

Chemical Research Group

Challenges for Advanced Industrializing CO₂ Capture Technologies

CO₂ capture and storage (CCS) is composed of CO₂ capture from fossil fuel combustion gases and its injection into geological formations for storage or sequestration.

The current CO₂ capture cost from emission sources is estimated to be about 60% of CCS costs. Therefore reduction of CO₂ capture costs is important aspect for practical application of CCS.

Our Chemical Research Group studies various CO₂ capture technologies, with a special focus on chemical absorption and membrane separation methods.

We developed a COCS project aimed at reducing the CO₂ capture cost in ironworks by chemical absorption, in which we developed an innovative chemical absorbent that reduced the CO₂ capture cost for flue gas to 3000 JPY/ton-CO₂. We are continuing to develop a chemical absorbent to further reduce this CO₂ capture cost to 2000 JPY/ton-CO₂.

Moreover, we have developed an excellent CO₂ absorbent that is effective for pressurized gas, and are planning to put this into practical use.

By developing molecular gate type membrane technologies to capture CO₂ selectively from H₂-containing pressurized gases such as that in the integrated coal gasification combined cycle (IGCC), we are aiming for a CO₂ capture cost target of 1500 JPY/ton-CO₂.

We have discovered that new types of dendrimer polymers have excellent properties for separating CO₂ from H₂ gas mixtures, and are therefore developing membrane modules incorporating dendrimeric materials. Furthermore, we have begun testing module performance using simulated gas of coal gasification gas.

For CO₂ capture technology using adsorption processes, we have developed new solid adsorbents that do not lose CO₂ capture efficiency even in the presence of water vapor. We are planning to develop a low-cost CO₂ capture process by eliminating the requirement for a dehumidification tower.

Above all, we have begun to develop new solid sorbents, onto which amine is immobilized, for the purpose of developing low-cost CO₂ capture technology.

As mentioned above, we are promoting innovative CO₂ capture technologies, which lay the foundations for the next generation, while developing practical technologies that are acceptable to industries.

Moreover, we have seed technologies such as CO₂ separation by zeolite membranes, H₂ separation by palladium membranes, a hybrid CO₂ capture system that combines membranes with a wet scrubbing system, baroplastics that have low temperature flow under high pres-

sure state, etc., to be used for various purposes.

Development of CO₂ capture technology by chemical absorption systems

CO₂ capture by chemical absorption is a prospective technology for separating CO₂ from a CO₂-containing gas by means of thermal dissociation of CO₂ that is chemically absorbed in an amine-based solution. This is suitable for CO₂ separation from the normal pressure gas generated on an industrial scale. Our objective is to develop new, efficient absorbents that will decrease the CO₂ separation cost, which is the main concern for chemical absorption systems.

We planned and coordinated, from FY 2004 until FY 2008, a "Cost-saving CO₂ Capture System" (COCS) project to capture and separate CO₂ from ironworks blast furnace gas at half the previous cost of a chemical absorption system, and achieved this goal (Fig. 1).

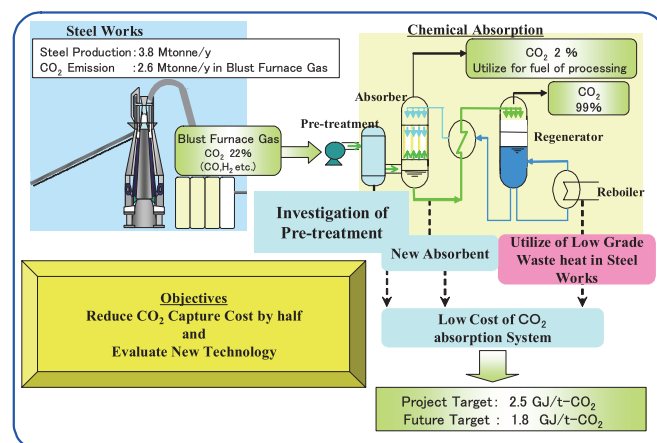


Figure 1 The outline of cost saving CO₂ capture system (COCS project)

The characteristics required of new absorbents to capture and separate CO₂ are lower heat of reaction and dissociation energy for CO₂ and a higher CO₂ absorption capacity. In particular, amines possess excellent characteristics in this regard.

In the first step of the COCS project, hundreds of amines were chosen from commercially available amines. We studied their basic characteristics, such as CO₂ absorption rate in solution, heat of reaction, CO₂ absorption capacity and so on, in a laboratory scale and determined the relationship between the chemical structure of the amines and their characteristics as absorbents. Furthermore, as a result of exploring amine composition and combining the characteristics of various amines, we developed several new efficient types of absorbent solution

(RITE-3 and 4 series) (Fig. 2). In the second step, we also developed more efficient absorbents (RITE-5 and 6 series) by designing, synthesizing and evaluating various kinds of amines using a methodology of computational chemistry based on our acquired data and quantum chemistry. The best performance for CO₂ capture energy of the absorbents developed in this project is 2.5 GJ/ton-CO₂, compared with the CO₂ capture energy of MEA (monoethanolamine) used as a standard of 4.0 GJ/ton-CO₂. We thus achieved the project target (Fig. 3).

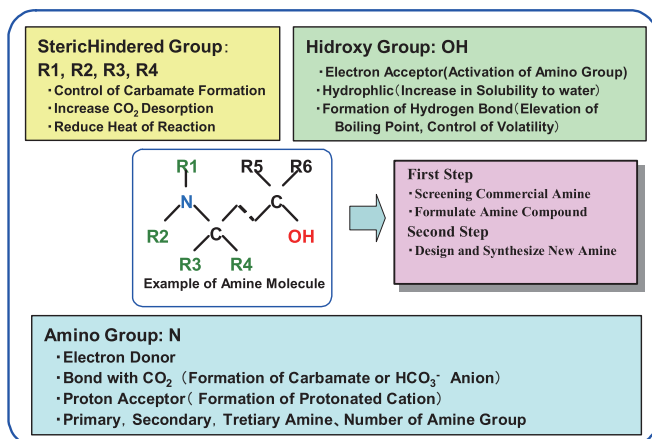


Figure 2 Development of new absorbents

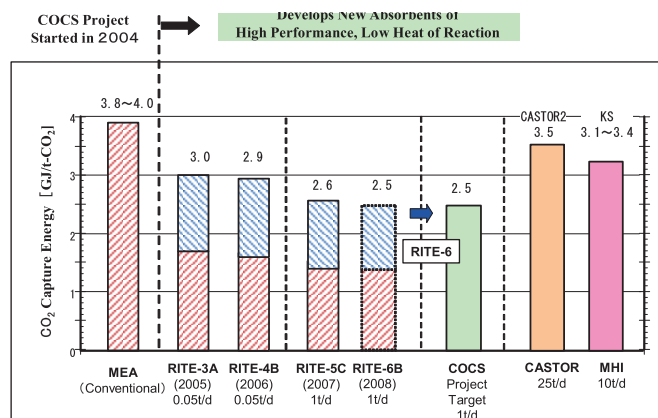


Figure 3 Reduction of CO₂ capture energy by new absorbents

The outcomes of the COCS project were succeeded by another project, “CO₂ Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 50” (COURSE50, from FY 2008 until FY 2012), aiming at CO₂ capture from the ironworks process gas.

We are now endeavoring to find new, more efficient, absorbents (CO₂ capture energy: 2.0 GJ/ton-CO₂) that are appropriate for the above-mentioned project and are also conducting tests of these absorbents in a process evaluation plant (30 ton-CO₂/d processing capacity).

From FY 2007 to FY 2009, we worked on the research and development of appropriate absorbents for CO₂ cap-

ture under high-pressure conditions, based on our accumulated research experience and found amine-based absorbents with excellent CO₂ absorption and dissociation performances. We will propose a chemical absorption system using these amine absorbents as a new technology for CO₂ capture from gases under high pressure.

CO₂ and H₂ separation with a polymeric membrane

Japan's government declared a goal to reduce CO₂ emissions to half of those in 2005 as the objective “Cool Earth 50”. One promising means of reducing CO₂ emission is the development of an integrated coal gasification combined cycle with CO₂ capture & storage (IGCC-CCS). In the IGCC-CCS process, CO₂ separation membranes will play an important role for reducing CO₂ capture costs. Estimates indicate that the CO₂ capture cost from a pressurized gas stream using a membrane might be 1500 JPY/ton-CO₂ or less.

We are currently developing a CO₂ molecular gate membrane, with the goal of producing a new, high-performance separation membrane. Fig. 4 shows the basic outline of the CO₂ molecular gate function. The pathway for gas molecules is occupied solely by CO₂, which acts as a gate to block the passage of other gases. Consequently, the amount of N₂ or H₂ permeating to the other side of the membrane is greatly limited and high concentrations of CO₂ can be obtained. An RITE dendrimer, which possesses excellent CO₂/H₂ selectivity, is fixed stably in a cross-linked polymer matrix to form the separation membrane. Fig. 5 shows a conceptual diagram of a material incorporating PAMAM dendrimer and its CO₂/H₂ separation properties, along with the data reported in Science and other high-impact journals. Our PAMAM dendrimer/polymer hybrid material shows the world's largest CO₂/H₂ selectivity of 30 or more.

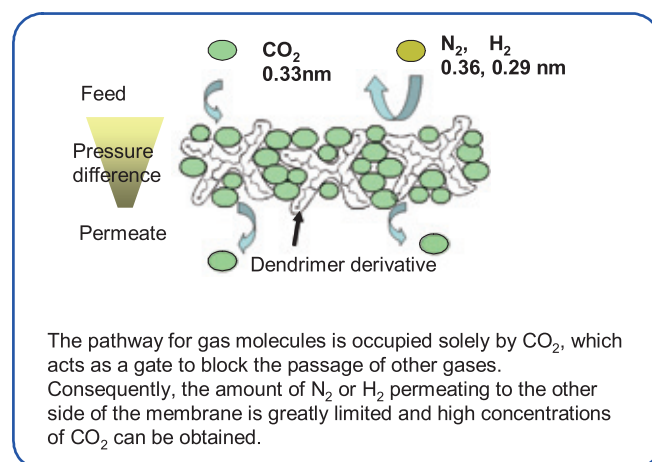


Figure 4 Conceptual diagram of the CO₂ molecular gate

In the development of a commercial membrane module using the PAMAM dendrimer/polymer hybrid material, RITE has recently involved four major membrane companies, Daicel Chemical Industries, Ltd.; Kuraray Co., Ltd.; Nitto Denko Corporation; and Toray Industries. RITE and Nippon Steel Engineering Co., Ltd. will test trial membrane modules with a recently developed simulator and demonstrate the utility of the membrane module for capturing CO₂ from a pressurized gas stream such as that in coal gasification (Fig. 6).

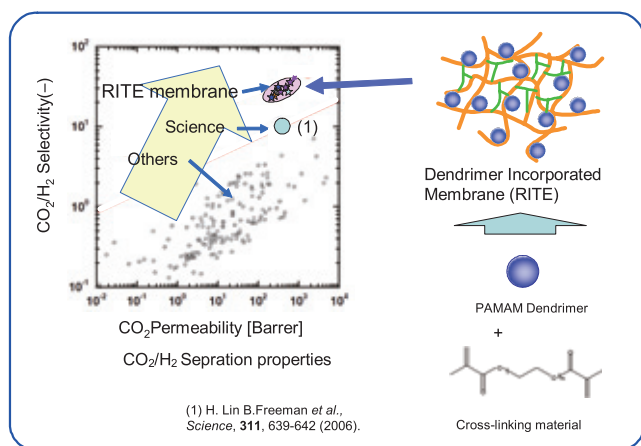


Figure 5 Dendrimer incorporated membrane and its performance

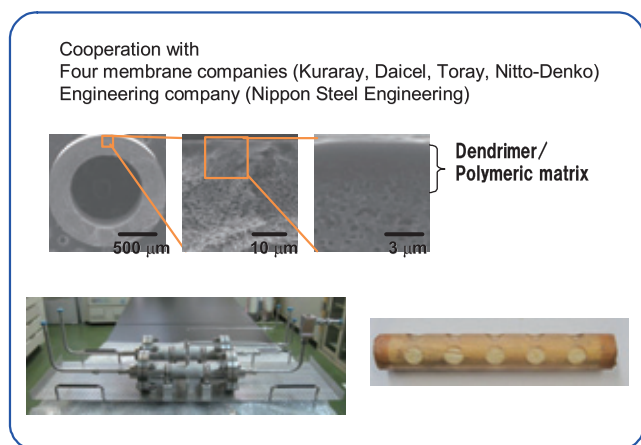


Figure 6 Development of membrane modules in cooperation with private companies

In developing this CO₂ 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) in a recognized project for the Carbon Sequestration Leadership Forum (CSLF), the University of Texas at Austin and the Norwegian University of Science and Technology.

Development of an energy-saving CO₂-PSA process using hydrophobic adsorbents

Novel hydrophobic adsorbents have been proposed as CO₂ adsorbents for the separation of CO₂ from high-pressure gas. CO₂ adsorption capacities of 13X zeolite and new synthetic adsorbents are shown in Fig. 7.

It has been confirmed that the adsorbent synthesized

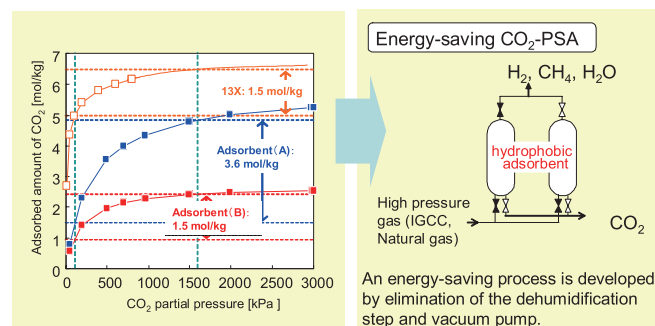


Figure 7 Development of an energy-saving CO₂-PSA process

in our study adsorbed considerable amounts of CO₂ at high pressure. It was also confirmed that they adsorbed CO₂ even in the presence of water vapor. From CO₂ separation experiments using CO₂-H₂ mixed gas flows, it was confirmed that the new adsorbent was effective for separating CO₂ from the gas flow in the presence of water vapor. Evaluation of the process cost is now under way.

Advanced stage of technology development on CO₂ capture by amine-based absorbents

CCS is a highly viable technology for tackling global warming. It is strongly desirable that this be implemented in the market as soon as possible. Recent R&D on CCS has focused on energy-saving, low-cost CO₂ capture technologies, demonstration and feasibility studies of commercial-scale systems, and so on. RITE began a new project funded by METI in 2010FY, in which the research objectives were to develop novel solid sorbents and to establish evaluation standards CO₂ capture using liquid amine solvents.

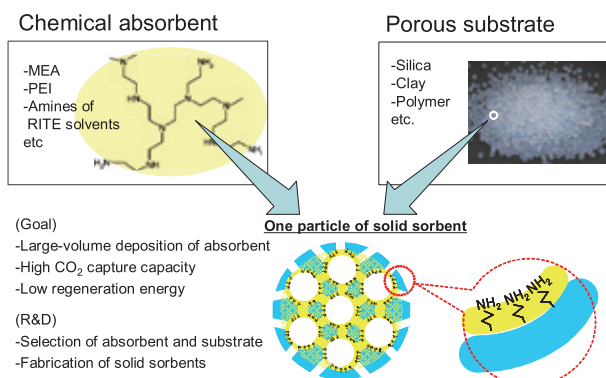


Figure 8 Development of novel solid sorbents

With respect to solid sorbents, amines can be immobilized onto a support or encapsulated within a porous substrate (Fig. 8). Although solid sorbent techniques use amine-based absorbents, similar to liquid amine solvent methods, it has the advantage of a lower anticipated heat duty for regeneration. RITE investigates novel solid sorbents using RITE-developed solvents through cooperative R&D activities with NETL, from which major research on the solid sorbents has already been presented.

Improved evaluation techniques are required to accelerate commercialization of liquid amine solvent methods. Process simulation for advanced amine solvents must be established and improved so as to more accurately estimate the performance of scaled-up processes. Also, the environmental impact of amine-based absorbents has become a crucial issue.

Advanced CO₂/H₂ separation materials incorporating active functional agents (GCEP)

RITE has conducted developmental work entitled “Sub-nano structure controlled materials: development of innovative gas separation membranes” as part of the Global Climate and Energy Project (GCEP) of Stanford University, USA.

Under the theme of advanced CO₂/H₂ separation materials incorporating active functional agents, supercritical and subcritical CO₂ acts as a structure-directing agent for CO₂ affinity materials. Fig. 9 shows a schematic of the concept. Excellent CO₂ separation membranes will be obtained by strict morphology regulation at the molecular scale. In the figure, supercritical CO₂ regulates the CO₂ affinity membrane materials into a morphology that is preferential for CO₂ permeation (State A). After removing supercritical CO₂, the preferential morphology will be maintained to form an excellent CO₂ separation membrane.

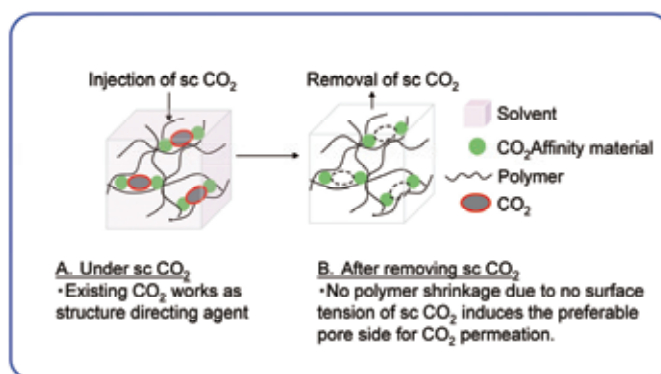


Figure 9 Concept of super critical (sc) CO₂ structure directing method