

## Chemical Research Group

### Looking ahead to Future CO<sub>2</sub> Separation Technologies and their Challenges

The cessation of thermohaline circulation in the ocean because of global warming, which will have a destructive influence on the Earth's environment, is an issue that needs to be addressed. We need to determine to what extent the CO<sub>2</sub> concentration in the atmosphere should be controlled scientifically to prevent this phenomenon. The probability of cessation of thermohaline circulation in the ocean is several percent at a CO<sub>2</sub> concentration of 550 ppm, and this probability increases by several tens of percent at a CO<sub>2</sub> concentration of 650 ppm.

In the Stern Review released in 2006, although the above catastrophic phenomenon was not taken into consideration, it was predicted that all countries in the world will suffer a 5% gross domestic profit (GDP) loss due to global warming if the global warming problem is not addressed. The review stated that a contribution of 1% of GDP to combat global warming is reasonable from an economic point of view. The Japanese government recently moved to build a new framework to reduce global CO<sub>2</sub> emission after the signing of the Kyoto Protocol.

A CO<sub>2</sub> concentration of 550 ppm is twice the concentration that was present during the Industrial Revolution. If we set a target CO<sub>2</sub> concentration of 550 ppm for 2100, it has been predicted that not only energy savings, fuel switching, renewable energy sources (solar cells, wind power and biomass) and nuclear energy, but also CO<sub>2</sub> capture and underground storage will be necessary to achieve this goal. As the cost of CO<sub>2</sub> capture from CO<sub>2</sub> sources is estimated to be 70% of the total cost of CO<sub>2</sub> capture and underground storage, it is important for the commercialization of this technology that the CO<sub>2</sub> capture cost for CO<sub>2</sub> capture and storage (CCS) is reduced.

Conversion technologies of fossil energy will progress, and we consider the power generation system of a boiler steam turbine evolving into a combined cycle with a gas turbine for power generation and a combined cycle with a fuel cell. Various CO<sub>2</sub> capture technologies such as chemical absorption, physical absorption, membrane separation, and the oxy-fuel method have been developed.

Progress in these technologies will result from development of the best combination of fuel conversion processes and CO<sub>2</sub> capture processes, so that CO<sub>2</sub> capture technologies that have economic benefits, as shown in Figure 1, are developed.

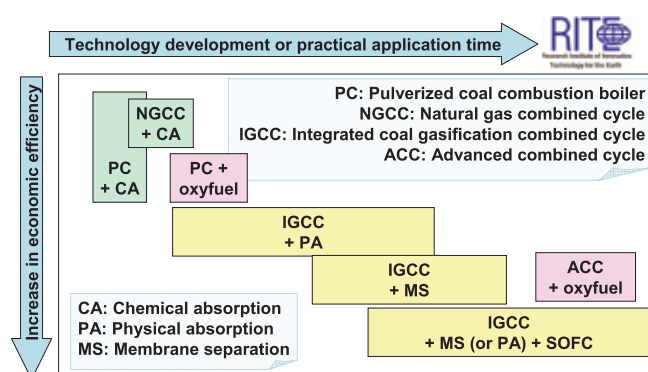


Fig. 1 Vision of power plant and CO<sub>2</sub> capture

Our chemical research group studies various CO<sub>2</sub> capture technologies, with an emphasis on chemical absorption and membrane separation methods. We use chemical absorption to reduce the CO<sub>2</sub> capture cost for flue gas in an ironworks factory to 3400 JPY/ton-CO<sub>2</sub>. We are developing a chemical absorbent to reduce this CO<sub>2</sub> capture cost to 2000 JPY/ton-CO<sub>2</sub>. Moreover, we have discovered an excellent membrane material for the separation of CO<sub>2</sub> from H<sub>2</sub>-containing gas. We are engaged in the development of the structure of a new membrane composed of this material and are developing a membrane module for demonstration with real coal gasification gas.

#### CO<sub>2</sub> capture technology with chemical absorbents

The chemical absorption process, where amine solvent selectively absorbs CO<sub>2</sub> in flue gas and desorbs CO<sub>2</sub> with heating, has the potential to capture CO<sub>2</sub> at large and atmospheric stationary emission sources in practical applications. The most important issue in the chemical absorption process is the development of new solvents to reduce the CO<sub>2</sub> capture cost.

The Research Institute of Innovative Technology for the Earth (RITE) has promoted a project named "A Cost-effective CO<sub>2</sub> Capture System Using Low-grade Waste Heat" since 2004 as a five-year project, with the RITE being responsible for the development of new solvents. The objective is to reduce the CO<sub>2</sub> capture cost in removing CO<sub>2</sub> from the blast furnace gas stream in integrated steel works by almost half compared to the cost of current technology (Figure 2).

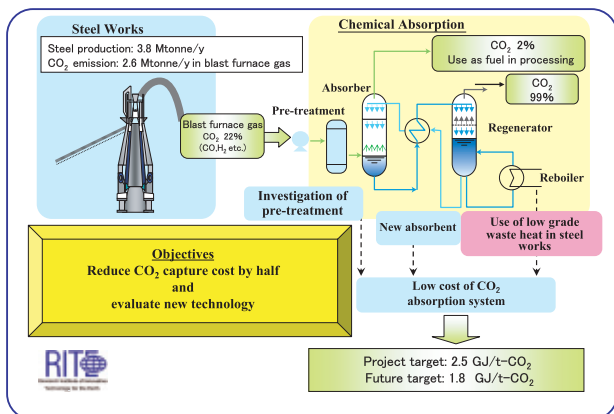


Fig. 2 Outline of cost savings in the CO<sub>2</sub> capture system (COCS project)

Desirable performances of the new solvent are low reaction heat, fast CO<sub>2</sub> absorption rate, and large separation capacity for CO<sub>2</sub>. Through these performances, CO<sub>2</sub> has been separated from a gas stream using less energy. Figure 3 shows a scheme for the development of new solvents. Initially, we investigated reaction characteristics of several hundred commercial amine solvents that have good CO<sub>2</sub> capture performances. We then measured the reaction rate with CO<sub>2</sub>, CO<sub>2</sub> absorbance capacity and the reaction heat using laboratory apparatus. Furthermore, we attempted to create a novel mixture of several amines in which each amine compensates for their deficiencies of others. We made a new solvent and repeatedly improved its performance. In this way, three types of high performance solvents (RITE-3, -4 and -5 Series), which have different characteristics, have been developed to date. Furthermore, high-performance solvents (RITE-5 and -6 series) have been developed from our experimentally formulated database and a theoretical approach to determining the molecular structure of new amine compounds using quantum theory analysis. The best energy performance for CO<sub>2</sub> capture among these solvents was 2.7 GJ/ton-CO<sub>2</sub>, which is very low compared to the 4.0 GJ/ton-CO<sub>2</sub> of the standard MEA (monoethanolamine) solution. It is estimated these absorbents can achieve a 40% reduction in CO<sub>2</sub> capture costs.

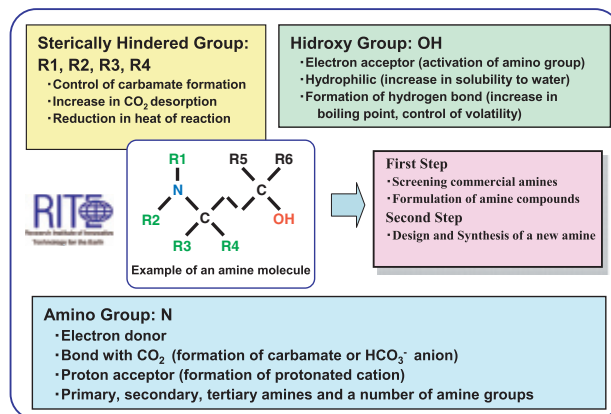


Fig. 3 Development of new absorbents

Future work will be an experimental study of the high performance absorbents and to find optimum conditions for the absorbents in building the most cost-effective CO<sub>2</sub> capture system.

### Chemical absorbent under high pressure

Based on current knowledge of solvents in CO<sub>2</sub> capture from a gas stream under atmospheric pressure, a research and design program for new solvents suitable for a high pressure gas stream has been running since 2007. In general, amine solvents for an atmospheric pressure condition can easily react with CO<sub>2</sub> independent of reaction temperature. However, we have confirmed that some amine solvents have large CO<sub>2</sub> capacity depending on reaction temperature under a high-pressure condition; nevertheless, they cannot react under atmospheric pressure (Figure 4). We intend to propose a new system for CO<sub>2</sub> capture from pressurized point sources through the development of these solvents.

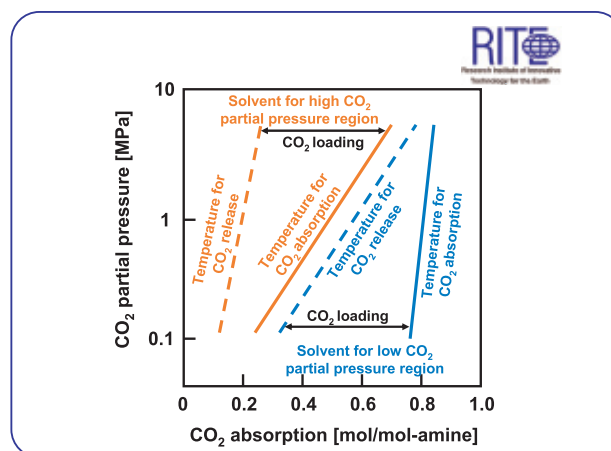


Fig. 4 Comparison of characteristics of chemical solvents applicable in high and low ranges of CO<sub>2</sub> partial pressures

### Novel techniques for regenerating the chemical absorbent

We are developing a regeneration technique for accelerating CO<sub>2</sub> desorption with a pressure difference to reduce the energy consumption in a chemical absorption system. To date, the following observations have been made. Desorption can be accelerated by flashing the solution into a reduced pressure space, which can reduce electric energy consumption by more than half in comparison with the conventional method that uses high temperatures. Moreover, by using low-temperature waste heat, as shown in Figure 5, it is possible to achieve an electric energy consumption about 1/4 (0.1 kWh/kg-CO<sub>2</sub>) of that of the conventional chemical absorption method. We will attempt to apply this method to the separation of CO<sub>2</sub> from flue gases, chemical processes, bioprocesses, etc., while efforts are made to further reduce energy consumption.

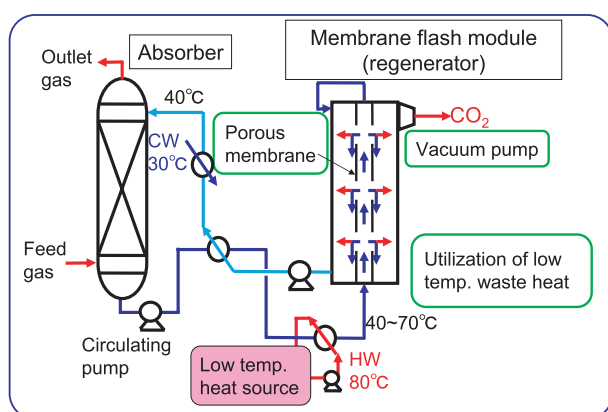


Fig. 5 Example of membrane flash flow with heating

### CO<sub>2</sub> and H<sub>2</sub> separation with a polymeric membrane

One promising means of decreasing the cost of CO<sub>2</sub> separation is the development of new, high-performance CO<sub>2</sub> separation membranes that allow CO<sub>2</sub> recovery via membrane separation from pressurized gas streams. An integrated gasification combined cycle (IGCC) with CCS such as the FutureGen project in the USA provides a pressurized gas stream containing about 40% CO<sub>2</sub> with H<sub>2</sub>. CO<sub>2</sub> would be separated with a membrane injected under the ground for the CCS, and H<sub>2</sub> would be used as a clean fuel. The cost of CO<sub>2</sub> capture from the pressurized gas stream with a membrane might be 1500 JPY/t-CO<sub>2</sub> or less.

We are currently developing a CO<sub>2</sub> molecular gate membrane with the goal of producing a new, high-performance separation membrane. Figure 6 shows the basic outline of the CO<sub>2</sub> molecular gate function. The pathway for gas molecules is occupied solely by CO<sub>2</sub>, which acts as a gate to block the passage of other gases. Consequently, the amount of N<sub>2</sub> or H<sub>2</sub> permeat-

ing to the other side of the membrane is greatly limited and high concentrations of CO<sub>2</sub> can be obtained. The RITE dendrimer having excellent CO<sub>2</sub>/H<sub>2</sub> selectivity is fixed stably in a cross-linked polymer matrix to form the active layer of a resulting composite membrane. The composite membrane showed a record CO<sub>2</sub>/H<sub>2</sub> selectivity of at least 20 at an elevated pressure. The RITE is now improving the selectivity and developing practical membrane modules of the dendrimer composite membrane.

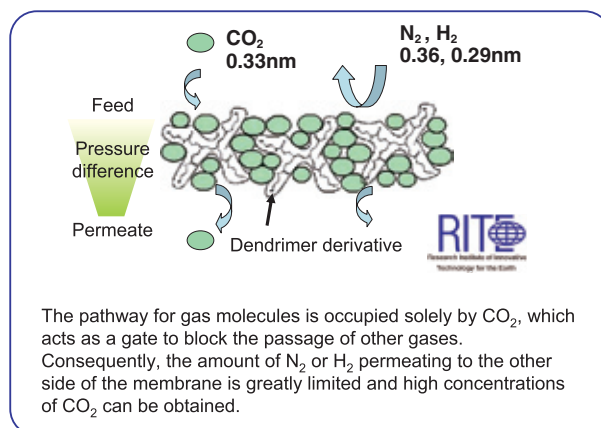


Fig. 6 Conceptual diagram for the CO<sub>2</sub> molecular gate

In developing this CO<sub>2</sub> molecular gate membrane, the RITE conducted joint research with the US Department of Energy's National Energy Technology Laboratory (NETL) as a recognized project of the Carbon Sequestration Leadership Forum (CSLF). Testing of the dendrimer composite membrane module developed by the RITE (Figure 7) was carried out at the NETL (Figure 8).

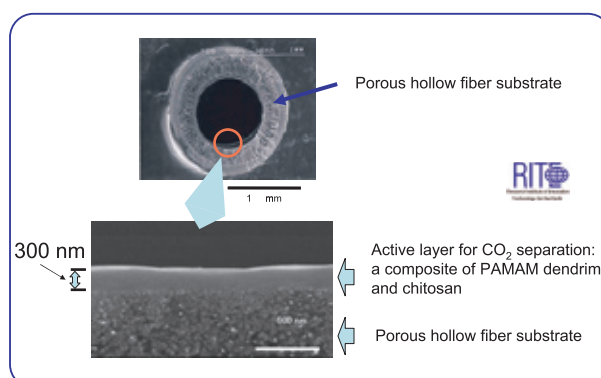


Fig. 7 Dendrimer composite membrane at ambient pressure

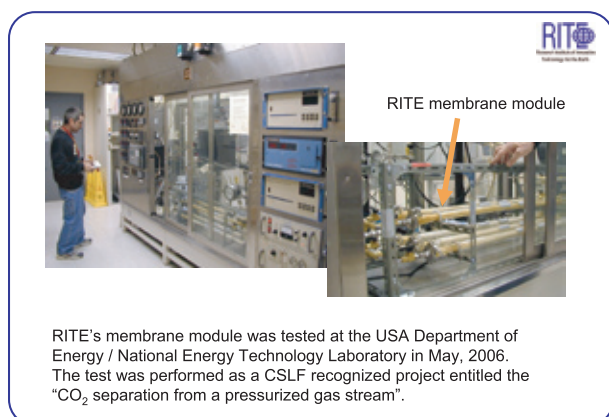


Fig. 8 RITE's membrane module test at USA DOE/NETL

### Inorganic membrane for the catalytic membrane at high temperature

Because zeolite and mesoporous silica possess well-defined micro/mesopores with low thermal expansion/mobility of the framework, considerable attention has been focused on the production of membranes that are capable of separating gases with high selectivity. Based on the simulation results, we selected candidate zeolite structures for CO<sub>2</sub> separation and have begun synthesis of new zeolite membranes.

On the other hand, since mesoporous silica has uniform, large pores as well as a high surface area, a variety of guest molecules can be introduced into the pores. A new hydrogen separation membrane was prepared by the impregnation of Pd salt in the mesoporous silica membrane and the additional growth of Pd nanoparticles by electroless plating. As shown in Figure 9, it was found that Pd nanoparticles seeds for electroless plating, which were of almost equivalent size to the mesopores, were successfully prepared into the pores by impregnation of Pd salt and the membrane showed H<sub>2</sub> selectivity from a mixture of H<sub>2</sub> and CO<sub>2</sub>. We are now planning: (1) improvement of the performance of the membrane, (2) evaluation of its durability, (3) production of a larger module and (4) application of the membrane reactor under changing reaction conditions.

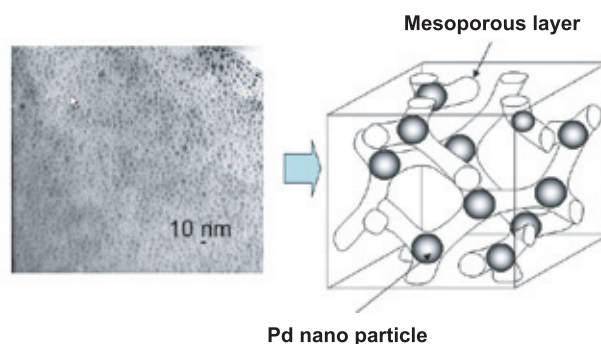


Fig. 9 Hydrogen separation membrane with Pd nano particles within mesopores

### Plasma PM removal system for diesel vehicles

Recently, the emission control for particulate matter (PM) from diesel vehicles is becoming extremely severe, although no satisfactory PM removal technologies have yet been developed. The plasma PM removal technology has potential as an innovative technology for the after treatment of exhaust gases from diesel vehicles. This project (Comprehensive technological development of innovative, next-generation, low-pollution vehicles, and R&D of innovative after-treatment systems) is a joint study with Daihatsu Motor Co., Ltd., which is supported by the New Energy and Industrial Technology Development Organization. RITE is 1) to investigate the mechanisms of plasma discharges and plasma PM oxidation and 2) to develop a PM removal system that can be loaded onto a small diesel vehicle. The PM removal system includes a power supply and a small plasma reactor of high PM removal ability and low pressure loss (Figure 10).

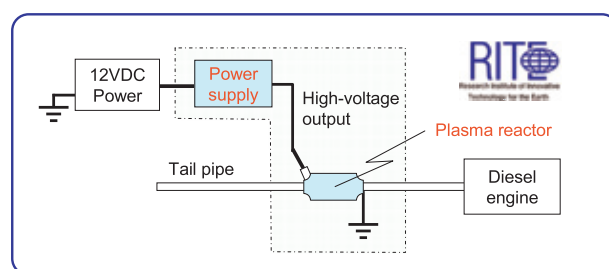


Fig. 10 Plasma PM removal system