## **Chemical Research Group**

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# Challenges Associated with the Advanced Industrialization of CO<sub>2</sub> Capture Technologies

## 1. Technologies for CO<sub>2</sub> capture

In December 2015, the Paris Agreement was adopted at COP21.\* To meet the conditions of the agreement, it is essential to promote innovative ways to dramatically reduce emissions on a worldwide basis. In June 2019, Japan released a long-term strategy as the growth strategy based on the Paris Agreement and the Integrated Innovation Strategy 2019, where it has been shown that the carbon capture, utilization and storage and carbon recycling (CCUS/carbon recycling) process is an important innovative technology that enables carbon neutrality in the world. In CCUS/carbon recycling, the combination of the reuse of separated and recovered CO<sub>2</sub> from fossil fuels and materials by treating CO<sub>2</sub> as a carbon resource (CCU) and the storage of separated and recovered CO<sub>2</sub> underground (CCS) is expected to have a significant CO<sub>2</sub> reduction effect. Furthermore, it has been shown that CO<sub>2</sub> separation and capture technologies are the basis for CCUS, and the targets for the technologies are to reduce the cost of CO<sub>2</sub> separation and capture to 1,000 yen/t-CO<sub>2</sub> by 2050 and to establish CO<sub>2</sub>

separation and capture technologies for various  $CO_2$ emission sources. Recently, in a policy statement speech of the 203rd extraordinary session of the Diet in October 2020, Prime Minister Suga said, "Eliminate greenhouse gas emissions to zero by 2050. In other words, we aim to realize a carbon neutral, decarbonized society by 2050." Negative emission technology is required to achieve carbon neutral, and direct air capture (DAC) of  $CO_2$  from the atmosphere, which has been attracting attention recently, is particularly important.

Against this background, it is necessary to promote the practical application of CCUS by proposing optimal separation and capture technologies for the various CO<sub>2</sub> emission sources. In particular, in order to introduce and put into practical use CCS, which is expected to reduce CO<sub>2</sub> on a large scale as a measure to address global warming, it is estimated that it will account for about 60% of the cost. CO<sub>2</sub> separation and recovery from emission sources as a means of cost reduction are important.

The Chemical Research Group studied the different

CO<sub>2</sub> capture technologies with a special focus on chemical absorption, adsorption, and membrane separation methods. This work involved the development of new materials and processing methods, as well as investigations of capture systems. The Group's studies have thus far generated significant outcomes and assisted in the progress of research in this particular field.

Specifically, we developed high performance chemical absorbents, and chemical absorbents with particular promise was selected for application in a commercial CO<sub>2</sub> capture plant owned by a private Japanese company.

With regard to solid sorbent technology, we have also been developing sorbents for CO<sub>2</sub> capture to efficiently reduce energy consumption. Currently, the lowtemperature regenerable solid sorbent that we developed is being evaluated for practical use. Research on practical application is now underway in collaboration with a private company. In the near future, we will install a test facility at a coal power plant for practical application.

Membrane separation is expected to be an effective means of separating CO<sub>2</sub> from high-pressure gas mixtures at low cost and with low energy requirements. As a member of the Molecular Gate Membrane module Technology Research Association, RITE has been developing membranes to selectively capture CO<sub>2</sub> from pressurized gas mixtures containing H<sub>2</sub>, such as those generated in the integrated coal gasification combined cycle (IGCC) at low cost and with low energy use. We are also developing membranes with large areas using the continuous membrane-forming method and developing membrane elements for the mass production of membranes and membrane elements in the future. In addition, we evaluated the separation performance and process compatibility of our membrane elements using coal gasification real gas and are proceeding with development aimed at commercialization.

RITE joined the International Test Center Network (ITCN) and now actively uses overseas networks towards the commercialization of CO<sub>2</sub> separation and recovery technology.

\*COP21: 2015 United Nations Climate Change Conference

## 2. Chemical absorption method for CO<sub>2</sub> capture

In the absorption method, CO<sub>2</sub> is separated by using the selective dissolution of CO<sub>2</sub> from a mixed gas into a solvent. In particular, the chemical absorption method based on the chemical reaction between amine and CO<sub>2</sub> in a solvent can be applied to gases with a relatively low CO<sub>2</sub> concentration, such as combustion exhaust gas, and the method is one of the most mature CO<sub>2</sub> capture technologies.

Energy consumption in the process of solvent regeneration and the degradation of amines are factors in the cost increase of the chemical absorption method. Focusing on the fact that the structure of amine molecules is closely related to these factors, RITE started a new amine solvent: since the COCS project (METI's Subsidy Project) started in 2004, RITE has been working on the development of a high-performance amine solvent that reduces the cost of  $CO_2$  capture.

In the COURSE50 project (NEDO's consignment project) since 2008 with the goal of reducing CO<sub>2</sub> emissions by 30% in the steelmaking process, RITE is working with Nippon Steel Corporation to upgrade the chemical absorption method. The chemical absorbent and process developed by the COURSE50 project was adopted by the energy-saving CO<sub>2</sub> capture facility ESCAP ® of Nippon Steel Engineering Co., Ltd., which was commercialized in 2014.

ESCAP<sup>®</sup> Unit 1 was constructed on the premises of Muroran Works for general industrial use including beverages (120t-CO<sub>2</sub>/day). This is the world's first commercial facility using the chemical absorption method for the combustion exhaust gas from a hot blast furnace at a steelworks as a CO<sub>2</sub> source. In 2018, ESCAP® Unit 2 started operation at the Niihama Nishi Thermal Power Station (143t-CO<sub>2</sub>/day). This is the first commercial facility in Japan to capture CO<sub>2</sub> by the chemical absorption method from the combustion exhaust gas of coalfired power generation as the CO<sub>2</sub> source. The recovered CO<sub>2</sub> is used as a raw material in a nearby chemical factory.



Fig. 1 Equipment of energy-saving CO<sub>2</sub> absorption process ESCAP<sup>®</sup> at Niihama Nishi power station, Sumitomo Joint Electric Power Co., Ltd.

## 3. Solid sorbent method for CO<sub>2</sub> capture

Unlike a chemical absorbent in which amine is dissolved in a solvent, such as water, a solid sorbent is one in which amine is supported on a porous material, such as silica or activated carbon. In the process using a solid sorbent, the heat of vaporization and sensible heat caused by the solvent can be suppressed, so reduction of  $CO_2$  capture energy can be expected.



Fig. 2 Liquid absorbent and solid sorbent

In 2010, RITE started the development of solid sorbent materials mainly for CO<sub>2</sub> capture from the combustion exhaust gas of coal-fired power plants (METI consignment project). In the fundamental research phase (FY 2010–2014), we succeeded in developing a new amine suitable for solid sorbents and achieved a capture energy of 1.5 GJ/t-CO<sub>2</sub> or less in a laboratory scale test. This solid sorbent is an innovative material that enables not only low energy capture but also a low temperature process at 60°C.

In the practical application research phase (METI/NEDO consignment project) from FY 2015 to 2019 with Kawasaki Heavy Industries, Ltd., as a partner, scale-up synthesis of solid absorbent (>10 m<sup>3</sup>), bench scale test (>5 t-CO<sub>2</sub>/day), and real-gas exposure tests at a coal-fired power plant were conducted, which achieved a CO<sub>2</sub> capture cost of less than 3,000 yen/t-CO<sub>2</sub>. Compared to other projects that used amine solid sorbents, the capture scale, energy, and cost of this project were all at the top level globally.

In 2020, RITE was adopted by the NEDO commissioned project with Kawasaki Heavy Industries, Ltd. In this project, with the cooperation of Kansai Electric Power Co., Ltd., a pilot scale test facility (~40 t-CO<sub>2</sub>/day) will be constructed at the Maizuru power plant, and CO<sub>2</sub> capture tests from the combustion exhaust gas emitted from the coal-fired power plant will start in 2022. Currently, RITE is proceeding with rationalization and the cost reduction of solid sorbent material manufacturing technology, elucidation of a material degradation mechanism, development of degradation prevention technology, and the upgrading of process simulation technology toward pilot scale tests.





#### 4. Membrane separation

 $CO_2$  separation by membranes involves the selective permeation of  $CO_2$  from the pressure difference between the feed side and the permeate side of the membrane. So,  $CO_2$  capture at low cost and energy is expected by applying the membrane processes to precombustion (Fig. 4). For this reason, we are currently developing novel  $CO_2$  selective membrane modules that effectively separate  $CO_2$  during the IGCC process.





We found that novel polymeric membranes composed of dendrimer/polymer hybrid materials (termed molecular gate membranes) exhibited excellent CO<sub>2</sub>/H<sub>2</sub> separation performance. Fig. 5 presents a schematic that summarizes the working principles of a molecular gate membrane. Under humidified conditions, CO<sub>2</sub> reacts with the amino groups in the membrane to form either carbamate or bicarbonate, which then blocks the passage of H<sub>2</sub>. Consequently, the amount of H<sub>2</sub> diffusing to the other side of the membrane is greatly reduced, and high concentrations of CO<sub>2</sub> can be obtained. A poly(vinyl alcohol) (PVA) polymer matrix is used for pressure durability and to immobilize the dendrimers.





We developed new types of dendrimer/polymer hybrid membranes that provide superior separation of CO<sub>2</sub>/H<sub>2</sub> gas mixtures. Based on this work, the Molecular Gate Membrane module Technology Research Association (MGMTRA consists of the Research Institute of Innovative Technology for the Earth [RITE] and a private company) is researching new membranes, membrane elements (Fig. 6), and membrane separation systems.

## **R&D** Activities • Chemical Research Group





**Membrane element** (4-inch; L = 200 mm)

Membrane module (2-inch)

Fig. 6 CO<sub>2</sub> selective membrane, membrane element, and membrane module.

Membrane element: The structure with a large membrane area composed of the membrane, support, and spacer. Membrane module: The structure in which the membrane element is placed.

Based on the achievements of the project by the Ministry of Economy, Trade and Industry (METI), Japan, the CO<sub>2</sub> Separation Membrane Module Research and Development Project (FY 2011–2014) and CO<sub>2</sub> Separation Membrane Module Practical Research and Development Project (FY 2015–2018) in the current NEDO project, CO<sub>2</sub> Separation Membrane Module Practical Research and Development (FY 2018–2021), we are developing membranes with large areas using a continuous membrane-forming method while developing membrane elements. As a result, two-inch and fourinch membrane elements with enough pressure durability were successfully prepared.

In addition, we conducted pre-combustion CO<sub>2</sub> capture tests of the membrane elements using coal gasification gas at the Wakamatsu Research Institute, Electric Power Development Co. Ltd. in Japan in order to identify and then solve the technical problems of the membrane elements (Fig. 7). As a result, it was confirmed that the membrane elements were durable against the real gas (containing impurities, such as H<sub>2</sub>S).





Simulated gas: CO<sub>2</sub>/He/N<sub>2</sub>.

In the future, we plan to develop commercial-scale membrane modules and the membrane systems, based on the results of the projects.

## 5. New challenges

As mentioned above, the Chemical Research Group has been focusing on the development and practical application of  $CO_2$  capture technologies for large-scale  $CO_2$  emission sources, such as steel industries and power plants. Finally, we will introduce two examples of new challenges. One is the capture of  $CO_2$  from the atmosphere, or direct air capture (DAC), and the other is the development of technology to immobilize  $CO_2$  as carbonate.

In order to achieve carbon neutrality, a technology that can remove CO<sub>2</sub> emitted into the atmosphere, that is, a negative emission technology, is indispensable. In recent years, DAC has been attracting attention as one of the representative negative emission technologies, and is being studied overseas. It is hoped that the recovered energy and costs will be significantly reduced for future implementation. In Japan, challenging research and development is being carried out in NEDO's "Moonshot R & D Project" that started in 2020. RITE has started studying the optimum materials and systems for DAC in cooperation with Kanazawa University and private companies in this project: the following three items will be developed to establish carbon recycling technologies that capture  $CO_2$  from the atmosphere and convert the recovered  $CO_2$  into valuable resources.

R&D items 1: Development of a new solid sorbent material for low-concentration CO<sub>2</sub> capture and a system to recover low-concentration CO<sub>2</sub> with high efficiency.

R&D items 2: Development of CO<sub>2</sub> conversion technology (Fischer–Tropsch synthesis) using an inorganic separation membrane for synthesizing liquid hydrocarbon fuel from CO<sub>2</sub> with high efficiency and low energy consumption.

R&D items 3: Life cycle assessment (LCA) evaluation and economic evaluation regarding the conversion process to liquid hydrocarbon fuel using CO<sub>2</sub> recovered from the atmosphere.





In the technology of CO<sub>2</sub> fixation as a carbonate, RITE developed a unique process over many years. From 2020, JFE Steel Co., Ltd., Taiheiyo Cement Co., Ltd., and RITE set up a study group to target steel slag and waste concrete and then use alkaline earth metals extracted from these for utilization with the CO<sub>2</sub> emitted from factories and other facilities. We are cooperating in the development of technology for recovering as carbonates,

which is a stable compound, by reacting with CO<sub>2</sub> (Fig. 9). By combining the unique processes developed by RITE and R&D skills with the technological capabilities and broad insights of the two leading steel and cement industries, synergistic effects are expected for technological development.



Fig. 9 CO<sub>2</sub> fixation as carbonates

### 6. Conclusion

As stated above, the Chemical Research Group has energetically promoted the development of CO<sub>2</sub> separation and recovery technology mainly for the chemical absorption method, the solid sorbent method, and separation. The chemical absorption membrane method has been deployed from the demonstration stage to commercial machines for blast furnace exhaust gas and combustion exhaust gas from coal-fired power plants and has already been put to practical use as a CO<sub>2</sub> separation and recovery technology. In the solid sorbent method, we have begun studying combustion exhaust gas from coal-fired power plants for a 40 t-CO<sub>2</sub>/day scale pilot test from FY 2020. In membrane separation, we confirmed the separation ability of CO<sub>2</sub> and H<sub>2</sub> in an actual gas test using a membrane element from coal gasification gas. In addition, we have just begun to develop DAC technology newly adopted in NE-DO's Moonshot R&D Project and CO2 fixation technology using steel slag and waste concrete.

The Chemistry Research Group will work vigorously on individual research topics with these themes. Among

them, for the themes close to the practical stage, we will carry out scale-up studies and actual gas tests with the aim of establishing the technology at an early stage. At the same time, we would like to develop innovative technologies and propose CO<sub>2</sub> separation and recovery technologies that can save more energy and reduce costs.