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JAPANESE R&D ON LARGE-SCALE CO₂ CAPTURE

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ABSTRACT

The Special Report on Carbon dioxide Capture and Storage was recently accepted by IPCC (1). In the context of optimization and integration of CO₂ capture and sequestration, CO₂ capture is a particularly important step. This paper presents a broad overview of key issues of CO₂ capture technologies in the Japanese R&D, focusing on their application to large-scale power plants.

INTRODUCTION

Since 1990s the world has been groping for a new era of sustainable development and solutions to reduce CO₂ emissions. Much attention has been focused on the reduction of CO₂ emissions from fossil combustion for power generation since it makes the largest contribution to the atmospheric build-up of CO₂.

Focusing on CO₂ emissions from power generation today, electric power generation emitted roughly 300 million tons of CO₂ and was the source of approximately one third of CO₂ emissions in Japan. Fossil fuel combustion is the largest emission source of CO₂ in Japan as well as in the world. However, there is still predominant reliance on fossil fuels for primary energy supply and electricity production (2). Looking into the future, the reliance on fossil fuels is expected to continue worldwide. CO₂ emission reduction is a key factor in supporting the continued use of fossil fuels.

There are several options for the electric utilities to reduce the amount of CO₂ emissions. The potential solutions include increase of energy efficiency, switching to fuels with lower CO₂ emissions, selection of energy sources with no CO₂ emissions such as nuclear power and renewable energy sources, and CO₂ capture and sequestration.

The greenhouse effect issue has provided added impetus to R&D for improvement of energy conversion efficiency. Many advanced technologies for efficient use of fossil fuels have been developed in Japan. This includes IGCC(integrated coal gasification combined cycle), MCFC(Molten carbonate fuel cell), SOFC (Solid Oxide Fuel Cell), IGFC (Integrated Gasification Fuel Cell). However, we may have to wait for a decade for these emerging technologies to be commercialized. Any fossil fuel combustion emits carbon dioxide. It is quite natural to think of switching to fuels with lower CO₂ emissions, or renewable energy sources. Concerns over renewable and new types of energy are rapidly growing in Japan. Energy policy of the Japanese government foresees significant increase of share of these energy resources such as wind power, photovoltaic power and waste-fired power toward the year 2010 (3). However the anticipated development potential of them is too small to play a major role in power generation or CO₂ reduction in a short term.

Among the options, greater reduction of CO₂ from power plant flue gas in a medium term is expected to be technically possible, using CO₂ capture and sequestration. Capture and sequestration of CO₂ from flue gas, aiming at the greenhouse effect reduction, is a new approach for the electric utility industry. One of the key issues is the development of cost-effective technologies for CO₂ capture and sequestration. Cost reduction of CO₂ capture is particularly important.

HISTORIC OVERVIEWS OF CO₂ CAPTURE

CO₂ capture from flue gases at a power station was first installed in the early 1980's by Carbon Dioxide Technology Corporation at the Holly Street Power Station of Lubboch Power & Light Department (Texas) as response to the oil "crises" of the 1970's in the United States. The CO₂ capture facility, including liquefaction and pipeline systems, was to take CO₂ from a natural gas-burning power plant to supply 1,100 tons/day of CO₂ for enhanced oil recovery. The plant was designed to be self-sufficient in steam. Due to falling demands for electricity and declining oil prices the CO₂ recovery was shut down and dismantled in early 1984 (4).

This table shows the CO₂ capture facilities currently being operated to recover large quantities of CO₂ from flue gases at several sites. These are mostly amine-based CO₂ capture technologies and have long been used in the petroleum, natural gas and ammonia plants(5)(6).

Table 1 Large-scale CO₂ capture facilities

Flue gas source	Licenser	Technology	Capacity	Location	Use
Natural-gas fired power plants	Dow Chemical	Gas/Spec FT-1	1100 US tons/day operation started 1982 dismantled 1984	Lubboch, Holly Street Plant, Texas, USA	EOR
Coal petrocokes, and natural gas-fired boiler	Kerr-McGee/ ABB/Lummus Crest	CO ₂ Recovery	800 US tons /day operation started 1978	Trona, Seales Valley, California, USA	soda ash
Coal-fired boiler	Kerr-McGee/ ABB/Lummus Crest	CO ₂ Recovery	300 US tons /day operation started 1991	Sua Pan , Botswana	soda ash

Table 1. (continued)

Fluidized coal-fired bed cogeneration plant	Kerr-McGee/ABB/Lummus Crest	CO ₂ Recovery	200 US tons /day operation started 1991	AES Shady Point Power Plant, Oklahoma, USA	food
Natural gas combined cycle	Fluor Daniel	Econamine - FG	320 US tons /day operation started 1991	Bellingham, Massachusetts, USA	food
Steam reforming gas or flue gas	Mitsubishi Heavy Industry/ Kansai Electric Power Co.	MHI/KEPCO KS-1	160 tonnes/day started operation 1999	Kedah Darul Aman, Malaysia	food
Converter-reburning gas	Nippon Steel Co.	PSA Oil-pitch-derived activated carbon	170 tonnes/day started operation 1989	Kimitsu, Japan	CO ₂ production

CHARACTERISTICS OF FLUE GAS

When compared to gas treated in the petroleum, natural gas and ammonia plants, flue gas from fossil-fired power plants has unique characteristics as shown in table 2. These characteristics are primary variables to be considered for process development. The primary variables are low pressure, presence of oxygen, presence of pollutants (NO_x, SO_x, particulates), high temperature and huge gas flow rates.

Table 2. Characteristics of fossil-fuel-combustion flue gas for power generation

Characteristics	Details
Pressure	Atmospheric pressure
CO ₂ concentration	10 - 15 (% DVB) (LNG CC:3%)
O ₂ concentration	3.3 - 5.5 (% DVB)
Pollutants	Particulates, SO ₂ (coal, oil), NO _x
Flow rate	Very high (m ³ _N /hr) 3,400,000 coal combustion 1000MW 3,000,000 oil combustion 1000MW 2,500,000 LNG combustion 1000MW

R&D ACTIVITIES ON CO₂ CAPTURE OF THE JAPANESE ELECTRIC UTILITIES

The Japanese electric utilities have conducted R&D on CO₂ capture technologies for many years, including adsorption, absorption, and membrane methods (7)(8). Some of the activities are shown in Table 3.

Table 3. R&D on CO₂ capture technologies

Company	Fuel	Flue Gas Volume	Technology
Tokyo Electric Power Co.	COM	1,000 m ³ _N /hr	Chemical absorption
Tokyo Electric Power Co.	COM	1,000 m ³ _N /hr	PTSA
Tohoku Electric Power Co.	Coal	1,700 m ³ _N /hr	PSA
Kansai Electric Power Co.	LNG	600 m ³ _N /hr	Chemical absorption
Hokuriku Electric Power Co.	Coal	50 m ³ _N /hr	PTSA using moving bed
Tokyo Electric Power Co.& Tohoku Electric Power Co	Simulated gas	5-10 m ³ _N /hr	
CRIEPI	NG	880 m ³ _N /hr	Chemical absorption

COM: Coal-Oil-Mixture, LNG: liquefied natural gas, NG: natural gas, PTSA: pressure and temperature swing adsorption PSA: pressure swing adsorption

Tokyo Electric Power Company tested CO₂ capture from COM (Coal-Oil-Mixture)-fired flue gas using chemical solvents, and also PTSA with a zeolite adsorbent. 1000 m³_N/hr of the flue gas was treated. Tohoku Electric Power Company also tested CO₂ capture from coal-fired flue gas using the PSA technique with a zeolite adsorbent. 1,700 m³_N/h of the flue gas from 1000 MW coal-fired power plant was treated. An amine-based test plant has been operated by Kansai Electric Power Company. This treated 600 m³_N/hr of flue gas from 600 MW LNG-fired power plant at the Nanko power station. At the beginning of the test Fluor Daniel's Econamine FG[®] solvent was used but later KS[®] solvents were used. The KS[®] solvents were developed by Kansai Electric Power Company and Mitsubishi Heavy Industry. Hokuriku Electric Power Company had operated a test plant treating 50 m³_N/hr of flue gas from a coal-fired power plant at the Toyama-Shinko power station. The pressure swing adsorption technique with a zeolite on moving bed was used. A laboratory-scale test for R&D on adsorbent with higher performance and lower pressure loss was conducted by Tokyo Electric Power Company, jointly with Tohoku Electric Power Company using a test facility treating 5-10 m³_N/hr of flue gas.

In addition to these technologies, oxyfuel combustion, the Benfield process, hybrid processes combining cryogenic separation and pressure swing adsorption or membrane separation had been studied by other electric power companies. R&D on CO₂ fixation and utilization, with approaches ranging from biological processes to catalytic hydrogenation reactions, has been conducted.

Common objectives of the R&D activities of the electric power companies - improvement of the System Performance and evaluation of the Economics - are summed up in Table 4.

A lot of data has been collected and performance of the CO₂ removal methods was evaluated with respect to energy requirements against a number of variables. The major results indicated that CO₂ from power plant flue gas could be captured with efficiency exceeding 90 % by chemical absorption with amine-based solvents or zeolite-based adsorption process. Some preliminary studies of the CO₂ capture tests

Table 4. Common objectives of the R&D activities

System Performance	<ul style="list-style-type: none"> - Reduction of energy requirements for CO₂ recovery - Scale-up - Corrosion prevention - Control of impurities in flue gases (SO_x) - Environmental performance (odor, noise etc) - Stable and reliable long-term operation - Compliance with load Fluctuation
Economics	<ul style="list-style-type: none"> - Evaluation of economics

are shown in Table 5. However the CO₂ capture reduces significantly the power outputs, as shown in Table 3. To date, most of the tests have been terminated. Kansai Electric, together with Mitsubishi Heavy Industry, is still successfully conducting CO₂ capture tests which employ patented chemical solvents - sterically hindered amines called KS-1, KS-2 or KS-3 - that require less energy for regeneration. The regeneration heat of KS solvents is said to be 700 kcal/ kg CO₂. i.e. and 20% lower than that of MEA with 900 kcal/kg CO₂ (9)(10).

Table 5. R&D Activities of Japanese Electric Utilities on CO₂ capture

Technology	Type	Scale	CO ₂ concentration	Energy requirement *,
Chemical Absorption	Amine	600 m ³ N/h	4-13%	18% (LNG)
Physical Separation	PSA	1,700 m ³ N/h	9-16%	- (coal-fired),
Physical Separation	PTSA	1,000 m ³ N/h	8-16%,	40% (COM)

Removal efficiency > 90%, Purity > 99% * Based on nameplate output

Major problems, broadly summed up in Table 6, remain to be solved. It is likely that the CO₂ capture technologies, when they are applied to power plants, come at a high cost in terms of reduction of net power output.

Table 6. Major issues in CO₂ capture

Type	issues
Chemical Absorption (examples : MEA, Econamine-FG,Ucarsol)	Scale-up: larger by 10 times Improvement of energy (regeneration of absorbent) Modification of power plant for steam extraction
Physical Separation (examples : PSA)	Scale-up: larger by 10 – 100 times Improvement of adsorbent, large-scale vacuum valve and peripheral devices
Membrane Separation	Many issues for R&D

CHEMICAL ABSORPTION

At present chemical absorption, in particular amine-based absorption, seems to be

the only technology to allow evaluation of its applicability to large scale CO₂ capture from power generation, because currently a few large-scale commercial CO₂ capture plants, using chemical absorption, are operating on coal boilers and other gases.

More details of the development requirements for CO₂ capture, using chemical solvents, are discussed below, based on the experimental results of MEA (Monoethanolamine) process operated at CRIEPI(Central Research Institute of Electric Power Industry).

Data of Test Facility

The test facility for CO₂ capture consisted of a conventional gas cooler, absorber, regenerator and steam-heated reboiler. The absorber height-12.2 meters, and regenerator height -10.6 meters, are as shown in Figure 1. The natural gas-fired boiler was equipped to supply flue gas to the CO₂ capture system.

This facility was able to capture a maximum of three tonnes of CO₂ per day. This was a computer-supported facility. Process parameters such as gas compositions, temperature and pressure in the process were continuously monitored. In addition on-line analysis of mass transfer, heat transfer and other calculations were available, based on the process data collected during operation.

Flue gas, containing CO₂, is contacted in the absorber with a lean amine which captures CO₂ to produce rich amine solvent. The captured CO₂ is steam-stripped from the rich amine solvent in the regenerator and the resultant lean amine solvent is recycled to the absorber. The operation of MEA process depends on the reversible nature of the chemical reaction between amine solvent and CO₂. The reaction properties are most relevant to operating performance of the process and are expressed as CO₂ loadings (carbonation ratio which is expressed as CO₂ moles/ MEA mole present originally). The CO₂ loadings, in other words equilibrium between CO₂ and amine, are shifted by changing temperatures. The most important parameters, affecting the process performance, are the reboiler heat duty and circulation rate (11), thus the cost and size of amine plant.

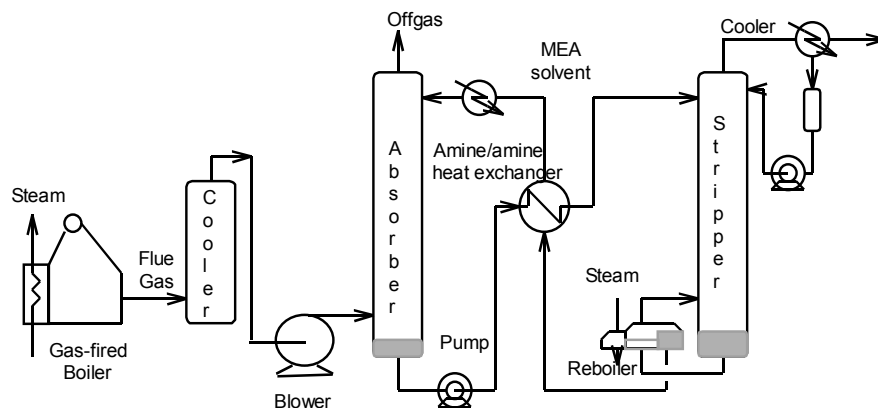


Figure 1. Test facility for CO₂ capture

The process performance which should be taken into consideration for the solvent

development is examined below showing the test results obtained:

Absorption Performance

The temperature profiles, gas-phase CO₂ concentration profiles, liquid-phase CO₂ loadings of the absorption column at the three different circulation conditions are respectively represented in Figures 2(a), 2(b) and 2(c). The three Figures show the process chemistry during CO₂ capture.

Temperature bulges on the Figure 2(a) are attributed to the heat of reaction when CO₂ is absorbed into the amine solvent. The bulge occurs at a point that is higher or lower than the midpoint of the packed section of the absorber depending on the solvent circulation rate. As the flue gas flows upwards from the bottom to the top of the absorber, the CO₂ concentration in the flue gas decreases as shown in Figure 2(b). As the solvent flows from the top of the absorber to the bottom, the CO₂ loading increases, responding to the trend in CO₂ concentration in the flue gas, as shown in Figure 2(c). The process chemistry in the absorber, which can be varied by changing amine circulation rates, provides useful information for the absorber performance optimization.

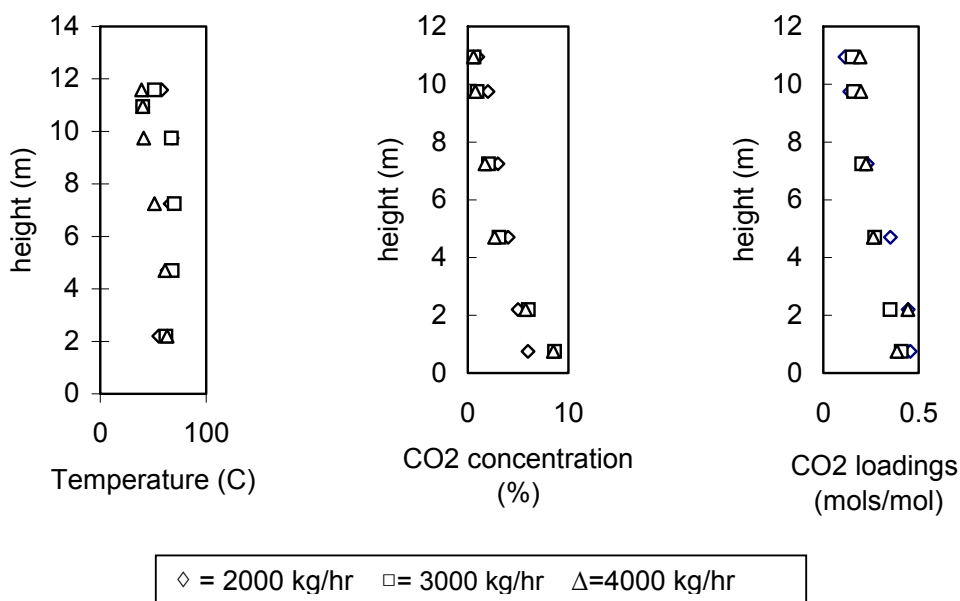


Figure 2(a)
Temperature profile

Figure 2(b)
Concentration profile

Figure 2(c)
CO₂ loadings

Reboiler Heat Duty

The steam supply in the reboiler, along with the solvent circulation rates, is a significantly important parameter in control of the energy requirement for CO₂ capture. Given a constant solvent circulation rate, with decreasing steam supply the lean

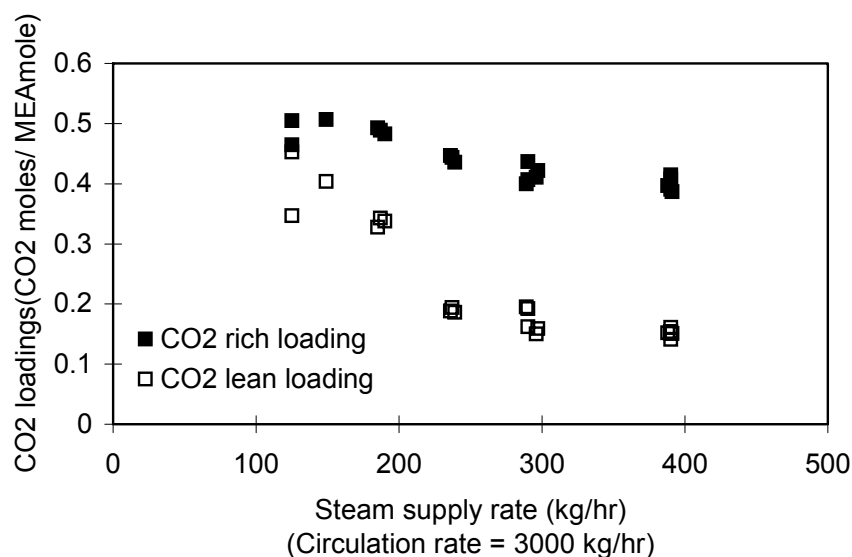
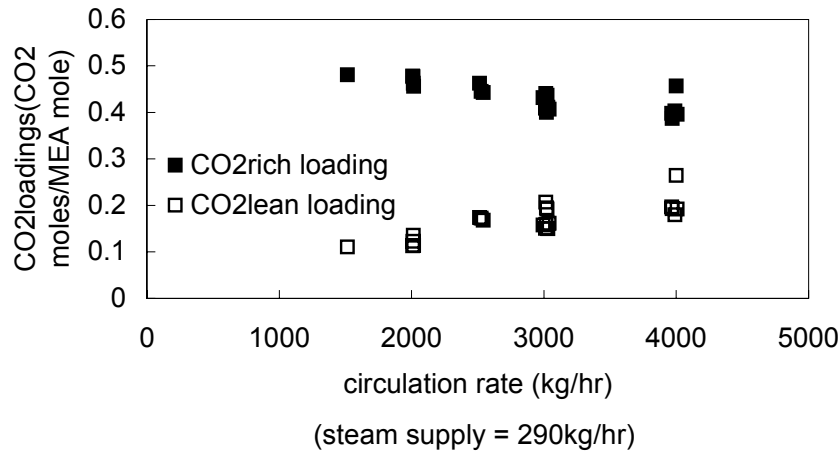


Figure 3 Steam supply rate vs CO₂ loadings

loading closely approaches the rich loading, eventually approaching the carbonation ratio of 0.5 which refers to the equilibrium usually assumed for the reaction between CO₂ and MEA. An increase in the steam supply leads to an increase of the net CO₂ loading, in other words, CO₂ carrying capacity(= rich CO₂ loading minus lean CO₂ loading), thus the amount of CO₂ captured as shown in Figure 3. Then the lean CO₂ loading and rich CO₂ loading tend to stabilize in the region of steam supply rate exceeding about 290 kg/hr. The region could be considered as optimal operational condition. The CO₂ carrying capacity is directly related to the reboiler heat duty (heat input required in the reboiler). Excess steam should not be used to avoid costly operation. These CO₂ loadings should be determined for a specific unit, if possible.

Circulation Rate

The CO₂ loadings are influenced by circulation rate as well as by steam supply, as shown in Figure 4. With increasing circulation rate, the rich loading decreases, while the lean loading increases. The difference between the rich loading and the lean loading at the same circulation rate gives the net CO₂ loading. In this case CO₂ capture efficiency was 80–94 %. The energy consumption increases as the circulation rate is raised. Increment of the CO₂ rich loading causes a decrease in the circulation rate, and thus energy. The circulation rate should be optimized by avoiding overcirculation of amine solvent, in addition to optimum CO₂ loadings in the rich and lean amine solvents.

Figure 4 Circulation rate vs CO₂ loadings

Development of Chemical Solvents

Some work on development of chemical solvents has been already done and will be further required to reduce the energy used in solvent regeneration. The CO₂ capture process is affected by a variety of operational factors mentioned above, as well as by design factors. In solvent development process, the performance analyses of potential chemical solvents should be carried out thoroughly, taking into account:

- lean/rich CO₂ loadings,
- energy required to regenerate a CO₂ loaded solvent,
- circulation rate,

In addition, loss of the solvent, degradation waste and corrosion and effect of co-existing gases should also be taken into account.

Size of CO₂ Capture Systems

A feasibility study has been carried out for the CO₂ capture of 5800 tons/day from 600 MW LNG-fired power plant using the conventional MEA process. The CO₂ capture system, including liquefaction and storage, was designed using minimum heat requirement obtained during the test operation on CO₂ capture. Power plant modification and CO₂ sequestration are not included⁽⁵⁾.

The CO₂ capture system for the large-scale gas treatment requires a four-train process system (four parallel absorber-stripper pairs) due to economic design constraints and operational requirements. One of the four units is illustrated in Figure 5. Maximum diameter of columns of the systems is 4.7 meters and the height of the absorber is 44 meters. The height of the cooling tower and strippers is about 25 meters. The whole unit size is enormous. It requires high capital and has high operating costs. The plot layout is illustrated in Figure 6. It also requires a vast area, also, almost equivalent that of the power plant.

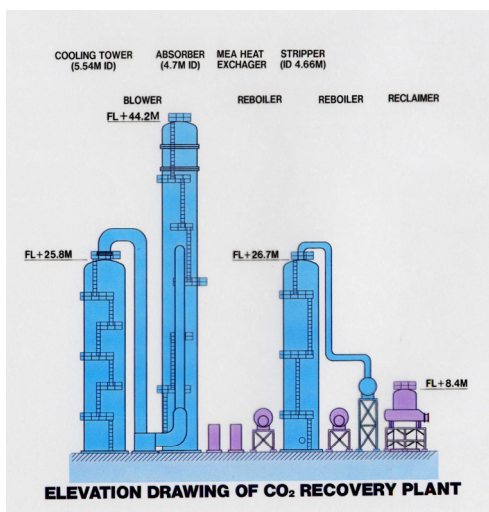


Figure 5. Elevation drawing of CO₂ capture plant(1 train of 4 train units)

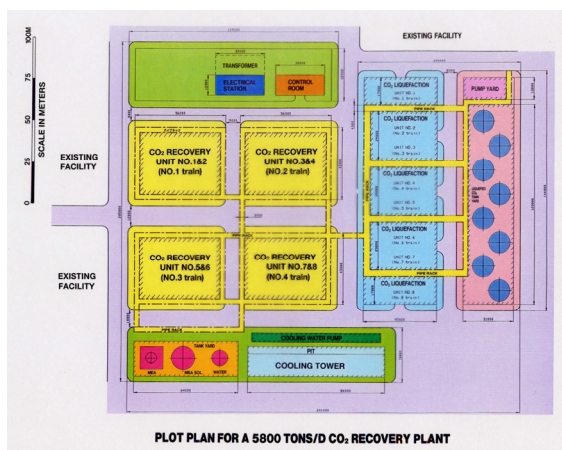


Figure 6. Plot layout for a 5800 tonnes /day CO₂ recovery plant

Plant Modification

In the feasibility study mentioned above, plant modification is an important matter, and attention needs to be given to the extent of modification required to an existing power plant to capture CO₂. The essential components of power plant such as steam cycle and/or flue gas stacks must be modified to integrate the CO₂ capture process to supply the steam to the reboiler system and/or flue gas to the CO₂ capture system. However, the modification of plant results in significant decrease in the overall power output and may affect the security of the national electricity supply if CO₂ capture plants are installed extensively. However, it is possible to design a CO₂ capture plant which is self-sufficient in steam and electricity as had been employed in the CO₂ capture system at the Holly Street Power Station of Lubboch Power & Light Department.

PHYSICAL ADSORPTION AND MEMBRANE

The key issues on physical adsorption and membrane, compared to chemical absorption, are briefly reviewed below.

Physical Adsorption

Compared to the CO₂ capture by chemical absorption from power generation, the CO₂ capture by adsorption is less attractive. To reduce the energy requirement, and dimensions of system components, several developments would be required as summed up in Table 7:

Table 7. Key issues on CO₂ adsorption

Problem	Further research needs
Adsorbent	Development of higher performance adsorbents is needed: adsorbents with lower pressure gradient such as honeycomb structure, adsorbents with higher capacity throughout the range of CO ₂ partial pressures, adsorbents with increased selectivity and improved reactivity to CO ₂ .
System component	The system components such as fans, blowers, vacuum pumps, vacuum valves for large-scale application must be developed and demonstrated.
Size	Enormous number of adsorption vessels would be required for CO ₂ capture system by adsorption because of the limited availability of existing vessel sizes. This makes the CO ₂ removal system complex and expensive.

Membrane

Laboratory scale studies on membrane separation technologies have been conducted by the Research Institute of Innovative Technology for the Earth (RITE). A hollow-fiber membrane module with a newly developed cardo-type polymer has developed. Also a facilitated transport membrane using a water-swollen-gel for the membrane structure and a mixed water-solution of caesium carbonate and 2,3-diaminopropionic acid as the carrier has been developed (12). Performance projection for a large scale coal-fired power plant, including liquefaction showed that a cardo-type polymer membrane with a CO₂/N₂ separation factor of 35 recovered CO₂ effectively. However, the new equipment required considerable space(13). Further development, as indicated below, is required before membranes could be used on a large scale in power plants:

- Membrane material development
- Production methods for practical-size-modules
- Membrane system development and demonstration
- System components such as vacuum pumps for large-scale application

COMMENTS

Challenging issues do still remain to be solved in CO₂ capture technologies. In particular, extensive and careful examination is further required for integration of the CO₂ capture and sequestration system. Dependence on fossil fuels is expected to increase worldwide with the greatest growth in developing countries. Transfer of energy efficient technologies will become increasingly important for reduction of CO₂ emissions.

Global climate change is a new factor that must be considered in the development of technologies and strategies for energy use. Although a superficial analysis might conclude that coal utilization would be reduced as switching to gas and oil in response to carbon taxes and other measures to reduce CO₂ emissions, the global energy supply situation is not that simple. Long term strategies to reduce CO₂ emissions must be comprehensive and take into account all energy supply options

and reserves, advanced fossil fuel utilization technologies, end user technologies, and demand side management. The ultimate objective of providing a sustainable, economically and environmentally sound energy supply system must be firmly kept in mind.

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