Chemical Research Group

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Challenges Associated with the Advanced Industrialization of CO₂ Capture Technologies

1. Technologies for CO₂ capture

The Paris Agreement was adopted at COP 21 in December 2015, and in order to minimize the adverse effects of climate change, such as abnormal weather, the rise in global average temperature before the Industrial Revolution was kept well below 2°C. Pursuing efforts to keep the temperature down to 1.5°C was the goal. After that, in response to the heightened sense of crisis, such as further temperature rises and the enormous natural disasters occurring on a global scale, the Glasgow Climate Agreement at COP 26 in November 2021 demonstrated the determination to pursue efforts to limit the temperature rise to 1.5°C with the world's first numerical target of 1.5°C. According to the IPCC, the 1.5°C target requires a 45% reduction in CO₂ by 2030 compared to 2010 and net zero by 2050.

In Japan as well, in response to the 2050 Carbon Neutral Declaration in October 2020 and the Green Growth

Strategy for 2050 Carbon Neutral formulated in December 2021 (detailed in June 2021), various types are available. Efforts to prevent global warming are being promoted from various areas. CCUS (Carbon dioxide Capture, Utilization, and Storage) / Carbon Recycling is an important innovative technology that enables carbon neutrality. In CCUS/carbon recycling, the combination of the reuse of separated and recovered CO₂ from fuels and materials by treating CO₂ as a carbon resource (CCU), and the storage of separated and recovered CO₂ underground (CCS) is expected to have a significant CO₂ reduction effect. Furthermore, it has been shown that CO₂ separation and capture technologies are the basis for CCUS, and the targets for the technologies are to reduce the cost of CO₂ separation and capture to 1,000 yen/t-CO₂ by 2050 and to establish CO₂ separation and capture technologies for various CO₂ emission sources. Negative emission technology is required to achieve carbon neutrality, and direct air capture (DAC) of CO₂ from the atmosphere, which has been attracting attention recently, is particularly important. In the Carbon Recycling Technology Roadmap (Ministry of Economy, Trade and Industry) revised in July 2021, DAC was added as a new technology field with progress.

Against this background, it is necessary to promote the practical application of CCUS by proposing optimal separation and capture technologies for the various CO₂ emission sources. In particular, in order to introduce and put into practical use CCS, which is expected to reduce CO₂ on a large scale as a measure to address global warming, it is important to reduce the cost of separating and recovering CO₂ emitted from large-scale sources.

The Chemical Research Group studied the different CO₂ 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 were selected for application in a commercial CO₂ capture plant owned by a private Japanese company.

With regard to solid sorbent technology, we have been engaged in research and development of solid absorbent materials with high CO₂ efficiency recovery and low energy consumption and have found solid absorbent materials and systems with good CO₂ desorption performance at low temperatures. Currently, in the NEDO consignment project, we are preparing for a scale-up test using actual combustion exhaust gas from a coal-fired power plant in collaboration with a private company.

Membrane separation is expected to be an effective

means of separating CO₂ 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 CO₂ from pressurized gas mixtures containing H₂, 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.

In addition, as part of the NEDO moonshot R&D project, we have begun studying technologies for capturing CO₂ from the atmosphere by direct air capture (DAC) and using it as fuel or raw materials. While promoting the development of amine compounds suitable for the separation and recovery of low concentration CO₂, we are working on the development of a DAC system that can separate and recover CO₂ from the atmosphere with high efficiency in cooperation with Kanazawa University and private companies.

As described above, RITE is working on the development of innovative technologies that will be the foundation for a wide range of next generation, leadingedge research and development for CO₂ reduction and aiming to establish technologies that can be implemented in society. In addition, we joined the International Test Center Network (ITCN) and now actively use overseas networks towards the commercialization of CO₂ separation and recovery technology.

*COP 21: 2015 United Nations Climate Change Conference

2. Chemical absorption method for CO₂ capture

In the absorption method, CO₂ is separated by using the selective dissolution of CO₂ from a mixed gas into a solvent. In particular, the chemical absorption method based on the chemical reaction between amine and CO₂ in a solvent can be applied to gases with a relatively low CO₂ concentration, such as combustion exhaust gas, and the method is one of the most mature CO₂ capture technologies.

Energy consumption in the process of solvent regeneration and the degradation of amines are factors in the cost increases 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 consignment project) since 2008 with the goal of reducing CO₂ 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 CO₂ capture facility ESCAP® of Nippon Steel Engineering Co., Ltd., which was commercialized in 2014.

ESCAP® Unit 1 was constructed on the premises of Muroran Works for general industrial use, including beverages. 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 CO₂ source. In 2018, ESCAP® Unit 2 started operation at the Niihama Nishi Thermal Power Station. This is the first commercial facility in Japan to capture CO₂ by the chemical absorption method from the combustion exhaust gas of coal-fired power generation as the CO₂ source. The recovered CO₂ is used as a raw material in a nearby chemical factory.

In addition, the latest research found the possibility of further reducing energy consumption by using the absorption solvent with an organic compound instead of water and continues to explore new ones. The solvent can control the reaction mechanism of CO₂ absorption and the effect of polarization.



Fig. 1 Equipment of energy-saving CO₂ absorption process ESCAP[®] at Niihama Nishi power station, Sumitomo Joint Electric Power Co., Ltd.

3. Solid sorbent method for CO₂ capture

Unlike a chemical absorbent in which amines are dissolved in a solvent, such as water, a solid sorbent is one in which amines are 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 for CO₂ 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 in a laboratory scale test, we obtained the prospect of capture energy of 1.5 GJ/t-CO₂ or less. This solid sorbent system is an innovative material that enables not only low energy capture but also a low temperature process at 60°C. Compared to other businesses that use amine-based solid absorbents, this business is at the top level globally in terms of low-temperature regeneration.

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 m³), bench scale test (>5 t-CO₂/day), and real-gas exposure tests at a coal-fired power plant were conducted.





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_2 /day) will be constructed at the Maizuru power plant, and CO_2 capture tests from the combustion exhaust gas emitted from the coal-fired power plant will start in 2022. Currently, RITE is proceeding with the production of solid absorbents on a 100 m³ scale optimized on the basis of the results of the scale-up synthesis of solid absorbents and bench scale tests for pilot scale tests. We are also elucidating the material deterioration mechanism, developing deterioration prevention technology, and studying efficient operating conditions using process simulation technology.

4. Membrane separation

CO₂ separation by membranes involves the selective permeation of CO₂ from the pressure difference between the feed side and the permeate side of the membrane. So, CO₂ capture at low cost and with low energy is expected by applying the membrane processes to pre-combustion (Fig. 4). For this reason, we are currently developing novel CO₂ selective membrane modules that effectively separate CO₂ during the IGCC process.



Fig. 4 Schematic of the IGCC process with CO₂ capture by CO₂ selective membrane modules

We found that novel polymeric membranes composed of dendrimer/polymer hybrid materials (termed molecular gate membranes) exhibited excellent CO₂/H₂ separation performance. Fig. 5 presents a schematic that summarizes the working principles of a molecular gate membrane.

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Under humidified conditions, CO_2 reacts with the amino groups in the membrane to form either carbamate or bicarbonate, which then blocks the passage of H₂. Consequently, the amount of H₂ diffusing to the other side of the membrane is greatly reduced, and high concentrations of CO₂ 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 CO₂/H₂ 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.

Based on the achievements of the project by the Ministry of Economy, Trade and Industry (METI), Japan, the CO₂ Separation Membrane Module Research and Development Project (FY 2011–2014) and CO₂ Separation Membrane Module Practical Research and Development Project (FY 2015–2018), we developed the membranes with large areas using a continuous mem-



CO₂ selective membrane





Membrane module

(2-inch)

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

Fig. 6 CO₂ 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.

brane-forming method while developing membrane elements in the NEDO project, CO_2 Separation Membrane Module Practical Research and Development (FY 2018– 2021). As a result, two-inch and four-inch membrane elements with enough pressure durability (2.4 MPa) were successfully prepared. In addition, we conducted pre-combustion CO_2 capture tests of the four-inch membrane elements using coal gasification gas, and it was confirmed that the membrane elements were durable against the real gas (containing impurities, such as H₂S).

In the new NEDO project, CO2 Separation Membrane System Practical Research and Development/Development of CO2-H2 membrane separation systems using high-performance CO2 separation membrane modules, we plan to conduct the practical research and development to improve the separation performance and durability of the membrane elements, to scale up the membrane modules and to design the membrane systems suitable for the CO₂ utilization process based on the results of the previous projects.

5. CO₂ capture technology from the atmosphere

RITE has been conducting a national project in the NEDO Moonshot R&D Project with the development of a highly effective direct CO₂ capture method from air and carbon recycling technologies in collaboration with Kanazawa University and private companies. This project is a part of the Environment Innovation Strategy launched by the Japanese government in 2020 that aims to establish technologies that enable Beyond Zero by 2050.

A method of capturing CO₂ directly from the atmosphere called Direct Air Capture (DAC) is one of the negative emission technologies. Seven research themes on DAC have been adopted in the Moonshot R & D Project. Fig. 7 shows our R & D items and a carbon cycle society as our goal.



Fig. 7 Development of highly efficient DAC and carbon recycling technologies

RITE is trying to synthesize new amines suitable for DAC and transform solid sorbents into low-pressure drop structured materials. Developed materials are tested in the actual air around RITE. Because of the dayto-day variations in the local atmosphere's conditions, we designed new equipment to control and test the effects of temperature, humidity, and CO₂ concentration in the atmosphere (Fig. 8).



Fig. 8 New designed lab test equipment for DAC

In order to realize an economically acceptable DAC, not only material development but also process development is important. We introduce a simulation technology to reveal the most suitable process without chemical/time consuming. This environmentally friendly development technique will be also used in the Moonshot R&D Project.

6. CO₂ fixation

 CO_2 fixation (CO_2 mineralization) has the same basic concept as enhanced weathering, which is one of negative emission technologies. It is a technology that reacts CO_2 with alkaline earth metals and immobilizes it as a chemically stable carbonate, which is attracting attention as a CO_2 fixation technology that does not affect the ecosystem. Especially in recent years, early implementation of the CO_2 fixation by using by-products and wastes containing alkaline earth metals is expected to build a sustainable society.

RITE developed a unique process over many years. From 2020, two Japanese private companies and RITE set up a study group to target steel slag and waste concrete and then use alkaline earth metals extracted from these for use with the CO₂ 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 CO₂ (Fig. 9).



Fig. 9 CO₂ fixation as carbonates

7. Conclusion

As stated above, the Chemical Research Group has energetically promoted the development of CO₂ separation and recovery technology mainly as the chemical absorption method, the solid sorbent method, and membrane separation. The chemical absorption 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 CO₂ 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-CO₂/day scale pilot test, which is planned for FY 2023-2024. In membrane separation, we confirmed the separation ability of CO₂ and H₂ in an actual gas test using a membrane element from coal gasification gas. In addition, we are working on the development DAC technology newly adopted in NEDO'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. 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 CO₂ separation and recovery technologies that can save more energy and reduce costs.

In particular, in sustainable development scenarios for decarbonization in the future, it is said that the contribution of CO₂ capture from natural gas and biomass combustion will increase, and negative emission technologies, such as DACCS, are also required. Therefore, in the future, it is necessary to proceed with technological development so that it can handle these lower-concentration CO₂ emission sources. As the CO₂ concentration decreases, the amount of gas to be treated increases and the high oxygen concentration also increases. Therefore, it will be important to develop materials with lower cost and higher deterioration resistance and system development corresponding to them.