleted oil and gas fields, and aquifers. Abundant aquifers have the highest potential as CO₂ storage sites, and some geological surveys are currently in operation worldwide to identify geological formations that can store CO₂.

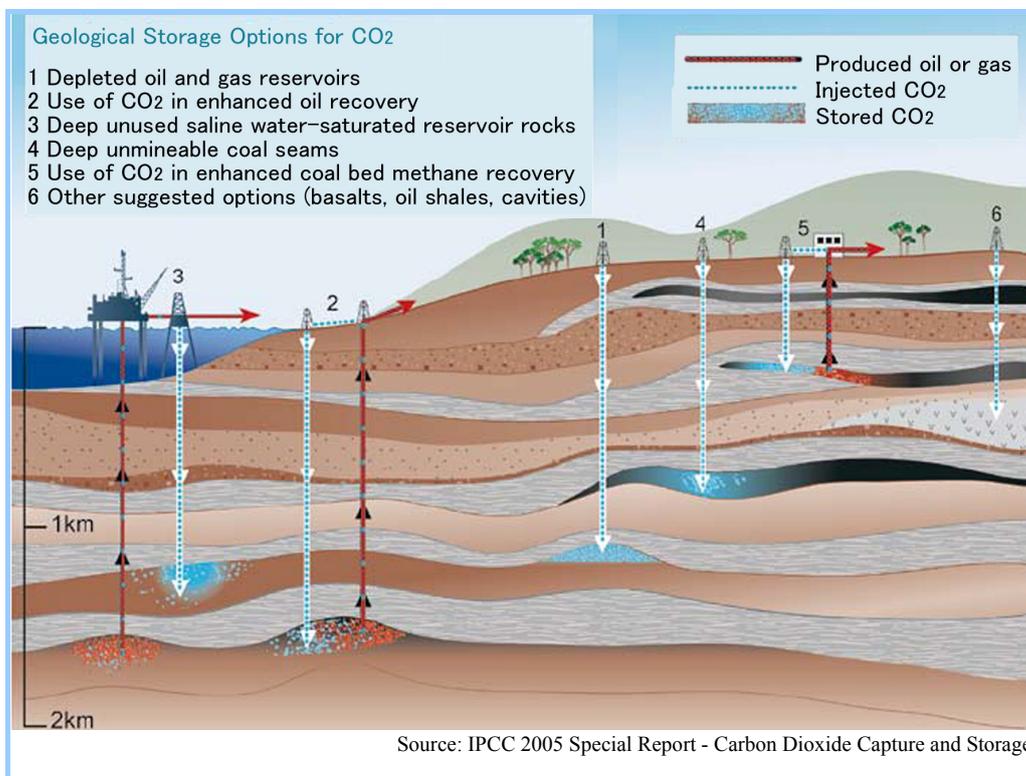


Figure 2 Geological storage options

Table 3 presents the estimated storage capacities of already-identified formations with huge CO₂ storage potential.

Aquifers have the highest potential and can store at least one trillion tons of CO₂. If undiscovered (unconfirmed) formations are included, this value reaches 10 trillion tons of CO₂.

Table 3 CO₂ storage sequestration capacity

Type of formation	Estimated minimum storage capacity (Gt CO ₂)	Estimated maximum storage capacity (Gt CO ₂)
Oil and gas fields	675*	900*
Depleted coal fields (ECBM)	3-15	200
Aquifers deep underground	1 000	Unconfirmed, but 10 ⁴

* These values increase by 25% if “undiscovered” oil and gas fields are included.

Source: IPCC 2005 Special Report: Carbon Dioxide Capture and Storage

3. Our CO₂ recovery technology

3.1 Experiences of our commercial plants

Table 4 shows experiences of our commercial plants.

Five commercial plants for natural gas (NG)-fired power plants have been in operation since 1999, when MHI installed the first plant to recover CO₂ in flue gas. As of December 2009, a commercial plant in Abu Dhabi has begun commissioning, and another in Bahrain is being prepared for commissioning. These two plants will begin full operation during the current fiscal year. Two additional plants are under construction in Pakistan and Vietnam, and operations are planned to begin in 2010.

Table 4 experiences of our commercial plants

					
Site	Malaysia	Japan	Aonla, India	Phulpur, India	Kakinada, India
Company	Petronas Fertilizer (Keda) Sdn. Bhd.	A chemical company	Indian Farmers Fertilizer Co.	Indian Farmers Fertilizer Co.	Nagarjuna Fertilizers And Chemicals Limited
Start operation	1999	2005	2006	2006	2009
Recovery rate	160 t/d	283 t/d	450 t/d	450 t/d	450 t/d
Emission source	NG-fired steam reformer flue gas	NG/oil-fired boiler flue gas	NG-fired steam reformer flue gas	NG-fired steam reformer flue gas	NG-fired steam reformer flue gas
Product	Urea	General use	Urea	Urea	Urea

* These experiences outline the performance of our commercial CO₂ recovery plants. The five commercial plants for NG-fired plants are currently in operation. Our CO₂ recovery plants for chemical industries have comprised a dominant share of the global market since 1999 and have been implemented not only locally, but also internationally (e.g., in Malaysia and India).

The commercial plant in Malaysia was started up in 1999 as the first plant employing our unique technology, and recovered CO₂ has been used to increase urea production. The process of urea production is comprised of ammonia production and urea production. In ammonia production, CO₂ in flue gas from the primary reformer is separated, captured, and then combined with ammonia to produce urea. The plant in Malaysia has operated smoothly and continuously for 10 years, proving its reliability. The commercial plant in Japan has been used for more general purposes. This plant recovers CO₂ in flue gas from a NG-fired boiler and partially from an oil-fired boiler. The three commercial plants in India are all designed for urea production. The CO₂ recovery rates of these plants reach a total of 450 t/d, achieving the world's largest capacity among flue gas CO₂ recovery plants. Thus far, we have implemented four of these plants as standard units for urea production with a CO₂ recovery rate of 450 t/d. As of December 2009, the 400-t/d-class unit in Abu Dhabi, which is under operation is the world's first commercial plant equipped with an energy-saving regeneration system.

As an additional global warming solution, MHI has also worked on the commercialization of CO₂ recovery technologies that target coal-fired power plants. In cooperation with Southern Company, one of America's largest generators of electricity, we are constructing a 500-t/d-class CCS demonstration plant for a coal-fired power unit. As outlined in Table 4, our CO₂ recovery

technology for NG-fired power plants has already been commercialized. However, our collaboration with Southern Company will be the world's first attempt to demonstrate 500-t/d-class recovery on flue gas from a coal-fired power unit, in which the coal flue gas exhibits high levels of impurity. This demonstration plant is under construction at the Barry Electric Generating Plant in Alabama (**Figure 3**); the Electric Power Research Institute (EPRI) has also joined this project.

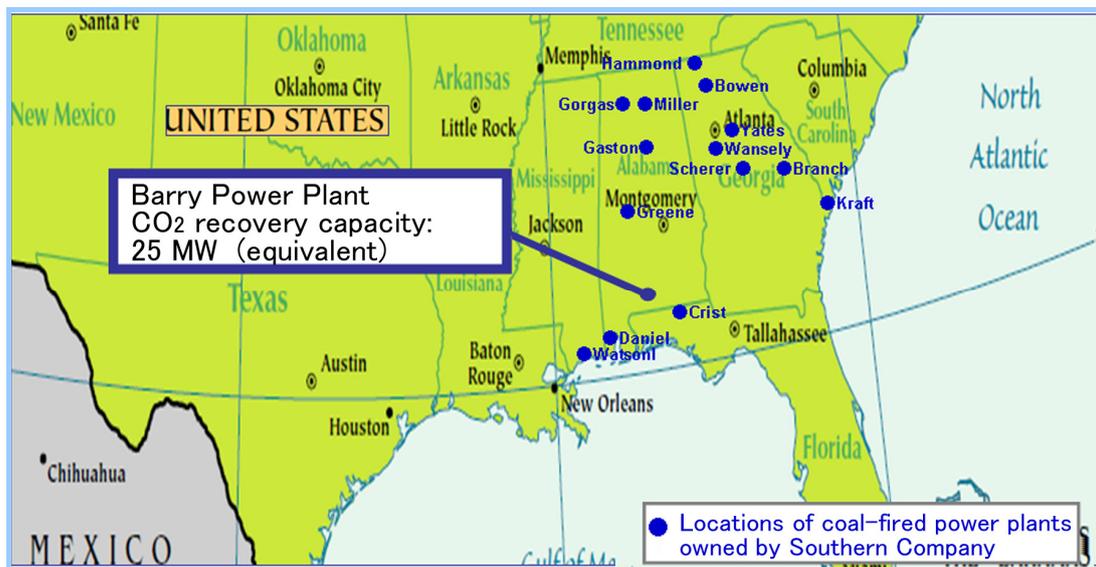


Figure 3 Location of Barry Electric Generating Plant

Location of the coal-fired Barry Electric Generating Plant owned by Alabama Power, a subsidiary of Southern Company. At this plant, an integrated demonstration project involving all processes from CO₂ recovery to geological storage will be implemented.

This demonstration project will include the construction of a demonstration plant to recover, capture, and compress CO₂ from flue gas, subsequently transporting it to an aquifer for storage. Operation and technology and performance validation will begin in April 2011. As a process licensor, MHI will take charge of tasks involved in not only basic planning and engineering, but also technical support and technology and performance validation during operation. CO₂ transport to aquifer storage will be conducted during the SECARB (South East Regional Carbon Sequestration Partnership Phase III program), a greenhouse gas (GHG) reduction project of the US Department of Energy (DOE). This demonstration project will serve as an integrated test covering all necessary processes from CO₂ recovery to geological storage.

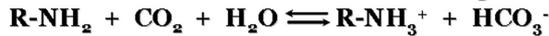
3.2 Features of our CO₂ recovery technology

In 1990, we initiated technological research and development to recover CO₂ from power plant flue gas in cooperation with the Kansai Electric Power Co., Inc. (KEPCO). We initially focused on the research and development of CO₂ recovery energy reduction as our main theme, ultimately achieving the practical use of an energy-saving CO₂ absorbent (KS-1 solvent) as well as a regeneration system and the optimal integration of a steam system covering power generation and CO₂ recovery units.

Figure 4 shows the reaction mechanism between amines and CO₂. The key reaction between the conventional monoethanolamine (MEA)-based absorbent and CO₂ proceeds with 2 mol of the amine and 1 mol of CO₂. However, the key reaction of KS-1 solvent requires a 1:1 molar ratio of amine:CO₂, i.e., KS-1 requires a lower molar quantity to recover CO₂ than does the MEA-based absorbent. One other advantage of KS-1 is that it involves less regeneration energy because carbamate (R-NH-COO⁻), a byproduct of the key reaction of the MEA-based absorbent, is so stable that the MEA reaction involves more regeneration energy. This advantage is evidenced by the fact that the KS-1 reaction generates less heat (dissociation heat) than does the MEA reaction. The KS-1 solvent is also superior to the conventional MEA-based absorbent in CO₂ loading per mole of amine under ambient temperature, requiring less CO₂ loading per mole of amine under the regeneration temperature range of about 120°C. The KS-1 solvent also has less corrosive properties and therefore does not require corrosion inhibitor.

■ Monoethanolamine (MEA)

(Key reaction)



■ KS-1



(Key reaction)



Figure 4 Reaction mechanism between amine and CO₂

The key reaction with the conventional monoethanolamine (MEA)-based absorbent and CO₂ stoichiometrically requires a 2:1 molar ratio of amine: CO₂, but the KS-1 solvent only requires a 1:1 ratio. In other words, the KS-1 solvent can recover the same amount of CO₂ with less solvent volume than that required by the MEA-based absorbent. KS-1 has another advantage: it involves less regeneration energy because carbamate (R-NH-COO⁻), a byproduct of the key reaction with the MEA-based absorbent, is so stable that the MEA reaction requires more regeneration energy.

Figure 5 outlines the process flow of CO₂ recovery from flue gas. Flue gas emitted from the power plant is cooled by the flue gas cooler and then transported to the absorber. CO₂ in the flue gas is recovered by contact with the absorbent running off from the upper end of the absorber. The flue gas whose CO₂ was extracted is then cooled and released from the top of the absorber to the atmosphere as low-CO₂ gas. The CO₂-containing absorbent is transported from the bottom of the absorber to the regenerator and is heated by steam to release CO₂. The regenerated absorbent is transported back to the absorber for re-use. MHI has developed a unique energy-saving regeneration system concept to re-use the waste heat of the regenerated absorbent for regeneration. In cooperation with KEPCO, we have developed and commercialized the KM CDR process[®] used to recover CO₂ with KS-1 solvent from flue gas. The KM CDR process[®] can recover CO₂ at a high purity level of 99.9% volume, allowing the CO₂ to be used as an industrial product for general purposes or chemical product materials.

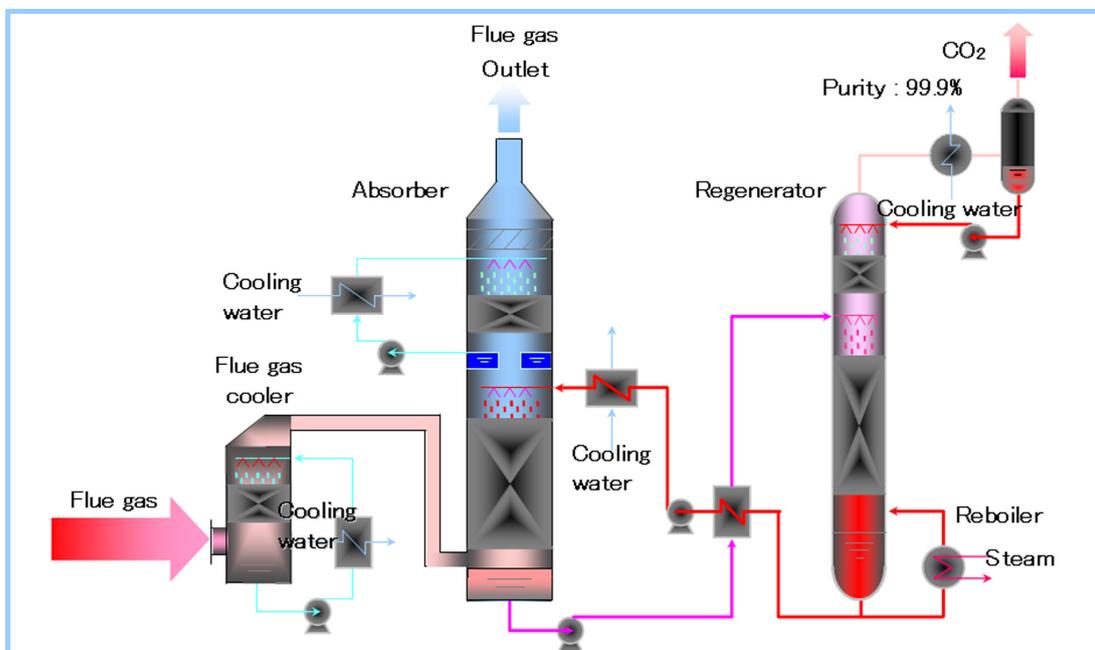


Figure 5 Process flow of CO₂ recovery from flue gas

Exhaust gas from power plants is cooled at the flue gas cooler and then transported to the absorber. CO₂ in the flue gas is recovered by contact with the absorbent running off from the upper end of the absorber. The CO₂-extracted flue gas is then cooled and released from the top of the absorber to the atmosphere as clean gas. The CO₂-containing absorbent is transported from the bottom of the absorber to the regenerator and is heated by steam to release CO₂. The regenerated absorbent is transported back to the absorber for re-use.

3.3 CO₂ recovery test experiences on coal-fired flue gas

If our CO₂ recovery technology is to be applied to coal-fired power plants, the effects of flue gas impurities on absorbents and on the entire recovery system must be evaluated. Therefore, MHI

constructed a 10-t/d-class demonstration system on the premises of J-Power's Matsushima power plant as part of a technological development plan to recover CO₂ from coal-fired boiler flue gas for global warming mitigation. The project was subsidized by the Research Institute of Innovative Technology for the Earth (RITE) and cooperated by the Electric Power Development Co., Ltd. (J-POWER). The plant was operated for 4,000 h from 2006 to 2007 on real pulverized coal-fired boiler flue gas, demonstrating effects on absorbents and recovery equipment and accumulating valuable data.

Larger scale validation tests were required to gather additional data on impurities in coal-fired boiler flue gas, as the CO₂ recovery volume in coal-fired power plants can reach several thousand t/d per unit. Therefore, MHI plan a project not only to recover CO₂ from the flue gas of a 500-t/d-class coal-fired boiler, but also to compress and dehydrate CO₂ before delivering it to a site where sequestration is carried out by SECARB (Southeast Regional Carbon Sequestration Partnership). In 2011, we will start this 500 t/d CO₂ capture demonstration together with CO₂ sequestration.

J-POWER's Matsushima power plant emits relatively clean flue gas. In FY2008, we demonstrated the responses of the coal flue gas at the US and European plants, which have higher particulate and SO_x levels. To confirm the effects of rises in particulate and SO_x levels in the demonstration, we bypassed the duct that pumps in 25% max. of the pre-desulfurization flue gas along with the conventional post-desulfurization flue gas. For the test at the Matsushima power plant, we also added ash captured by the electrostatic precipitator (EP) to the absorbent in advance to document the effects. The results indicated that SO_x was removed during the pre-treatment stage, even at higher impurity levels. No performance degradation was detected, even though particulates accumulated in the absorbent under test conditions of high particulate levels. The test achieved 1,000 h of continuous and stable operation without any problems.

As of FY2008, our test has achieved 5,842 h of continuous operation, with no indication of performance degradation, thus demonstrating that our CO₂ recovery technology is readily applicable to coal-fired power plants. The test also provided crucial proof of effective CO₂ recovery from coal-fired boiler flue gas. With the support of Southern Company, MHI intends to link this experience to the integrated CCS project demonstration in the USA for recovery of 500 t/d.

3.4 Scaling up

Until now, the CO₂ recovery rates of the systems we have implemented have reached as large as several hundred tons per day, depending on the intended purpose. However, technological development for scaling up the entire recovery plant is essential to achieve practical use in coal-fired power plants, as 500 MW-class commercial models generally emit about 10,000 t/d. Thus, as a key technology for this increase in scale, we demonstrated the absorbent distribution performance of an absorber in our own large-scale test plant (**Figure 6**) to collect data for a large-scale absorbent distribution plant. We also designed a CO₂ recovery plant that can recover 3,000 t/d (equivalent to a 150 MW-scale power plant) per train based on the scaling up of flue gas desulfurizers, which function to remove SO_x from flue gas. We have implemented over 200 of these desulfurizers.

MHI is currently developing technological advances aimed at a CO₂ recovery plant with 6,000 t/d per train. **Figure 7** presents an image of such a large-scale CO₂ recovery plant for coal-fired power plants.



Figure 6 Large-scale test plant



Figure 7 Proposed large-scale CO₂ recovery plant for coal-fired power plants

3.5 Energy-saving technology

CCS requires huge amounts of energy. Under the joint project with KEPCO, we constructed a pilot test plant (**Figure 8**) at KEPCO's Nanko power plant. During this project, we have been testing the system on real-flue gas since 1991 and have developed CO₂ absorbents and an energy-saving regeneration system that can re-use exhaust heat within a CO₂ recovery plant (see the Section 3.2 "Features of our CO₂ recovery technology" above). During the development stage, a promising absorbent MEA (monoethanolamine)-based solution posed several challenges, such as higher corrosive properties and higher energy requirements for CO₂ recovery, i.e., about 900 kcal/kg CO₂. Therefore, focusing on the molecular structure of the absorbents, we tested many candidates and successfully developed an energy-saving absorbent, the KS-1 solvent. KS-1 has since been used in many commercial-scale plants, thus accumulating necessary performance data. However, further energy saving technologies need to be developed for commercialization of CCS for coal-fired power plants, as the CCS systems for such plants still require a large portion of the energy that is generated by the plant. Therefore, MHI has continued our pursuit of further energy-saving technologies through both new absorbent development and energy-saving system improvements.

(1) Development status of a new absorbent

We have developed a new absorbent that requires lower CO₂ recovery energy than KS-1. This new candidate absorbent was tested in a pilot test plant in FY2009. The test results are presented in **Figure 9**. The new absorbent can absorb CO₂ 1.4 times more quickly than conventional KS-1, and the regeneration evaluation test results indicate that the new absorbent allows about a 10% reduction in CO₂ recovery energy compared to KS-1.

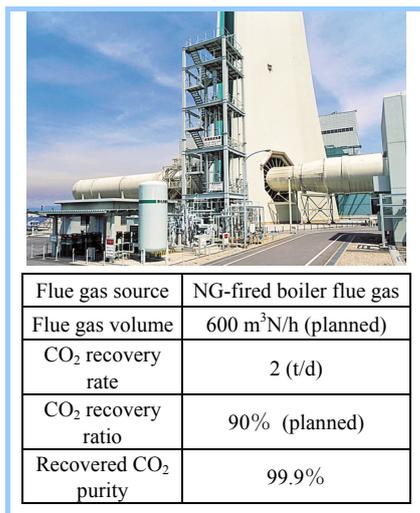


Figure 8 Outline of KEPCO's Nanko pilot plant

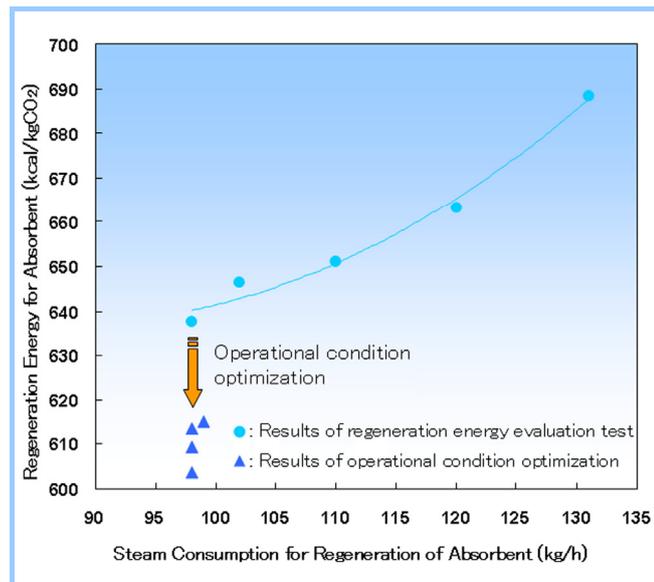


Figure 9 Test results of new absorbent performance

Our new absorbent, which is under development, exhibits 1.4 times higher recovery speed than that of conventional KS-1. The regeneration evaluation test results show that this new absorbent allows about a 10% reduction in CO₂ recovery energy compared to KS-1. Further reductions have also been achieved by the operational condition optimization.

(2) Operational condition optimization

MHI has worked to develop an energy-saving CO₂ recovery process by improving the system flow of CO₂ recovery. As one approach, we focused on the fact that the CO₂ recovery reaction between absorbents and CO₂ is exothermic, and we initiated the development of technology to increase the volume of CO₂ recovery per unit of absorbent by taking advantage of reaction characteristics that optimize the operational conditions in the absorber. This approach allows substantial CO₂ recovery energy reduction, and its effectiveness has already been well documented.

As described above, our goal is to reduce CO₂ recovery energy to about 600 kcal/kg CO₂ in a commercial plant by developing new absorbents and optimizing the operational conditions.

4. Future challenges

For the commercialization of CO₂ recovery plants for coal-fired power plants, MHI is currently constructing a 500-t/d-class CCS demonstration plant for a coal-fired power unit with the support of Southern Company, one of America's largest generators of electricity, based on the extensive knowledge acquired in the 10-t/d-class demonstration at J-POWER's Matsushima power plant. In this project, a portion of the flue gas from the power unit will be transported to the CO₂ recovery plant to separate and recover CO₂ at a high purity level. The CO₂ will then be pressurized and dehydrated and transported via a pipeline to an aquifer for storage. The operation is scheduled to begin in the spring of 2011. This project will be the world's first attempt to demonstrate at a large-scale CCS technology on coal-flue gas with high impurity levels. Based on the knowledge acquired in this project, we ultimately plan to shift to a 3,000-t/d-scale CCS demonstration.

MHI also intends to research more energy efficient systems that cover the entire energy flow of a power plant to reduce the enormous operation energy (i.e., steam and electricity) required by the CO₂ recovery plant. Our goal is total energy reduction of the entire system from generation to CO₂ recovery for future commercial application.

5. Conclusions

As humans continue to use fossil fuels, CCS technologies will be essential. In particular, application of CCS to coal-fired power plants, a large CO₂ emission source, offers an effective option for global warming mitigation. However, many challenges must be overcome in demonstrations and pilot projects. For example, we will need to evaluate the effects of impurities in coal-fired boiler flue gas as well as increase the scale of recovery plants. MHI has conducted absorbent distribution tests in a real-scale test plant and a 10-t/d-scale recovery demonstration on real-flue gas derived from coal-fired power plants. As a next step, we seek to commercialize our technology through a mid-scale demonstration of a CO₂ recovery rate of 500 t/d on coal-fired boiler flue gas in the USA, with a target date of 2015 for commercialization of CCS for coal-fired power plants.

References

1. CCS2020 by Japan's Ministry of Economy, Trade and Industry
2. IPCC Special Report on Carbon dioxide Capture and Storage