Flue Gas CO_2 Recovery and Its Application

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Mitsubishi Heavy Industries, Ltd. (MHI) and The Kansai Electric Power Co., Inc. have been developing flue gas CO_2 recovery technology since 1990 as a measure against Global Warming. As a result of the research and development efforts which have now been carried out for seven years, the new energy-efficient solvents KS-1 and KS-2 which are less corrosive and cause less degradation than those used previously, have been developed. In addition, a research has produced a new packing, KP-1, that can reduce the size of CO_2 absorbers and the horsepower requirements of flue gas blowers. The pilot plant, which is located in Nanko Power Plant of The Kansai Electric Power Co., Inc. has been used for the pilot tests of The Central Electric Power Council targeted for all utility companies in Japan and MHI since the fiscal year of 1995. The newest developments are presented in this paper, as well as a description of the subterranean disposal of CO_2 to help stop Global Warming. Ways to use CO_2 for industry and related economic matters are also discussed. We hope our new technology will contribute not only help prevent Global Warming, but also prove beneficial to various industries.

1. Introduction

At the United Nations (UN) earth summit held in Rio de Janeiro, Brazil, in June 1992, it was agreed that the industrialized nations should control the CO_2 emission at the level of 1990 by 2000. In December, 1997, at the UN Framework Convention on Climatic Change (COP3), it is planned to agree on the curtailment of CO_2 emissions after 2000.

Against this background, as a measure of reducing CO_2 emissions, MHI, jointly with the Kansai Electric Power Co., Inc., has been promoting technical development since 1990 for the removal and recovery of CO_2 from boiler flue gas released from thermal power plant by the chemical absorption method.

As CO_2 emission control methods, energy saving, improvement of efficiency, conversion to less CO_2-releasing energy (LNG etc.), promotion of nuclear power generation, and positive use of natural energy are being encouraged, but since the energy-saving level in Japan is very high, it is thought to be difficult to cut CO_2 emissions at a rate surpassing the economic growth.

In some other nations, for example, certain European nations and the United States, conversion from coal thermal power to natural gas thermal power is expected to proceed, but in the Netherlands presently depending mostly on natural gas and in Norway, vastly increasing the production of oil and natural gas in the North Sea, they are positively promoting research on the recovery and disposal of CO_2.

Under these conditions, although the prospects are uncertain about the COP3 and the international attitude toward CO_2 emission control, it is nevertheless important to establish a CO_2 recovery and disposal technology so as to be ready to apply it anytime.

On the other hand, using the established technology, aside from measures against global warming, extensive applications are expected in the chemical industry having a need for CO_2, general use, and enhanced oil recovery (EOR), among others, and MHI has already constructed 150 t/d CO_2 recovery plants from oil firing boiler flue gas for general CO_2 applications.

2. New flue gas CO_2 recovery technology and conventional technology

2.1 Conventional technology

The CO_2 recovery technology from boiler flue gas has been traditionally employed in CO_2 production, such as the carbonated beverage business. In the chemical industry, it has been also used for the purpose of feeding CO_2 for the production of soda ash production or urea.

Monoethanolamine (MEA) is used for CO_2 recovery from boiler flue gas. First, in this MEA method, in order to prove the technology by using an effective corrosion inhibitor, we have constructed a pilot plant at the Nanko Power Plant of The Kansai Electric Power Co., Inc., and conducted tests to evaluate the CO_2 recovery performance. As a result, the MEA technology was found to be high in thermal energy consumption for CO_2 recovery, and significant in the deterioration and consumption of MEA.

For an efficient and economical CO_2 recovery from boiler flue gas on a power plant scale at low energy consumption, MHI started fundamental research on the following topics:

(1) Reduction of regeneration energy of absorbent
(2) Reduction of flue gas blower power
(3) Larger power plant scale and compact equipment
(4) Reduction of amine loss
(5) Measures against impurities in flue gas
(6) Optimum steam integration system for power plants and flue gas CO_2

2.2 Development of new energy-saving absorbent[(1)]

The most important point in the chemical absorption method is the reduction in the regeneration energy. In the prior art of using MEA for the recovery of CO_2 from boiler flue gas, the regeneration energy of the absorbent was found to be 900 kcal/kg CO_2 in pilot plant tests. This value corresponds to about 20% of combustion energy in the boiler when only comparing energy alone.

In order to curtail the regeneration energy, MHI noticed the possibility of a greater reduction in regeneration energy when the degree of steric hindrance of amine was higher, and have

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tested 80 possible amines in this category, and have selected potential candidates and conducted further investigations by using a bench tester and wetted-wall test apparatus to check for problems in the absorption, regeneration performance and its property etc., and performed pilot-plants tests.

As a result, KS-1 and KS-2 were developed as two new excellent absorbents. Both proved to be capable of curtailing the regeneration energy by about 20% as compared with the conventional MEA.

Fig. 1 compares KS-1, KS-2, and MEA for steam consumption for regenerating absorbent in the pilot plant.

Concerning corrosion of the absorbent, in both the new absorbents, KS-1 and KS-2, were found in fundamental tests to have very low corrosiveness, and results suggest that it is unnecessary to take any corrosion countermeasure. **Table 1** shows the results of corrosion tests of MEA, KS-1, and KS-2 under stripper conditions than the regeneration conditions. Results have shown that conventional MEA cannot be used in carbon steel unless a corrosion inhibitor is used.

In pilot plant tests, we measured not only the energy required for CO_2 recovery, but also the degree of deterioration of absorbent by the increase of heat-stable salt, and consumption of absorbent. **Fig. 2** shows the rate of production of heat-stable salt by the new absorbents KS-1, KS-2, and MEA.

2.3 New low pressure loss type packing

In the CO_2 recovery process from boiler flue gas, the second largest energy consumption item after regeneration energy of absorbent is the power of the flue-gas blower. The boiler flue gas is very large in volume, and a slight reduction of the pressure loss results in a significant saving in blower power.

Accordingly, MHI developed new packing with very small resistance to flue gas. By trial and error, we developed a nearly ideal new packing KP-1 of the wetted-wall gas-liquid contact type, and evaluated its performance by using it in the CO_2 absorber of the pilot plant.

Fig. 3 compares the pressure loss in the CO_2 absorber with the conventional packing, and indicates that the pressure loss is reduced to 1/15 at the same gas flow rate, and also provides a notable improvement in CO_2 recovery performance. Hence, as the flue-gas flow rate is enhanced, a compact absorber can be designed, and a low loss of pressure is realized at the same time.

2.4 Steam system integration into the power generation plant

By the development of new absorbents KS-1, KS-2, the regeneration energy of the absorbents is substantially decreased, but a significant amount of energy is still needed. However, since the absorbent is regenerated at a low temperature, around 110 to 120°C, low-pressure steam (2 to 3 kg/cm²G) is sufficient. MHI constructed an integrated steam system, capable of maintaining low-pressure steam in the power plant, and effectively utilizing the waste heat of the flue-gas CO_2 recovery system in the power plant. In this system, it has become clear by calculation that the loss of power owing to CO_2 recovery in the LNG firing thermal power generation plant remains at around 5%.

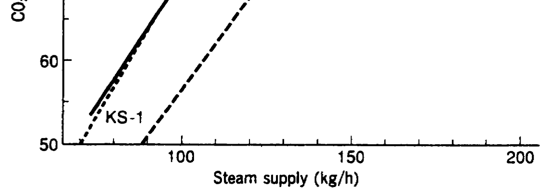

Fig. 1 Relationship between steam consumption and CO_2 recovery in the pilot plant

Table 1 Corrosion test results

(Unit: mils per year)

	Test 1	Test 2
MEA	93.0	76.4
MEA + inhibitor	9.5	8.3
KS-1	3.1	3.6
KS-2	2.0	2.2

Test condition: 130°C, in the presence of O_2

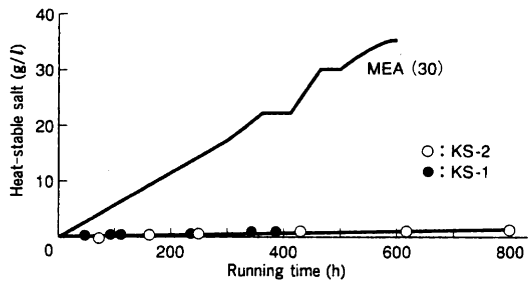

Fig. 2 Deteriorated product of MEA, KS-1, and KS-2

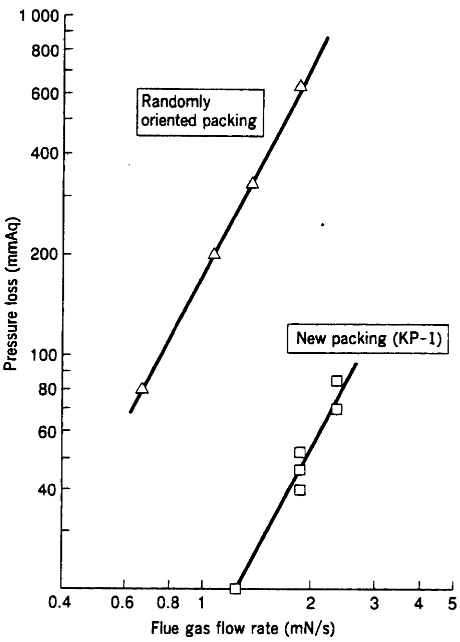

Fig. 3 CO_2 absorber absorption part pressure loss

Table 2 Comparison of conventional technology and newly developed technology

Item	Conventional	New	Remarks
Regeneration energy	1	0.8	Application of KS-1 or KS-2 absorbent
Deterioration of absorbent	1	1/40	Application of KS-1 or KS-2 absorbent
Loss of absorbent	1	1/20	Application of KS-2 absorbent and amine loss curtailing technology
Degree of corrosion	Corrosion preventive inhibitor is needed.	Corrosion preventive inhibitor is not needed.	Application of KS-1 or KS-2 absorbent
Release of ammonia from absorber	1	1/15	Application of KS-1 or KS-2 absorbent
Circulation amount of absorbent	1	0.65	Application of KS-1 or KS-2 absorbent
Pressure loss of absorber	1	1/7	Application of KP-1 packing
Drop of output in thermal power generation	1	1/4	Application of KS-1 or KS-2 absorbent, application of KP-1 and new steam system

2.5 Comparison of conventional technology and new technology

On the basis of the pilot plant test results and the evaluation of the integrated steam system, the conventional technology and new technology are compared in **Table 2**.

As shown in the table, including the decrease in energy for the CO_2 recovery from boiler flue gas, utility and equipment costs can be considerably lowered.

3. Subterranean disposal of CO_2

Among the measures against global warming, the CO_2 disposal method is equally important to that of CO_2 recovery, and a CO_2 recovery and disposal system cannot be established unless a proper disposal method is developed.

MHI has a long history in the design and construction of petroleum and natural gas production facilities. In this field, the underground injection of gas is general practice globally.

3.1 Example of underground injection of gas

In the field of petroleum and natural gas production and storage, gas is injected underground by the following methods.

(1) Gas injection for pressure maintenance of oil fields
(2) Gas recycling injection for recovery of gas condensate
(3) Injection of natural gas or CO_2 for Enhanced Oil Recovery (EOR)
(4) Underground storage of natural gas
(5) Subterranean injection disposal of H_2S gas

Of these, (1), (2) and (3) are technologies for the production of crude oil and gas condensate, and (4) and (5) are for the purpose of underground storage of gas. Accordingly, in (1), (2), (3), gas is injected in the oil field or gas condensate field, while methods (4) and (5) are widely applied in aquifers with a firm cap rock, aside from oil fields and gas fields. The underground injection of gas is a very common technology in the field of petroleum and gas production.

Actually, CO_2 is injected underground for the purpose of EOR and subterranean disposal of H_2S.

3.2 Disposal of CO_2 in aquifer

The subterranean sedimentary layers are alternate laminates of porous and dense layers, and when oil or gas is collected in the porous layer, an oil field or a gas field is formed. The porous layer without oil or gas is filled with water, which is called an aquifer, and most sedimentary layers in the world are aquifers. Therefore, aquifers exist in every part of the world, and only if a huge aquifer with a firm cap rock above the porous layer is found, CO_2 can be disposed of merely by pushing it into this layer.

In Norway, as the world's first commercial project of CO_2 disposal, injection of CO_2 separated from natural gas in the Sleipner West Gas Field was started in October 1996 at an annual scale of 1 million tons. **Fig. 4** shows the appearance of the offshore plant of this project.

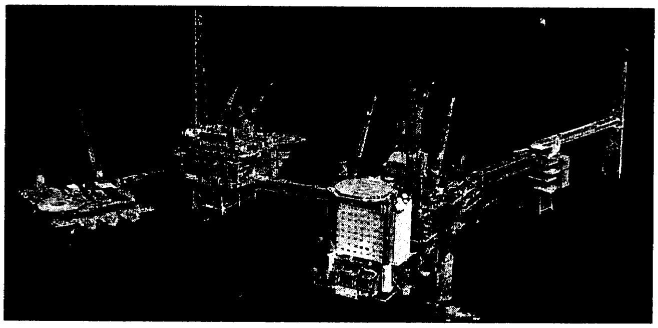

Fig. 4 Sleipner West offshore platform

In Indonesia, on the other hand, in relation to the development of the Natuna Gas Field, they are planning a project to separate CO_2 contained in natural gas (by 71%), inject it into the aquifer near the gas field, and shipping the natural gas in a form of LNG. When this project is put in full operation, 100 million tons of CO_2 will be injected into the underground aquifer every year.

In Japan, the Engineering Advancement Association of Japan, together with others, is surveying several potential sites for CO_2 disposal and investigating the CO_2 disposal technology.

3.3 CO_2 Enhanced Oil Recovery (EOR)

As for EOR using CO_2, a commercial project was started in the United States and other countries after the second petroleum crisis, and it is now contributing to the increase in crude oil production of 160 000 barrels/day in the U.S.

In the U.S., CO_2 is transported by pipeline mainly from CO_2 gas fields, and injected into the oil field.

It is also put in operation in Canada, Hungary, Turkey and elsewhere and MHI has delivered a supercritical pressure CO_2 dehydration system to Hungary.

CO_2 EOR, at a relatively low pressure (14 to 21 MPa), produces a miscible state with crude oil, and the flow of crude oil in the oil layer is greatly accelerated, so that the productivity and recovery of crude oil are enhanced dramatically.

To establish an economical CO_2 EOR project, both high performance CO_2 EOR in the oil field (to recover much crude oil with small amounts of CO_2), and a massive supply of CO_2 at low cost are both required. A commercial CO_2 EOR project generally includeds the following range.

- Performance of CO_2 EOR: 3 to 12 MSCF(Note) CO_2/BBL crude oil
- CO_2 supply cost: 0.5 to 1.5 US$/MSCF CO_2

(Note): MSCF: 10^3 standard cubic feet = 52.6 kg

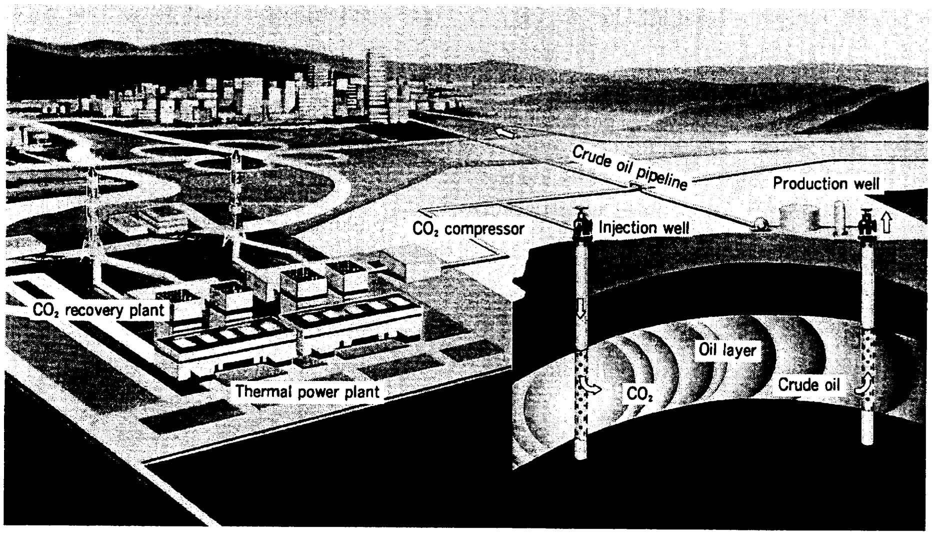

Fig. 5 Concept of flue gas CO_2 recovery for EOR

A concept of flue gas CO_2 EOR is shown in **Fig. 5**.

The economy of the system shown in Fig. 5 was evaluated by technologies developed by MHI, and the EOR was found to be very economical, provided that there is a power plant near the oil field and that the oil field greatly needs EOR.

Thus, the subterranean disposal of CO_2 has been already established, and when CO_2 disposal is executed on a global scale, it will be introduced gradually from economically advantageous cases from the CO_2 reduction cost and quantity aspects.

4. Use of CO_2 recovery plant in general applications and chemical plants

CO_2 is used widely in industry, and the principal applications include the following.

- General applications
  - Dry ice
  - Refrigeration
  - Carbonated drinks
  - Seawater desalination
  - Welding
- Chemical applications
  - Urea production
  - Methanol production
  - Soda ash production
  - Oxo-gas production

CO_2 for such general and chemical applications, is supplied at present, from off-gas from hydrogen plants or ammonia plants, and in areas without such CO_2 sources, CO_2 is recovered from boiler flue gas.

Fig. 6 shows a plant for recovering CO_2 gas from oil-firing boiler flue gas with a capacity of 150 t/d delivered by MHI in 1994. Since SO_2 is contained in the boiler flue gas, this plant is designed to remove SOx before CO_2 recovery.

Although this plant was constructed before the development of a new absorbent and packing for the flue gas CO_2 recovery system, numerous improvements made during the research for flue gas CO_2 recovery were incorporated in the design and construction.

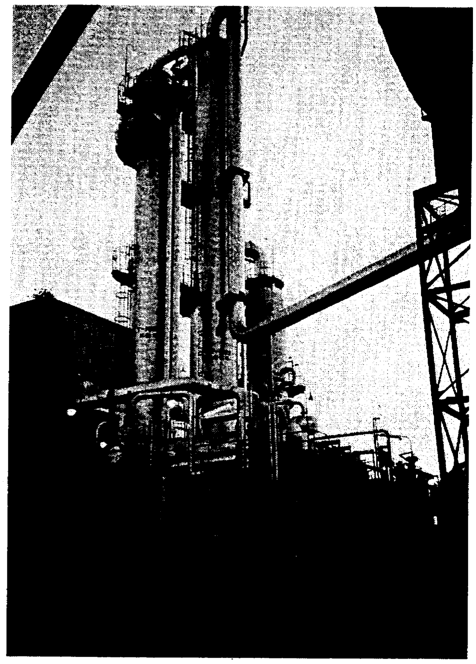

Fig. 6 Flue gas CO_2 recovery plant delivered by MHI

Urea plants and methanol plants have recently been constructed using natural gas as raw material, but since the natural gas is mainly composed of methane, the hydrogen ratio is high, and the carbon content is too low for synthesizing urea or methanol. Accordingly, by recovering and supplying CO_2 from the flue gas of a steam reformer, the productivity of urea and methanol can be enhanced.

5. Future problems

Considering CO_2 recovery and disposal from the viewpoint of a measure against global warming, CO_2 recovery on a power plant scale is needed.

It is hence necessary to construct a plant with a 5000 to 15000 t/d capacity of CO_2 recovery in one system, and this size is 30 to 100 times as big as that of the existing plant delivered by MHI.

Moreover, there is increased need for technology for curtailing the drop in power generation output due to CO_2 recovery.

MHI is promoting joint research programs with the Kansai Electric Power Co., Inc. and other power companies to solve the problems step by step, and is also continuing cost reductions and establishment of reliable technologies while constructing flue-gas CO_2 recovery plants for general industries and chemical and EOR applications.

6. Conclusion

Today, Japan's technology is contributing globally in the environmental fields, such as flue gas desulfurization and flue gas denitrification, and we will be very happy if the flue gas CO_2 recovery technology, as a measure against global warming, developed in Japan, would flourish throughout the world. MHI, together with co-researchers, will continue to further the research and development.

Reference

(1) Mimura, et al., Development of Energy Saving Technology for Flue Gas Carbon Dioxide Recovery in Power Plant by Chemical Absorption Method and Steam System, The Third International Conference on Carbon Dioxide Removal Massachusetts USA September 9-12 (1996)