# **Chemical Research Gruop**

# **Chemical Group Activity**

Extensive use of fossil fuels has caused an increase in  $CO_2$  emissions, resulting in a rapidly increasing atmospheric  $CO_2$  concentration that in turn is causing global warming. Atmospheric  $CO_2$  concentration needs to be stabilized at a low level to mitigate global warming.

There are two main measures for atmospheric  $CO_2$  stabilization. One is to reduce  $CO_2$  emissions, the other to sequestrate emitted  $CO_2$  into land or ocean (Carbon Capture and Storage, CCS).

A scenario for  $CO_2$  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  $CO_2$  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<sub>2</sub> 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  $CO_2$  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  $CO_2$  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  $CO_2$  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  $CO_2$  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,  $CO_2$  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  $CO_2$  obtained. At present, cooperation with the companies is promoted for applying this method to the separation of  $CO_2$ from flue gas, chemical process, bio-process, etc.

#### **Polymeric membrane**

One promising means of lowering the cost of  $CO_2$  separation is the development of new, high-performance  $CO_2$  separation membranes that allow  $CO_2$  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  $CO_2$ separation properties. The asymmetric hollow fiber membrane of the cardo polyimide shows the largest  $CO_2$  permeance among existing asymmetric membranes and the top level of  $CO_2$  selectivity in various polymeric membranes. A module of the membrane can recover  $CO_2$  from an exhausted gas of 25 %  $CO_2$  concentration at a comparable expense to amine solution by a system involving  $CO_2$  liquefaction. For a higher  $CO_2$  concentration flux, the membrane separation will have an advantage over amine solution in the system.

RITE is currently developing a  $CO_2$  molecular gate membrane with the goal of producing a new, high-performance separation membrane. Figure 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<sub>2</sub> or H<sub>2</sub> leaking to the other side of the membrane is greatly limited and high concentrations of  $CO_2$  can be obtained. The membrane of RITE dendrimer shows excellent  $CO_2$  selectivity of more than 1000, which would have a potential to replace amine solution.



In developing this CO<sub>2</sub> molecular gate membrane, RITE conducted joint research with the US Department of Energy's National Energy Technology Laboratory (NETL) and the University of Texas at Austin (UTA).

Partially carbonized membrane is a fresh subject under a founding from Global Climate and Energy Project (GCEP) in Stanford University.

#### **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 CO<sub>2</sub>, however, thermal expansion/mobility of polymer at high temperature causes degradation of CO<sub>2</sub> selectivity. Since mesoporous slicas 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 CO<sub>2</sub> 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 CO<sub>2</sub> capture and separation. Amine-grafted mesoporous silica MCM-48 membranes (thickness: 300-500nm) were prepared and they showed high CO<sub>2</sub>/N<sub>2</sub> separation properties and CO<sub>2</sub> permselectivities were 50-800 even at  $100^{\circ}$ C. This research proposal was awarded by GCEP(Global Climate & Energy Project) of Stanford University, and the project has started in September, 2005.

# CO<sub>2</sub> 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 CO<sub>2</sub> sequestration method. The major advantages of this process are, long term stabilized and environmentally safe CaCO<sub>3</sub> and/or MgCO<sub>3</sub> 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 NH<sub>4</sub>Cl. 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.