Chemical Research Group

Looking ahead to future CO_2 separation technologies and our challenges

Discussions about a new global framework to reduce CO_2 emission is progressing, the number of people recognizing the importance of countermeasures against global warming are increasing. Generally speaking, many people believe that a countermeasure in increasing order of small economical burden will be sequentially undertaken.

A CO_2 concentration of 550 ppm is twice the concentration that was present during the Industrial Revolution. If we set a target CO_2 concentration of 550 ppm for 2100, it has been predicted that not only energy saving, fuel switching, renewable energy sources (solar cells, wind power and biomass) and nuclear energy, but also CO_2 capture and underground storage will be necessary to achieve this goal. As the cost of CO_2 capture from CO_2 sources is estimated to be 70 % of the total cost of CO_2 capture and underground storage, it is important for the commercialization of this technology that the CO_2 capture cost for CO_2 capture and storage (CCS) is reduced.

Conversion technologies of fossil energy are going to 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_2 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 between fuel conversion processes and CO_2 capture processes, so that CO_2 capture technologies that will consistently increase the economic benefits of technical visions, as shown in Figure 1, are developed.

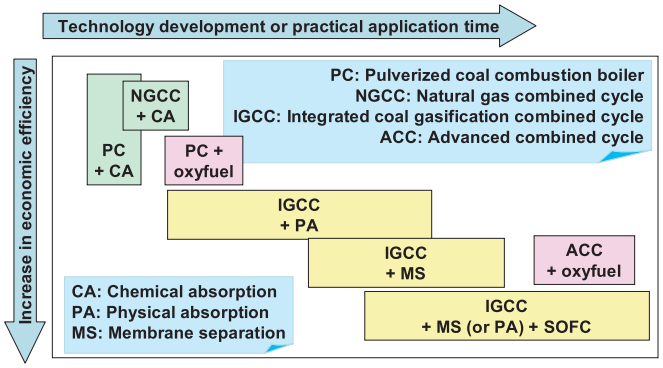

Fig.1 Vision of power plant and CO_2 capture

Our chemical research group studies various CO_2 capture technologies, with a special focus on chemical absorption and membrane separation methods. We can use chemical absorption to reduce the CO_2 capture cost for flue gas in an ironworks factory to 3000 JPY/ton-CO_2. We are developing a chemical absorbent to reduce this CO_2 capture cost to 2000 JPY / ton-CO_2. Moreover, we have discovered an excellent, world-class membrane material for the separation of CO_2 from H_2-containing gas. We are engaged in the development of the structure of a new membrane composed of this material and are developing the membrane module in order to demonstrate with real coal gasification gas. We are developing not only practical and acceptable technologies for the industries but also innovative technologies for foundation for next generation and also evaluate the various new technologies not to fail projects.

Development on CO_2 capture technology by chemical absorption system

CO_2 capture by chemical absorption has the potential to be used in practical applications for large stationary point sources of CO_2 in the near future, and a five-year project to this end was started in 2004 in collaboration with four Japanese companies.

The objective of this project is to reduce the CO_2 capture cost to half that of the existing technology for the flue gas (blast furnace gas) stream in an integrated steel works. The main objectives, shown in Figure 2, are the development of new absorbents to enable the capture of CO_2 with less energy use, and the development of a heat utilization technology to use waste heat at steel works to supply low cost steam for regenerating CO_2.

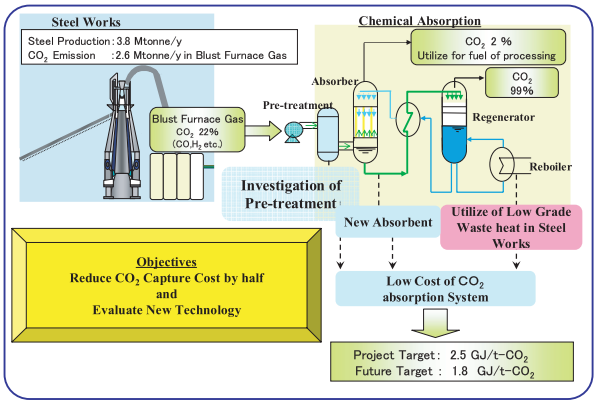

Fig.2 The outline of cost saving CO_2 capture system (COCS project)

RITE mainly develops new absorbents. The most desirable characteristics for new absorbents are: a lower heat of reaction with CO_2, fast CO_2 absorbance, and easy separation from CO_2. If this is achieved, CO_2 can be captured from a gas stream with a lower energy input. Among the solvents tested for CO_2 capture, amine

solutions have shown the best performance.

As a first step for the screening and development of new absorbents, the reaction characteristics, such as the reaction rate of CO_2, the amounts of CO_2 absorbed and the heat of reaction with CO_2, of almost 100's samples of commercial amine solvents selected were analyzed using laboratory apparatus. Furthermore, compound amine solutions, that can compensate for deficiencies in the amines, were prepared and their performance was investigated.

From these investigations, several type of high performance absorbents (RITE-3,4 series), that showed different characteristics, were developed. In succession, new absorbents (RITE-5,6 series) has been developed through the basis of our experimental database and theoretical design of molecular structure of new amine compounds using the quantum analysis approach(Figure 3). The energy for CO_2 capture of the best of these absorbents is estimated to be 2.5 [GJ/tonne-CO_2]. This value is very low compared to the 4.0 [GJ/tonne-CO_2] for a standard MEA (mono-ethanol amine) solution, so we have a prospect to accomplish the project target (Figure 4).

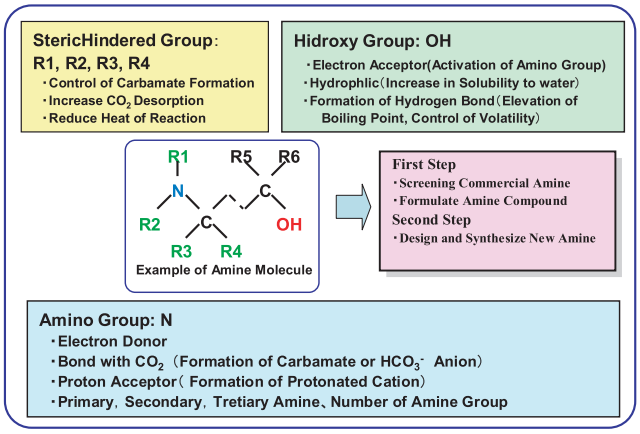

Fig.3 Development of new absorbents

The fruits of this project has succeeded to a new project of "COURSE 50" aiming at a drastic reduction of CO_2 emission in an integrated steel works. A development of new absorbents with a higher performance and application study by pilot-scale plant is scheduled hereafter.

Furthermore, based on the current knowledge on CO_2 absorbents, a development on new absorbents suitable for high pressure gas stream has also been carried out since 2007. In general, amine solvents can easily react with CO_2 under atmospheric pressure condition independent of reaction temperature. But we have confirmed that some amine solvents , nevertheless they do not react under atmospheric pressure, react with CO_2 depending on reaction temperature under high pressure condition. (Figure 4) We have proposed a new CO_2 capture system in pressurized point sources of CO_2 with these sorbents.

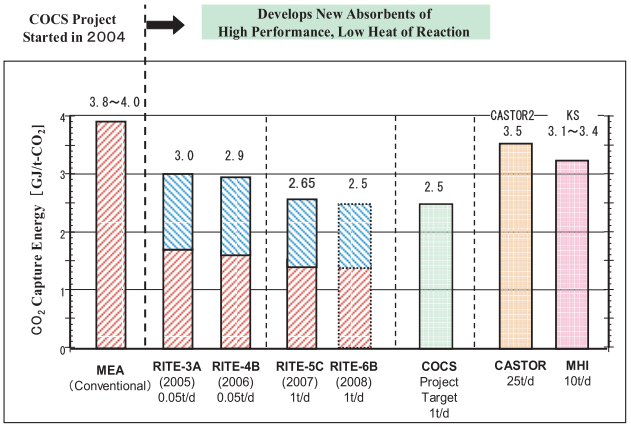

Fig.4 Reduction of CO_2 capture energy by new absorbents

The second step of the project has also been carried out, in which new types of amine compounds, designed and prepared based on the current knowledge, are evaluated by a similar method. Furthermore, research on the optimum conditions for the chemical absorption system has been carried out, so that the best performance can be obtained from the new absorbents. Currently, the aim of the project is to reduce the CO_2 capture energy down to the target value.

Novel techniques for regenerating the chemical absorbent

We are developing a regeneration technique for accelerating CO_2 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_2) of that of the conventional chemical absorption method. We will attempt to apply this method to the separation of CO_2 from flue gases, chemical processes, bioprocesses, etc., while efforts are made to further reduce energy consumption.

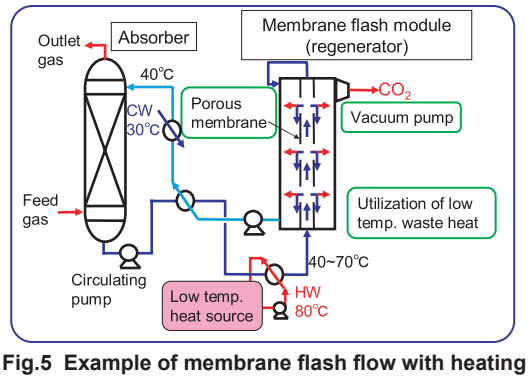

Fig.5 Example of membrane flash flow with heating

RITE and Taiyo Nippon Sanso Corp. have developed the equipment (Figure 6) which gets the high-concentration methane by removing CO_2 from biogases, and the practicability has been confirmed in continuous running for two months at the biogas generation site.

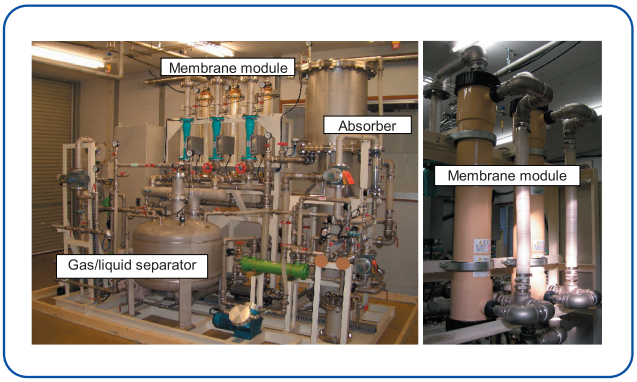

Fig.6 Biogas purification test equipment developed by RITE and Taiyo Nippon Sanso Corp.

CO_2 and H_2 separation with a polymeric membrane

Japan's government has declared the reduction of CO_2 emission to half by 2005 as "Cool Earth 50". One promising means of dimidiating CO_2 emission is the development of an integrated coal gasification combined cycle with CO_2 capture & storage (IGCC-CCS). In the process of IGCC-CCS, CO_2 separation membranes will play an important role of reducing CO_2 capture cost. The cost estimates indicate that CO_2 capture cost from the pressurized gas stream with a membrane might be 1500 JPY/t-CO_2 or less.

We are currently developing a CO_2 molecular gate membrane with the goal of producing a new, high-performance separation membrane. Figure 7 shows the basic outline of the CO_2 molecular gate function. The pathway for gas molecules is occupied solely by CO_2, which acts as a gate to block the passage of other gases. Consequently, the amount of N_2 or H_2 permeating to the other side of the membrane is greatly limited and high concentrations of CO_2 can be obtained. The RITE dendrimer having excellent CO_2/H_2 selectivity is fixed stably in a cross-linked polymer matrix to form the separation membrane. Figure 8 shows the CO_2/H_2 separation properties of the membrane along with the other membranes reported previously. Our dendrimer membrane shows the world largest CO_2/H_2 selectivity of 30 or more. The RITE is now improving the performance and developing practical membrane modules of the dendrimer membrane in cooperation with membrane companies.

In developing this CO_2 molecular gate membrane, the RITE conducted joint research with many foreign partners such as the US Department of Energy's National Energy Technology Laboratory (NETL) as a recognized project of the Carbon Sequestration Leadership Forum (CSLF), University of Texas at Austin and Norwegian University of Science and Technology.

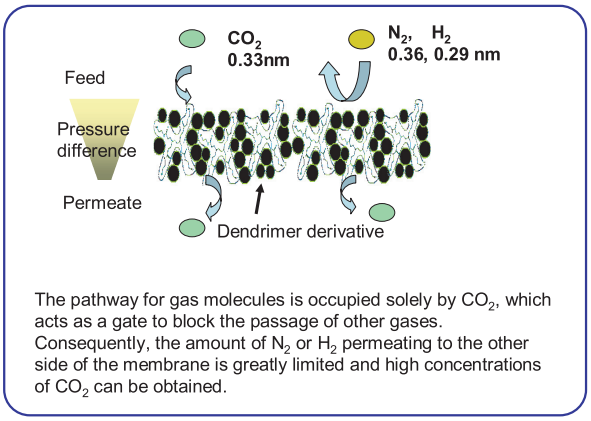

Fig.7 Conceptual diagram for the CO_2 molecular gate

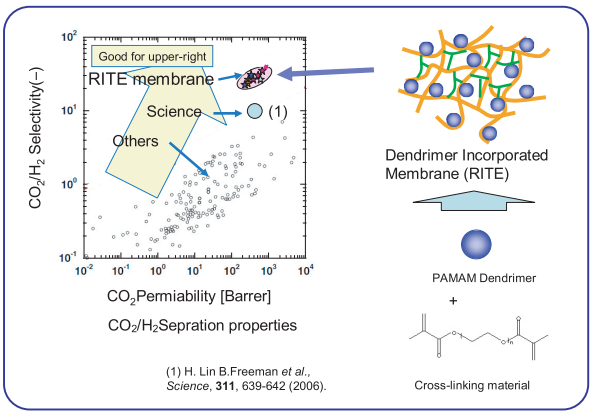

Fig.8 Dendrimer incorporated membrane and its performance

Development of an energy-saving CO_2-PSA process using hydrophobic adsorbents

The usual means of CO_2 separation, pressure swing adsorption (PSA) using polar hydrophilic adsorbent, is energy intensive: to regenerate the absorbent, the partial pressure of CO_2 must be changed by the vacuum pump. In addition, a dehumidification process which consumes approximately 30% of total energy is necessary for the conventional PSA process using hydrophilic 13X zeolite, because water vapour is adsorbed more strongly than CO_2 on 13X zeolite surface. 13X zeolite strongly adsorb both CO_2 and H_2O and had a Langmuir-type adsorption isotherm. The CO_2 adsorption capacity of hydrophilic zeolite is completely lost with the coexistence of water; therefore, hydrophobic adsorbent should be used for CO_2 separation in high moisture conditions, such as that for stack gas.

In this project, newly prepared hydrophobic adsorbents have been proposed as CO_2 adsorbents for the separation of CO_2 from high pressure gas. They

can overcome such obstacles to adsorption processes. Hydrophobic adsorbents have an advantage over traditional adsorbents such as activated carbon and zeolites because they can adsorb CO_2 in the presence of water vapour, which is usually present in flue gases from fossil fuel combustion. Furthermore, vacuum pump can be eliminated for the adsorption process from high pressure gas.

CO_2 adsorption capacities of 13X zeolite and newly synthesized adsorbents were shown in figure 9. It was confirmed that the adsorbent synthesized in our study had a hydrophobic property and adsorbed considerable amounts of CO_2 under high CO_2 pressure. It was also confirmed they adsorbed CO_2 even in the presence of water vapor.

Evaluation of the process cost is now in progress.

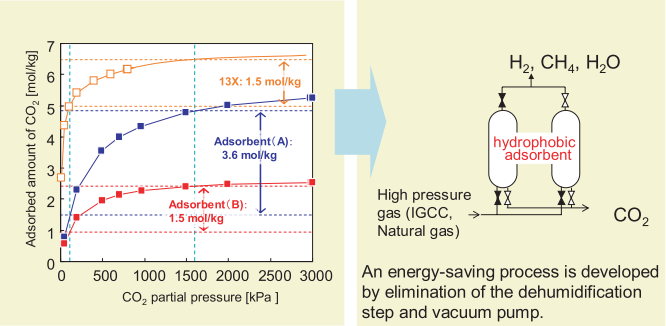

Fig.9 Energy-saving CO_2 - PSA

Development of an innovative after treatment system for diesel vehicles

Recently, the emission control for the diesel vehicles is becoming extremely severe; each diesel vehicles has to install an after-treatment system in order to satisfy the severe standards. The plasma technology has been getting great attention as an innovative technology for particulate matter (PM) removal from the exhaust gases of diesel vehicles. We carried out the study supported by NEDO (Comprehensive Technological Development of Innovative, Next-Generation, Low-Pollution Vehicles, R&D of innovative after treatment systems) to develop the plasma technology for PM removal from FY2004 to FY2008. After mechanism investigation of plasma discharge and PM oxidation/combustion, a plasma PM removal system (Fig. 10) of a pulse power supply and a plasma PM reactor has been developed for light-duty diesel vehicles. The plasma PM reactor has been evaluated by Japan Automobile Research Institute (JARI, Tsukuba). It was found that the PM emission from a light-duty diesel vehicle installed with the plasma PM reactor with 93 W discharge powers is 0.005 g/km (Fig. 11); this result suggested that if using the plasma PM removal system the PM emission satisfies the post new long-term emission standard (to be effective from 2009) for light-duty diesel vehicles.

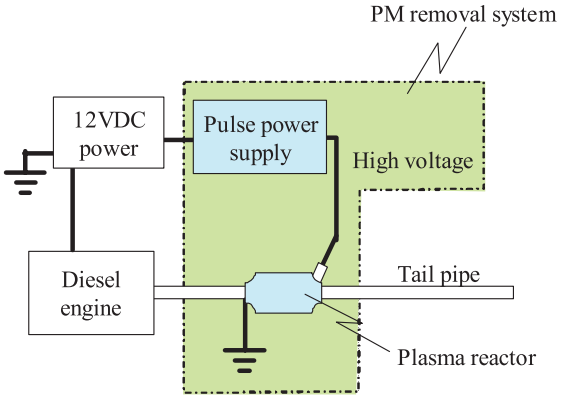

Fig.10 Non-thermal plasma PM removal system.

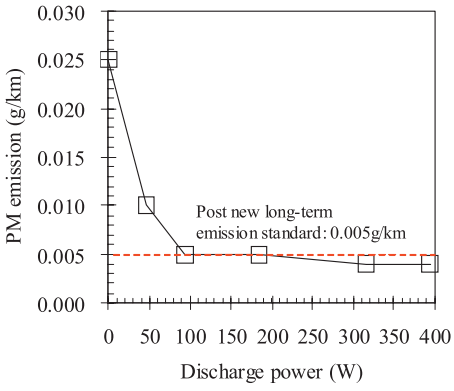

Fig.11 Relation of PM emission and discharge power under JC08 mode.