Chemical Research Group

Challenges for Advanced Industrializing CO_2 Capture Technologies

1. CO_2 capture technologies

CO_2 capture and storage (CCS) is composed of CO_2 capture from fossil fuel combustion gases and its injection into geological formations for storage or sequestration.

The current CO_2 capture cost from emission sources is estimated to be about 60% of CCS costs. Therefore reduction of CO_2 capture costs is important aspect for practical application of CCS.

Our chemical research group studies various CO_2 capture technologies, with a special focus on chemical absorption and membrane separation methods.

We developed a COCS project aimed at reducing the CO_2 capture cost in ironworks by chemical absorption, in which we developed an innovative chemical absorbent that reduced the CO_2 capture cost for flue gas to 3000 JPY/ton-CO_2. We are continuing to develop a chemical absorbent to further reduce this CO_2 capture cost to 2000 JPY/ton-CO_2 (by 2015).

Moreover, we have developed an excellent CO_2 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 CO_2 selectively from H_2-containing pressurized gases such as that in the integrated coal gasification combined cycle (IGCC), we are aiming for a CO_2 capture cost target of 1500 JPY/ton-CO_2 (by 2015).

We have discovered that new types of dendrimer polymers have excellent properties for separating CO_2 from H_2 gas mixtures. RITE and three private companies have established the technology research association, developing membrane modules and separation systems for the practical application.

For CO_2 capture technology using adsorption processes, we have developed new solid adsorbents that do not lose CO_2 capture efficiency even in the presence of water vapor. We are planning to develop a low-cost CO_2 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 CO_2 capture technology.

As mentioned above, we are promoting innovative CO_2 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 CO_2 separation by zeolite membranes, H_2 separation by palladium membranes, a hybrid CO_2 capture system that combines membranes with a chemical absorption process, baroplastics that have low temperature flow under high pressure state, etc., to be used for various purposes. Especially the membrane/absorption hybrid CO_2 capture technology has been used practically in a private company.

2. Development of CO_2 capture technology by chemical absorption systems

CO_2 capture by chemical absorption is a prospective technology for separating CO_2 from a CO_2-containing gas by means of thermal dissociation of CO_2 that is chemically absorbed in an amine-based solution. This is suitable for CO_2 separation from the normal pressure gas generated on an industrial scale. Our objective is to develop new, efficient absorbents that will decrease the CO_2 separation cost, which is the main concern for chemical absorption systems.

We planned and coordinated, from FY2004 until FY2008, a "Cost-saving CO_2 Capture System" (COCS) project to capture and separate CO_2 from ironworks blast furnace gas at half the previous cost of a chemical absorption system, and achieved this goal (Figure 1).

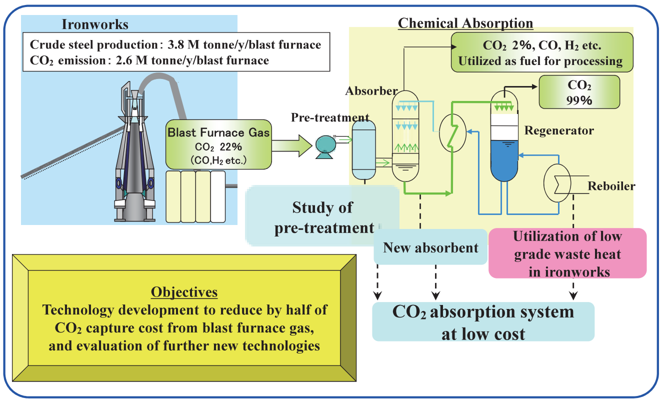


Figure 1 Outline of cost saving CO_2 capture system (COCS project)

In this project, we developed various types of efficient new absorbent. The CO_2 capture energy consumption of the absorbents developed in this project is drastically reduced in comparison with that of MEA (monoethanolamine) used as a standard.

These outcomes were succeeded by another project, "CO_2 Ultimate Reduction in Steelmaking Process by Innovative Technology for Cool Earth 50" (COURSE50, five years from FY2008), aiming at CO_2 capture from the ironworks process gas.

We are now endeavoring to find more efficiently new absorbents (CO_2 capture energy: 2.0 GJ/ton-CO_2) which

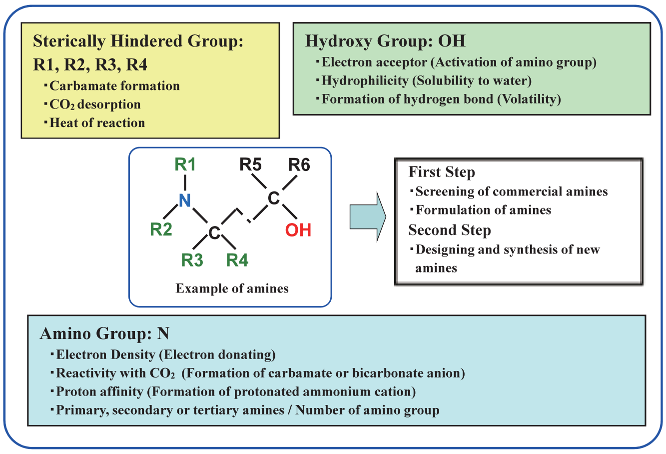


Figure 2 Development of new absorbents

are appropriate for the COURSE50 project(Figure 2).

In order to minimize CO_2 capture energy, it is necessary to minimize heat of chemical reaction in CO_2 capture and also necessary to maximize CO_2 capture rate in order to minimize plant size. In general, heat of reaction and reaction rate is trade-off, however the development of compatible absorbents is required.

Therefore, we are developing more efficiently new amine absorbents taking advantage of latest computational chemistry and synthetic chemistry with Nippon Steel Corporation and The University of Tokyo, and are evaluating the test results with 1t and 30t-CO_2/day scale pilot equipment(Figure 3) using BFG (blast furnace gas) in cooperation with Nippon Steel Engineering Co., Ltd.

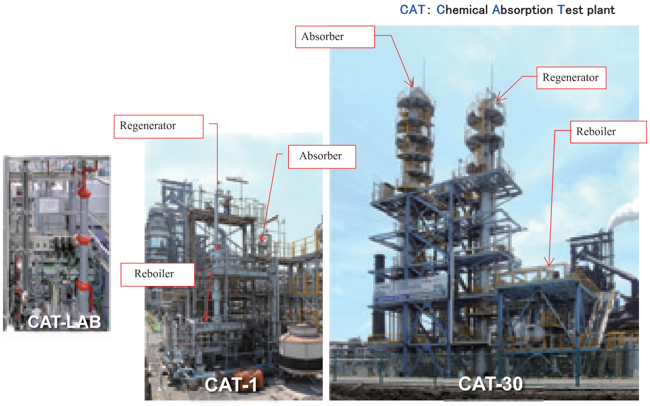


Figure 3 Snapshots of test equipment

To date, we successfully developed a new chemical absorbent (solvent 2) superior to the previously developed chemical absorbent (solvent 1) (Figure 4). The thermal energy consumption of solvent 2 is 2.5GJ/t-CO_2, and furthermore, ca. 0.1GJ/t-CO_2 improvement is expected at actual equipment.

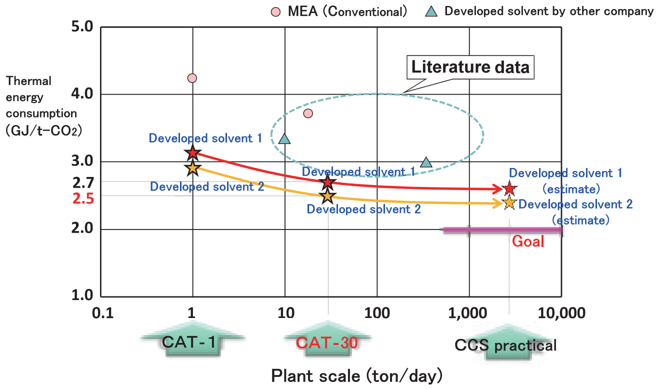


Figure 4 Evaluation of performance (thermal energy consumption)

From FY2007 to FY2009, we worked on the research and development of appropriate absorbents for CO_2 capture under high-pressure conditions, based on our accumulated research experience and found amine-based absorbents with excellent CO_2 absorption and dissociation performances. We will propose a chemical absorption system using these amine absorbents as a new technology for CO_2 capture from gases under high pressure.

In addition, we are interested in process development of chemical absorption for CO_2 capture. A new evaluation technique for solvent selection is required to accelerate commercialization of 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. The environmental impact of amine-based absorbents is also important in process development and has currently become a crucial issue. In 2010, a pilot plant operation of a RITE-developed solvent at a 10t/d-scale facility was conducted in order to evaluate solvent performance and to gather process data for the process simulation.

3. CO_2 and H_2 separation with a polymeric membrane

Japan's government declared a goal to reduce CO_2 emissions to half of those in 2005 as the objective "Cool Earth 50". One promising means of reducing CO_2 emission is the development of an integrated coal gasification combined cycle with CO_2 capture & storage (IGCC-CCS). In the IGCC-CCS process, CO_2 separation membranes will play an important role for reducing CO_2 capture costs. Estimates indicate that the CO_2 capture cost from a pressurized gas stream using a membrane might be 1500 JPY/ton-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 5 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. A RITE's dendrimer, which possesses excellent CO_2/H_2 selectivity, is fixed stably in a cross-linked polymer matrix to form the separation membrane. Figure 6 shows a conceptual diagram of a material incorporating PAMAM dendrimer and its CO_2/H_2 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 CO_2/H_2 selectivity of 30 or more.

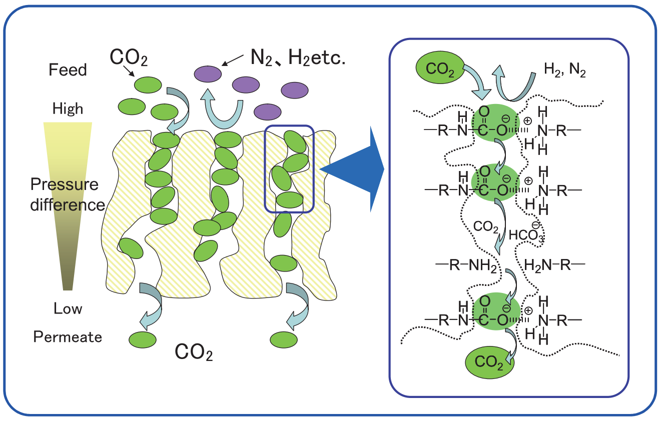


Figure 5 Conceptual diagram of the molecular gate membrane

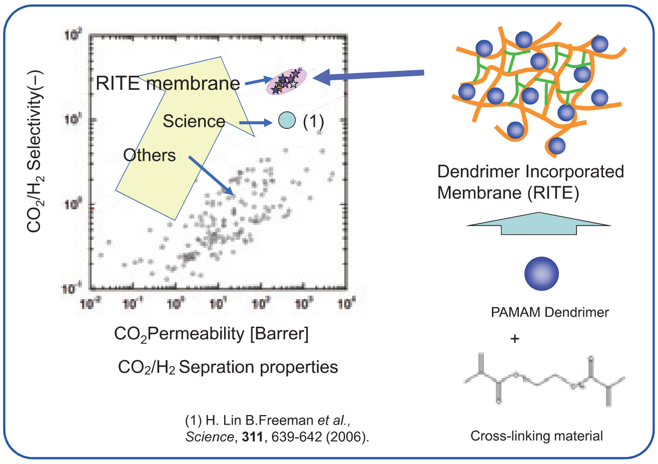


Figure 6 Dendrimer incorporated membrane and its performance

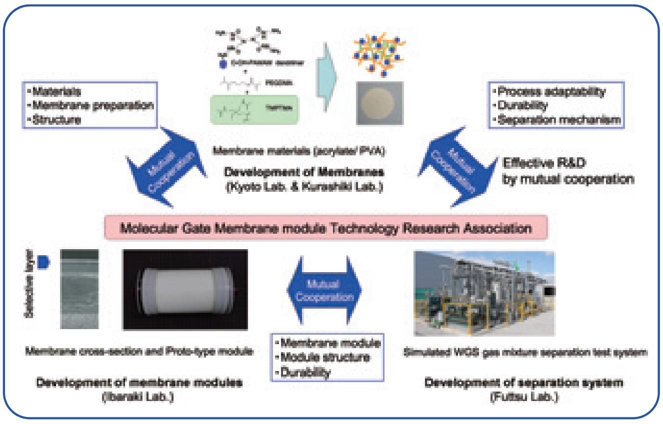


Figure 7 Development of membrane modules in cooperation with private companies

Based on these materials, modification of membrane materials, membrane thickness control etc. are ongoing to improve CO_2 separation performance further.

In the development of a commercial membrane module using the PAMAM dendrimer/polymer hybrid material, RITE, Kuraray Co., Ltd., Nitto Denko Corporation and Nippon Steel Engineering Co., Ltd. established Molecular Gate Membrane module Technology Research Association, and membranes, membrane modules and separation systems are being developed(Figure 7).

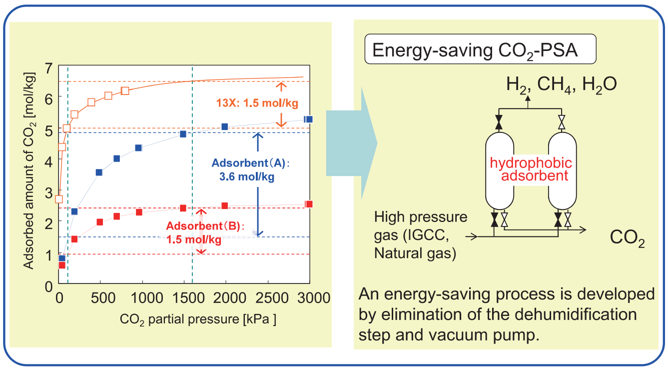
In developing this CO_2 molecular gate membrane, RITE conducted joint research with many foreign partners such as the US Department of Energy's National Energy Technology Laboratory (NETL) in a recognized project for the Carbon Sequestration Leadership Forum (CSLF)*, the University of Texas at Austin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

* Ministerial-level international climate change initiative that is focused on the development of improved cost-effective technologies for the separation and capture of carbon dioxide (CO_2) for its transport and long-term safe storage.

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

Novel hydrophobic adsorbents have been proposed as CO_2 adsorbents for the separation of CO_2 from high-pressure gas. CO_2 adsorption capacities of 13X zeolite and new synthetic adsorbents are shown in Figure 8.

It has been confirmed that the adsorbent synthesized in our study adsorbed considerable amounts of CO_2 at high pressure. It was also confirmed that they adsorbed CO_2 even in the presence of water vapor. From CO_2 separation experiments using CO_2-H_2 mixed gas flows, it was confirmed that the new adsorbent was effective for separating CO_2 from the gas flow in the presence of water vapor. Evaluation of the process cost is now under way.



An energy-saving process is developed by elimination of the dehumidification step and vacuum pump.

Figure 8 Development of an energy-saving CO_2-PSA process

5. Advanced stage of technology development on CO_2 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 CO_2 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 CO_2 capture using liquid amine solvents.

With respect to solid sorbents, amines can be immobilized onto a support or encapsulated within a porous substrate (Figure 9). 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. It has been confirmed that a new RITE-solvent based solid sorbent synthesized in our study desorbed CO_2 at lower temperature compared with traditional solid amine sorbent. Evaluation for the practical use is now under way.

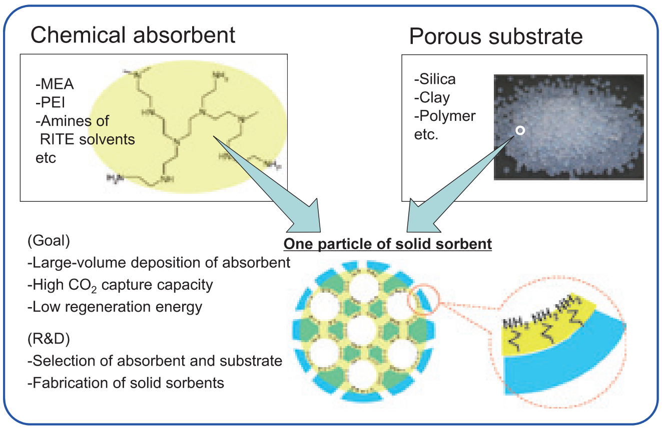


Figure 9 Development of novel solid sorbents

6. Advanced CO_2/H_2 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 CO_2/H_2 separation materials incorporating active functional agents, supercritical and subcritical CO_2 acts as a structure-directing agent for CO_2 affinity materials. Figure 10 shows a schematic of the concept. Excellent CO_2 separation membranes will be obtained by strict morphology regulation at the molecular scale. In the figure, supercritical CO_2 regulates the CO_2 affinity membrane materials into a morphology that is preferential for CO_2 permeation (State A). After removing supercritical CO_2, the preferential morphology will be maintained (State B) to form an excellent CO_2 separation membrane.

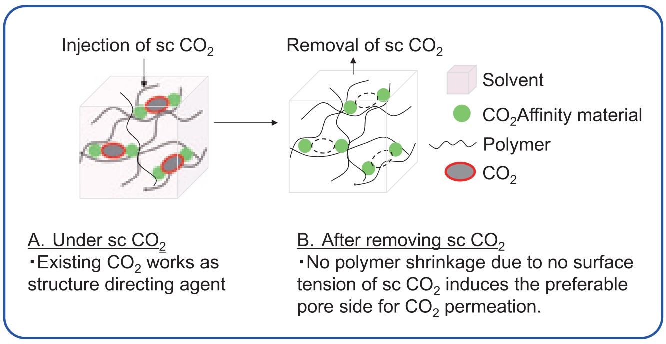


Figure 10 Concept of super critical (sc) CO_2 structure directing method