Chemical Group Activity

Extensive use of fossil fuels has caused an increase in CO\textsubscript{2} emissions, resulting in a rapidly increasing atmospheric CO\textsubscript{2} concentration that in turn is causing global warming. Atmospheric CO\textsubscript{2} concentration needs to be stabilized at a low level to mitigate global warming.

There are two main measures for atmospheric CO\textsubscript{2} stabilization. One is to reduce CO\textsubscript{2} emissions, the other to sequestrate emitted CO\textsubscript{2} into land or ocean (Carbon Capture and Storage, CCS).

A scenario for CO\textsubscript{2} stabilization determines scales and schedules of the implementation of measures. The stabilization level generally considered is 550ppm by 2100 which is a level two times higher than the CO\textsubscript{2} concentration before the industrial revolution.

Stabilizing at 550ppm would be difficult if there is only implementation for improvements in efficient energy use, or fuel switching to renewable energy sources.

Therefore, additional stabilization options such as CCS technologies, which have high potential for stabilization, should be developed for practical use. Reduction of energy consumption and the cost of a CCS system is essential for its practical use.

For achieving this, basic technologies in three fields of materials, processes and systems are necessary as innovative technology elements.

Our chemical group has worked toward the establishment and gathering of such technologies, and is also involved in the process of advancing them.

We are presently focusing our research activities toward the establishment in ten years of a CCS system that uses our technology elements.

Our R&D work in this area relates not only to CCS, but also to new energy systems that enable the construction of a sustainable carbon cycle society.

Chemical Absorption Process

A new CO\textsubscript{2} capture project by chemical absorption process has been started with collaboration of three Japanese companies since fiscal year 2004 as a five-year project.

The project aims at reducing a CO\textsubscript{2} capture cost to half and includes two main research objectives: One is to develop higher-performance chemical absorbents and the other is to utilize low-grade waste heat in integrated steel works in order to provide CO\textsubscript{2} capture process with low-cost energy.

RITE has mainly worked on developing the new absorbents. In 2004, both experimental and theoretical studies on the reaction of amine compounds with CO\textsubscript{2} were conducted and structural characteristics of hopeful absorbents were clarified. Then, the current results contributed to developing the new absorbent which was graded as one of the current highest-performance ones. In the next term, RITE aspires to develop the best absorbent ranked beyond the others.

Practical development of membrane/absorption hybrid separation technique

Membrane/absorption hybrid method has been studied as a new CO\textsubscript{2} separation technology. (The work was supported by NEDO and guided by Prof. Teramoto, Kyoto Inst. of Technology, in 2001-2003 fiscal year.) In this method, CO\textsubscript{2} is absorbed in the absorbent liquid in one side of the porous membrane and emitted in the other side with the liquid permeation under the reduced pressure. This method is characterized by drastically little energy consumption compared to the current separation method and highly concentrated CO\textsubscript{2} obtained. At present, cooperation with the companies is promoted for applying this method to the separation of CO\textsubscript{2} from flue gas, chemical process, bio-process, etc.
Polymeric membrane

One promising means of lowering the cost of CO₂ separation is the development of new, high-performance CO₂ separation membranes that allow CO₂ recovery via membrane separation. RITE is now involved in developing just such polymeric separation membranes.

Cardo polyimide having fluorene moiety was modified in the chemical structure for good CO₂ separation properties. The asymmetric hollow fiber membrane of the cardo polyimide shows the largest CO₂ permeance among existing asymmetric membranes and the top level of CO₂ selectivity in various polymeric membranes. A module of the membrane can recover CO₂ from an exhausted gas of 25 % CO₂ concentration at a comparable expense to amine solution by a system involving CO₂ liquefaction. For a higher CO₂ concentration flux, the membrane separation will have an advantage over amine solution in the system.

RITE is currently developing a CO₂ molecular gate membrane with the goal of producing a new, high-performance separation membrane. Figure 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 leaking to the other side of the membrane is greatly limited and high concentrations of CO₂ can be obtained. The membrane of RITE dendrimer shows excellent CO₂ selectivity of more than 1000, which would have a potential to replace amine solution.

Inorganic membrane

Since zeolites and mesoporous silicas possess well defined micro/meso-pores, considerable attention has been focused on the production of membranes that are capable of separating gases with high selectivities. Polymer membrane shows good affinity for CO₂, however, thermal expansion/mobility of polymer at high temperature causes degradation of CO₂ selectivity. Since mesoporous silicas have uniform and large pores as well as high surface area, a large number of active sites or adsorption sites can be introduced uniformly on inorganic rigid pore wall by chemical grafting of surface OH group with organosilane molecules. If such a material is prepared in the thin film, a molecular movement of the functional group connected with a rigid inorganic pore wall is restricted, and it seems that the decrease in the CO₂ selectivity because of an increase in a free volume by thermal expansion/movement of polymeric material in the high temperature region can be controlled. We have studied surface functionalization of the pore wall of various mesoporous silicas that are specialized for CO₂ capture and separation. Amine-grafted mesoporous silica MCM-48 membranes (thickness: 300-500nm) were prepared and they showed high CO₂/N₂ separation properties and CO₂ permselectivities were 50-800 even at 100 °C. This research proposal was awarded by GCEP(Global Climate & Energy Project) of Stanford University, and the project has started in September, 2005.
**CO₂ fixation as carbonates**

Fixation of carbon dioxide as carbonate by the reaction with calcium and magnesium sources containing waste materials, such as iron- and steelmaking slag, waste concrete and minerals has recently been paid attention as one of the CO₂ sequestration method. The major advantages of this process are, long term stabilized and environmentally safe CaCO₃ and/or MgCO₃ production. Additionally, the overall carbonation process is exothermic and hence, has the potential to become economically feasible. However, the development of a new system with simple process, short reaction time, and lower energy consumption is necessary for practical use. We have proposed and investigating a new process of CO₂ fixation via carbonation of calcium contents in waste concrete or slag by using a solution of NH₄Cl. Studies for the new process have been carrying out to verify the possibility of the system.

**Development of an Innovative After Treatment System for Diesel Vehicles: A Non-Thermal Plasma System**

(A NEDO project from FY2004, joint study with Daihatsu Motor Co. Ltd.)

RITE had developed a plasma technology for natural gas (methane) conversion to acetylene and hydrogen using a high-frequency pulsed plasma in a R & D project of environmental friendly catalysis technology supported by funds from NEDO (FY1991-2000). In 2001, RITE started a three-year plasma particulate matter (PM) removal study financially supported by the Ministry of Education, Culture, Sports, Science and Technology, in which the pulsed plasma technology was used to establish a plasma PM removal system. This plasma PM removal system included a plasma reactor and a pulse power supply.

Recently, the emission control is becoming extremely severe for diesel vehicles, although no satisfied PM removal technologies have been found yet. The plasma PM removal technology has potential as an innovative technology for the after treatment of the exhausts from diesel vehicles. We then began a new project supported by NEDO (project of comprehensive technological development of innovative, next-generation, low-pollution vehicles, R&D of innovative after treatment systems) to continue the plasma PM removal study from 2004. This new project is a joint study with Daihatsu Motor. RITE is to develop a small plasma reactor and pulse power supply that can be loaded on a small diesel car.
1. Overview of CO₂ Geological Storage Technology

The CO₂ geological storage technology is to store carbon dioxide (CO₂) in geological formations safely for reducing greenhouse gas emissions. The technologies of Enhances Oil Recovery (EOR), Enhanced Coal Bed Methane recovery (ECBM), injection in oil and gas fields and saline formations are developed for the mitigation of the global warming.

RITE is developing the aquifer storage technology which is possible for long-term stable isolation with cap rock layer. CO₂ aquifer storage is thought to be one of the most effective and practical technology because the knowledge of underground natural gas storage and the experience of EOR are applicable.

2. Outcome of the recent project

R&D project of CO₂ geological storage technology was launched in 2000 with the support of Ministry Economy Trade Industry. From 2000 to 2004, the possibility of the aquifer storage in Japan was confirmed. Especially the injection experiment in Nagaoka city of Niigata prefecture showed that 10,400 t-CO₂ was able to be stored in a year and half between July 2004 and January 2005. The cross-well seismic tomography, well loggings, measurements of pressure and temperature of reservoir formation, and micro-seismicity monitoring were carried out for developing the simulator of CO₂ behavior. There is not any CO₂ leakage from the reservoir, even when the Nagaoka site was hit on October 23, 2004 by the huge earthquake (M6.8) of which epicenter was about 20km far from the CO₂ injection well. It has been kept to monitor the injected CO₂ for improving the model of CO₂ behavior, until now.

3. R&D subjects of the project.

The scientific possibility of aquifer storage in Japan has been cleared by the current study. Around same time, the technology of geological storage has been progressed with recognition as mitigation technology in the world. So, the technology verification of CO₂ carbon storage (CCS) should be needed for its implementation. RITE is focusing the studies of total analysis and safety analysis to make the road map of CCS for the large scale CO₂ emission sources.

a. Total analysis
   (a) Research on validity
   Storage system will be classified in terms of emission source, capture methods, transporting methods, reservoir types and injection methods. Storage potentials, costs, consumed energy and mitigating effects will be analyzed for each classification. A basic scenario plan which will quantitatively explain the validity of aquifer storage in Japan will be made.
   (b) Submission of road map for implementation of CCS
   Technological issues of CCS implementation in Japan will be summarized, and a first draft of research and development road map which clears milestones of solutions of subjects will be made.
   (c) Engineering study for supposed sites
   Assumed model areas will be chosen and issues of implementation will be extracted by engineering
study including safety and environmental assessment on emission sources, transportation methods, reservoir conditions and storage methods. Solutions for the issues will be proposed.

(d) Storage potential evaluation in Japan

The storage potential of aquifer in Japan will be re-estimated based on the existing data. Locations and types of emission sources will be considered. Issues of the estimation method will be summarized and a new storage model will be proposed.

(e) Survey for implementation and public outreach of CCS

Investigation on political and technical trends of CCS will be carried out including overseas and a framework for public outreach of CCS will prepared. Investigation of implementation will be carried out in terms of operating scheme, legal framework, regulations, overseas business potentials and public outreach.

(f) Investigation on safety and risk

Safety and risk analysis will be carried out and a guideline of safety assessment and environmental assessment will be presented.

b. Safety analysis

(a) Monitoring of Iwanohara site

CO₂ injected at Iwanohara site in Ngaoka will be monitored to improve the simulation model of CO₂ behavior in aquifer for confirming the safety of storage.

(b) Laboratory experiment for basic research

In order to improve the CO₂ behavior model, the following laboratory experiments will be carried out: influence of CO₂ dissolved into water on mechanical stability of cap rock, quantification of mineral dissolution rates under CO₂ presence, mechanisms of super critical CO₂ substitution for saline water in porous media, etc.

(c) Model integration of underground CO₂ behavior

Based on data and knowledge of the monitoring at Iwanohara and the laboratory experiments, CO₂ behavior in aquifer for a short and long period will be scientifically summarized. The improved model will be presented for safety confirmation.

4. Future of the project

It is scheduled as shown in Fig.3 that total analysis and safety analysis of CO₂ geological storage project will be summarized for the future implementation of CCS in Japan in accordance with the R&D of CO₂ capture technology. A workshop entitled “International Workshop on CO₂ Geological Storage, Japan ‘06” was held on February 20, 21, 2006 at the Toranomon Pastoral Hotel Tokyo Japan. This workshop provided the research result of the Nagaoka Project including overseas CCS trend information and the next step of the project. See details in the page 18 of this report.
R&D of CO₂ Ocean Sequestration Project

1. Overview of CO₂ Ocean sequestration technology

Increasing of atmospheric CO₂ is one of the factors of global warming. This is the result of imbalance between the dissolution of atmospheric CO₂ in the ocean and the emission of anthropogenic CO₂, mainly due to the combustion of a fossil fuel. This imbalance is also due to the long time scale requires for the absorption of atmospheric CO₂ in the ocean in contrast with the rapid increase of emissions. However, there is a sufficient potentiality to dissolve anthropogenic CO₂ in the middle and deep layers of the ocean. Therefore, a bypass technology of direct injection of atmospheric CO₂, captured from high emissions, into the deep ocean was proposed. The main objection for the utilization of this technology is the resulting biological impacts when the initial concentration of injected CO₂ is high. From the viewpoint of suppressing environmental impact to the minimum extent, RITE is developing a dilution & injection technology to the middle and deep ocean layer using “Moving Ship” approach, as shown in Fig. 1.

2. Purpose of R&D

In order to implement the anthropogenic CO₂ sequestration into the ocean as a practical used technology, it is important a prior understanding of the environmental impacts, especially onto the biosphere, to prevent possible damages caused by the application of this new technology. Therefore CO₂ sequestration technology can be clearly understand with a wide social receptiveness among the international frameworks, such as Framework Convention on Climate Change (FCCC) and Convention on the Prevention and of Marine Pollution by Dumping of Wastes and other Matter (London Convention, LC). This project is being carried out with the purpose of clarifying these subjects towards the utilization of CO₂ ocean sequestration. In addition, during the phase 1, carried out from FY1997 to FY2001, macroscopic CO₂ action grasp in the adjacent seas of Japan, including predictions and investigations of environmental effects, mainly on the biota, produced by the nozzle back discharge of CO₂, were conducted. Followings are the aims of the present projects as the phase 2 which is carried out from FY2002 to FY2006.

a. Technology assessment of CO₂ ocean sequestration
   (a) Technical evaluation of CO₂ sequestration capacity
   (b) Economic evaluation of the CO₂ sequestration
   (c) Investigation on the legal issue related to international laws

b. Development of assessment technology for CO₂ environmental impact
   (a) Investigation of marine environment
   (b) Understanding of deep-sea ecosystem
   (c) Investigation of biological impact
   (d) Development of Biological impact model

c. Development of CO₂ dilution technology
   (a) Development of CO₂ injection technology
   (b) Improvement of the simulation model of CO₂ behavior
3. Present state of the project

The phase 2 of this project started from the FY2002, and now it is the 5th year. A interim assessment of this project was carried out by the subcommittee of METI in the FY2004. As the result, the following comments and advices have been reported. "Ocean sequestration technology is an effective measure for the mitigation of global warming. However, the environmental impact assessment is an important task. Public relation, especially for oversea, international collaboration, and so on should be carried out actively." So, RITE is enhancing public outreach (PO) and the corporation with research institute of overseas, though RITE has already succeed to organize the international work shop on “Advances in Biological Research for CO₂ Ocean Sequestration” in 2003. From FY2004, the collaboration of carbon dioxide impact on marine ecosystem has been carried out with the Norwegian Institute for Water Research (NIVA) in which an experiment was carried out in a fjord of Norway in 2005 and its results will be reported in 2007. In order to promote PO actions, the special symposium of Japan Ocean Society “CO₂ ocean sequestration: what is the appropriate assessment for the environmental impact” was carried out in 2006. Moreover, in order to make clear the image of ocean sequestration, the engineering study of its implementation under the case which is the ocean sequestration of about 50 million tons of CO₂ annually into the ocean near Japan, was carried out and its biological impact is evaluated.

4. Future of the Project

Development of a CO₂ dilution technology and environmental-impact-assessment technology is progressing using laboratory experiments, field observations and numerical simulations. For an effective utilization of the ocean sequestration technology, it is necessary to prove the developed technology using field experiments in the ocean. Finally, it is necessary to trace the CO₂ behavior in several 100 km scale, and to investigate the biological impact. Therefore, field experiments covering a wide range of scale from small-scale to a real scale is desired in the next step of this project. For the final purpose, it is necessary to promote the understanding ocean sequestration in academia and obtain the agreement to the implementation of ocean sequestration in the arena of LC and other international ocean regulation, because the ocean is a human common property and the implementation of CO₂ ocean sequestration needs to build up an international consensus.