CO2 Recovery from Flue Gas Using Hindered Amines

Masaki Iijima
Mitsubishi Heavy Industries, Ltd.
3-3-1, Minatomirai, Nishi-Ku Yokohama 220-8401, Japan
E-mail: masaki01_iijima@mhi.co.jp

1. Abstract

Mitsubishi Heavy Industries. (MHI) and Kansai Electric Power Co. (KEPCO) in 1990 founded research and development for CO2 recovery flue gas technologies resulting in forefront global environmental, energy efficient solvent and process improvements. Commercially applied in 1998, six plants currently in operation or under construction.

The main feature of MHI's flue gas CO2 recovery technologies are its solvent efficiencies, progressed by advanced equipment process and simplistic operation, gained through years of commercial application and resource conservation experience. CO2 capture and process delivery investment, sustaining target emission control initiatives in CO2 EOR throughout the Middle East region will be discussed at the symposium.

Application of CDM for CO2 capture and EOR projects will require mutual collaboration and co operation with liaison between oil producing and developing countries. These communications progressing by way of open forum with attending audience symposium delegates.

2. Introduction

The Kansai Electric Power Co. (KEPCO) and Mitsubishi Heavy Industries, Ltd. (MHI) have been carrying out joint work on research and development of new technology for CO_2 recovery from power plant boiler flue gas and gas turbine exhaust gas. From the results of this research and development work, an energy proficient solvent and energy efficient process were developed and commercialized. The first commercial plant having commenced operations October 1999 in Malaysia with seven (7) commercial and demonstration plants either in operation, or under construction mainly for chemical purposes.

MHI's detailed cost study for CO_2 recovery, compression and dehydration identify very attractive commercial results for CO_2 EOR operations. Flue gas CO_2 sources are widely available globally and if oil fields and flue gas sources are located near by, CO_2 EOR would be the most promising economical option to increase crude oil recovery ratios.

MHI proposes the concept of flue gas CO_2 recovery and apply for CO_2 EOR as shown in Figure-1.The concept will contribute not only to enhance oil recovery but at the same time mitigate CO_2 emission reduction to atmosphere.

Figure –1. Concept of Flue Gas CO_2 Recovery and EOR

3. Feature of KEPCO/MHI's Flue Gas CO_2 Recovery Technology

98% of Co2 emissions are derived from fossil fuel combustion, exhausted to atmosphere by flue gas stacks from furnace boilers, gas turbines and engine emission.

The major characteristic of these flue gases is that they are released at atmospheric pressure usually containing Oxygen, Nox, Sox and dust particulate impurities.

This means special developed technology is required for efficient flue gas CO2 recovery with consideration having to be acknowledged for:

- Very low CO2 partial pressure condition.
- CO2 recovery solvent requires strong durability to resist O2.
- For CO2 recovery to be effected proficiently pre treatment of flue gas Sox, NOx and dust particulate is a paramount necessity.

Research proved conclusively KEPCO/MHI solvents have evolution developed as proprietary solution process in control of flue gas emission conditions.

In parallel to advanced solvent development for CO2 recovery are enhanced heat energy savings with dramatically improved solvent regeneration efficiencies that have proved total large scale plant expansion capability are now ready for commercial use.

3.1 Solvent

Monoethanol amine (MEA) is the most fundamental amine currently produced and has been used for more than 50 years for boiler flue gas CO_2 recovery by very small scale operations with recovered CO_2 having been used for beverages and dry ice.

MHI laboratory tests and pilot plant tests show that MEA consumes larger amount of energy for regeneration, and at the same time consume large amounts of solvent. Therefore MHI commenced laboratory tests followed by the pilot plant tests and developed an energy efficient advanced durable solvent KS-1.

Figure-2 shows the comparison of CO_2 and amine reaction mechanism.

MEA mainly react with two moles of amine and one mole of CO_2, however MHI developed solvent (KS-1) primarily react with one mole of amine and one mole of CO_2. Therefore MHI solvent (KS-1) produces higher CO_2 absorption efficiencies.

Figure-3 shows the comparison of the solubility of CO_2 in KS-1 and MEA solution.

At absorption conditions, KS-1 is higher CO_2 absorption efficiency than MEA and at regeneration conditions, KS-1 can be easily

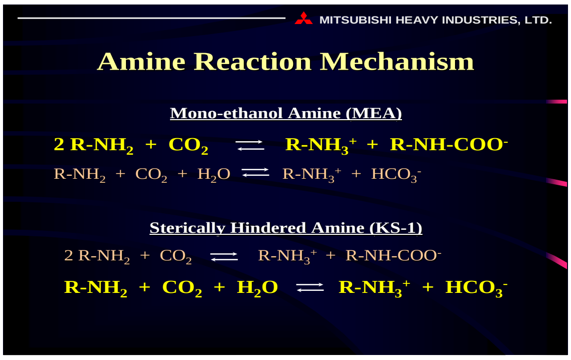


Figure -2

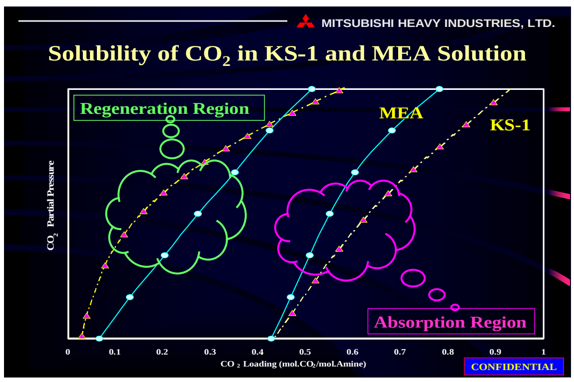


Figure - 3

regenerated compared to conventional MEA solution.

Figure-4 shows the comparison of heat of CO_2 dissociation from the solvent.

When amine absorb CO_2, absorption heat is emitted and amine desorbs, dissociation heat is necessary.

KS-1 is approximately 20% less heat of dissociation needed than MEA.

Figure-5 shows the corrosion test results compared with MEA and KS-1. MEA itself is very corrosive, therefore requiring corrosion inhibitors where carbon steel materials are used.

KS-1 is very low level of corrosion tendency, therefore KS-1 does not need corrosion inhibitors.

Figure-6 shows the deteriorated product formation comparison between MEA and KS-1. Because flue gases contain oxygen, and oxygen accelerates deterioration of amines. MEA quickly deteriorated, therefore demanding solvent clean up operations much more frequently. Usually when heat sable salts content reach 3 wt%, solvent clean up operation (reclaiming) is needed, therefore MEA demand reclaiming operations every month, whereby MHI KS-1 solvent's reclaiming operation is once in 6 months.

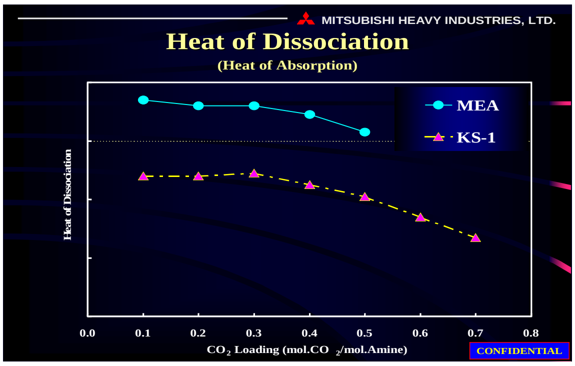
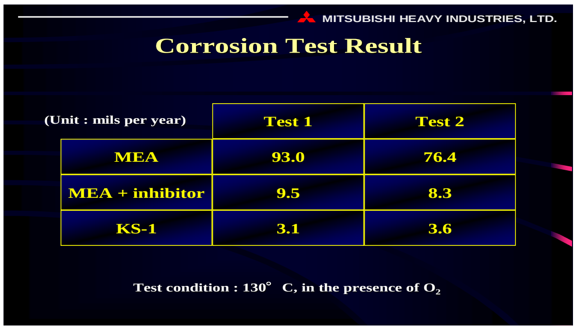


Figure - 4



(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

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

Figure - 5

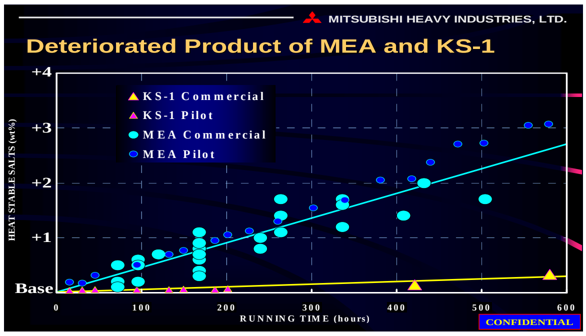


Figure - 6

3.2 Energy Efficient Process

KEPCO/MHI developed the process, incorporating KS-1 solvent, and recently developed energy efficient regeneration process by unique concept as shown in Figure-7.

The process itself reduces solvent regeneration energy about 15% from conventional process.

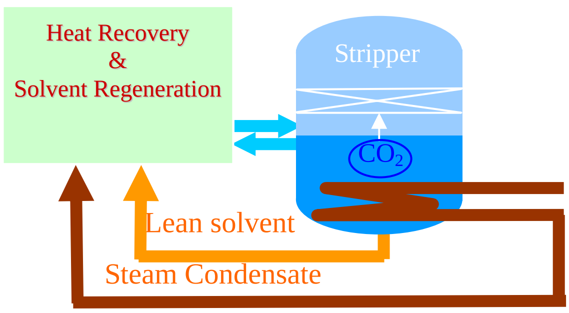


Figure – 7 Energy Efficient Process for Solvent **Regeneration**

3.3 Energy Efficient Process

We are exploring for the equipment enlargement to expand scale of economy. MHI has comprehensive experiences of large capacity flue gas desulfurization process, handling 3 million normal cubic meters per hour of flue gas by single train. By using these technologies and know-how, MHI developed 3,000 T/D (60 MMSCFD) CO_2 recovering capacity by single train. Figure-8 shows a birds eye view of 3,000 T/D plant.MHI is developing large scale plant to 6,000 T/D (120 MMSCFD) CO_2 recovery capacity.

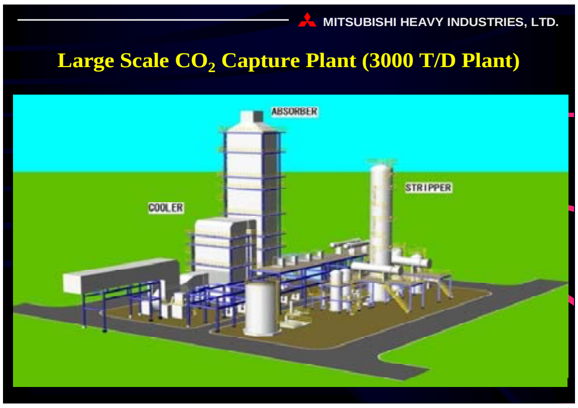


Figure - 8

4. Recent Experiences

The first commercial plant by MHI new technology has been in operation since October 1999 in Malaysia utilizing advanced KS-1 solvent. Figure-9

The plant recovers 200 T/D CO_2 from steam reformer flue gas and use CO_2 for urea production. The energy efficiency and low amine consumption are confirmed by the extended period of commercial operation.

Figure-10 shows the second commercial plant which commenced operations in Japan, November 2005, with CO_2 recovered from boiler flue gas being used for dry ice, and beverages. Maximum CO_2 recovery capacity is 330 T/D.

Another two CO_2 recovery plants are under construction in India for CO_2 recovery, capacity 450 T/D each and one is under construction in Abu Dhabi. At these plants recovering CO_2 will be used for urea production. Also an addtidional CO_2 recovery plant in under construction in China for methanol production purpose, CO_2 recovery capacity 800 T/D. Finally a coal fired power station flue gas CO_2 recovery demonstration plant is under construction in Japan. KEPCO and MHI have several testing facilities from bench scale to the pilot plant for the purpose of improving flue gas CO_2 recovery technology and their demonstration purposes.

Figure - 9 (Commercial Plant in Malaysia)

Figure - 10 (Commercial Plant in Japan)

5. CO_2 Recovery Costs for Enhanced Oil Recovery (EOR)

5.1 Required CO_2 Conditions for EOR

For the purpose of CO_2 EOR the following conditions are required.

1) CO_2 Purity

For the purpose of achieving miscible conditions in the oil reservoir, required CO_2 purity is more than 94~95 vol.%.

MHI technology produces very high purity CO_2 such as 99.9 vol.% with more at dry base, therefore CO_2 recovered from flue gases is suitable for CO_2 EOR.

2) Amount of CO_2

CO_2 requirement for EOR is between 3 and 8 MSCF/BBL of CO_2 is considered economical.

3) CO_2 Pressure

Usually CO_2 delivery pressure of 2000 psig, is used at the inlet of the CO_2 pipeline.

CO_2 then being compressed at the wellhead to suit the wellhead pressure accordingly.

5.2 Study Basis

A comprehensive economic study was carried out on CO_2 recovery plants in Middle East area for the purpose of Enhanced Oil Recovery (EOR) based on various parameters which included (i) the capacity of the CO_2 recovery unit, (ii) the utility cost, (iii) the pipeline cost and (iv) any other operational requirements.

The following four cases were selected for the study. These conditions were reviewed and considered, as they represent typical large scale CO_2 recovery plants for EOR purpose.

Table - 1

	CO_2 content	CO_2 Recovery Capacity
Boiler Case-1	8.5 vol%	100 MMSCFD
Boiler Case-2	8.5 vol%	60 MMSCFD
Gas Turbine Case-1	3.0 vol%	90 MMSCFD
Gas Turbine Case-2	3.0 vol%	50 MMSCFD

1) Capital Cost Estimation

CAPEX consists of the initial investment cost of the CO_2 recovery, the cost of its compression and the cost of its auxiliary utilities. The plant costs are based upon MHI's experience of commercial plants currently operating in the Middle East. The initial capital investment was depreciated at 10% per year in the study.

2) Operation and Maintenance Cost Estimation

OPEX consists of the operation expenses including the cost of all utilities, operational personnel, maintenance, consumables, spare parts and general charges of the plant management. The cost portion of operational personnel, maintenance, consumables, spare parts and general charges were considered as constant, since they are not large percentage.

Utility unit costs are varied for the study.

Table - 2

	Study case		
Fuel Gas (US$/$10^6$BTU)	0.5	1.0 (Base)	1.5
Cooling Water (US¢/T)	1.0	1.5 (Base)	2.0
Electricity (US¢/Kwh)	2.0	3.0 (Base)	4.0

Base case study results based upon utility unit cost for the following are shown in Table-3.

- Fuel Gas:···············1.0 US$/$10^6$BTU
- Cooling Water:·······1.5 US¢/T
- Electricity: ··············3.0US¢/Kwh

Table - 3 Base Case Study Results

Case	CO_2 Content in Flue Gas	CO_2 Recovery Capacity	On Stream Factor (%)	CAPEX (US$/MSCF)	OPEX (US$/MSCF)	Cost Total (US$/MSCF)
Boiler Case-1	8.5	100	90	0.472	0.444	0.916
Boiler Case-2	8.5	60	90	0.533	0.515	1.048
Gas Turbine Case-1	3.0	90	90	0.609	0.830	1.439
Gas Turbine Case-2	3.0	50	90	0.609	0.838	1.446

5.3 Factors affecting CO_2 recovery and compression cost

1) CO_2 recovery capacity

The relationships between CO_2 recovery and compression cost (delivery cost) and CO_2 recovery capacity are shown in Figure - 11.

The single train CO_2 recovery plant for gas turbine flue gas is limited to 50 MMSCFD. Therefore if an increase of 100 MMSCFD is required, then two train plants are necessary.

On the other hand, a single train CO_2 recovery plant of up to 100 MMSCFD is possible for boiler flue gas. Therefore scale of economy can be enjoyed in boiler flue gas cases. CO_2 delivery cost also depends on CO_2 content of flue gas. The higher CO2 concentration results in the smaller size of equipment. CO_2 recovery plant for boiler flue gas gives less CO_2 delivery cost than that for gas turbine flue gas.

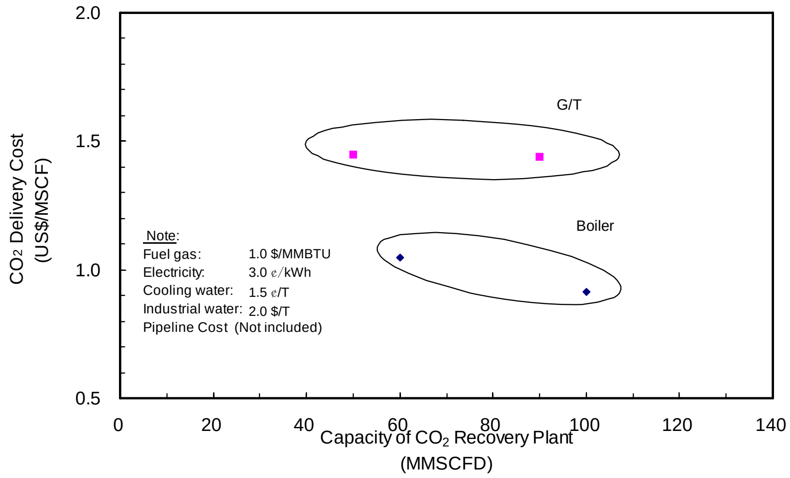


Figure - 11 Relationship between CO_2 Delivery Cost and CO_2 Recovery Plant Capacity

2) Fuel gas cost

The relationships between CO_2 recovery and compression costs (delivery costs) and fuel gas unit costs are shown in Figure - 12.

Since CO_2 recovery and compression plants need large amounts of energy, CO_2 delivery costs are affected by the unit cost of fuel gas. Actually one of the most significant effect on CO_2 delivered costs is fuel gas cost.

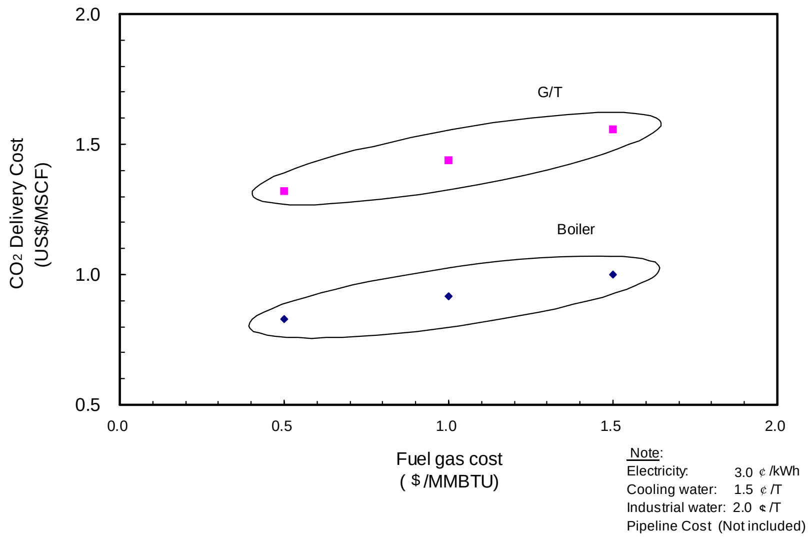


Figure - 12 Relationships between CO_2 Delivery Cost and Fuel Gas Cost

3) Cooling Water Cost

The relationships between CO_2 recovery and compression costs (delivery costs) and cooling water unit costs are shown in Figure - 13.

Since combustion flue gas cooling and CO_2 recovery plants need large amounts of cooling media, CO_2 delivery costs are affected by the unit cost of cooling water.

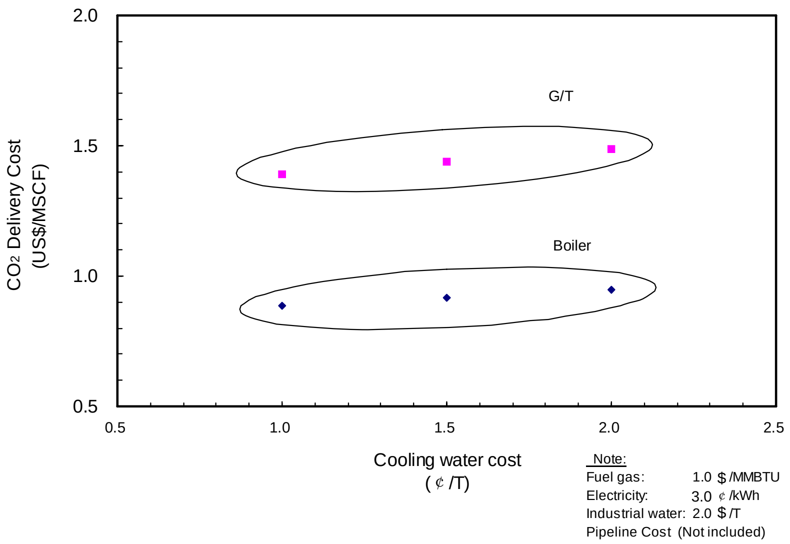


Figure - 13 Relationship between CO_2 Delivery Cost and Cooling Water Cost

4) Pipeline Cost

CO_2 pipeline costs were between 6 US¢/MSCF/100 km and 10 US¢/MSCF/100 km in the Middle East. Therefore if CO_2 recovery and compression cost (delivery cost) is 1.0 US$/MSCF and the CO_2 is transported by a 100 km long pipeline to the oil fields, then CO_2 arrival costs are 1.06 to 1.10 US$/MSCF.

If CO_2 sources such as large boilers are located near oil fields (within 100~300 km) then the delivery cost of CO_2 at the oil field is a little above 1.0 US$/MSCF, which is equivalent to CO_2 cost in west Texas area where CO_2 EOR projects are widely carried out. Therefore CO2 recovery from flue gases are economical for enhanced oil recovery. 5 ~ 6MSCF CO_2 is usually needed for CO_2 EOR for one barrel of incremental oil production. Therefore, CO_2 cost for EOR is usually 5 ~ 6 US$/barrel of oil. If CO_2 EOR performance is better, CO_2 requirement and cost of CO_2 can be reduced.

CO_2 can be utilized for EOR and at the same time CO_2 can be stabilized in the oil reservoir, therefore flue gas CO_2 recovery and EOR can contribute to a reduction of CO_2 released into the atmosphere contributing to global CO_2 emission reduction initiatives.

If flue gas CO_2 recovery and EOR projects are applied for Joint Implementation (JI) or Clean Development Mechanism (CDM), then CO_2 emission rights to become valuable and can be traded.

Such trade benefits can be enjoyed for flue gas CO_2 recovery and EOR projects.

1US$/MSCF of CO_2 is equivalent to 19US$/Ton CO_2. Therefore if the CO_2 emission trade price becomes more than 20 US$/Ton then the delivery cost can be completely offset by the emission trade price. In such cases, CO_2 EOR projects will have huge financial benefits.

6. Application of CDM for CO_2 Capture and EOR Projects

Since CO_2 capture from flue gases and utilize CO_2 for EOR can reduce CO_2 emissions to atmosphere, therefore, CO_2 capture and EOR projects contribute for global warning prevention issue. By Kyoto Protocol, Annex 1 countries (developed countries) which ratify the Kyoto Protocol and non Annex 1 countries can collaborate together and reduce CO_2 emissions to atmosphere, such project would be applied as CDM (Clean Development Mechanism). However based on CDM rules, CDM have to clarify baseline scenario and additionality scenario have to be clarified for each projection. Baseline scenario means that the project can reduce CO_2 emission when the project is executed. This scenario is easier to explain if the monitoring procedures are clarified. On the other hand, additionality scenario means that the project can not be executed without the economical benefit by the income of CDM. CO_2 EOR projects has to be economical without CDM income, therefore this additionality scenario may be very difficult to explain. Although rules of CDM exist in Kyoto Protocol, CO_2 capture from flue gases and utilize CO_2 for EOR projects actually reduce CO_2 emissions to atmosphere and stabilize CO_2 into oil reservoir, therefore the projects can contribute global warning prevention issues. Oil producing counties and Annex 1 counties such as Japan and EU have to collaborate together to influence to the CDM board of United Nations to realize the projects of CO_2 capture and EOR as the CDM project.

CO_2 capture and EOR projects can actually contribute not only for increased oil recovery remaining in reservoirs, but also simultaneously contribute to global warming prevention issues.

<Reference>

1) 1MSCF CO_2 = 10^3 standard cubic feet of CO_2
   = 52.6 kg CO_2

2) Iijima M., et al. 2002 Greenhouse Gas Control Technologies, Kyoto Japan "Flue Gas CO_2 Recovery and Compression Cost Study for CO_2 Enhanced Oil Recovery."