Adsorption and desorption technology

Adsorptive Separation and Catalytic Reaction: Indispensable Technologies for Sustainable Society

Dr. Takayasu FUJIURA[*1]

[*1] Mechanical Engineering Research Laboratory, Technical Development Group (currently, Business Development Department)

Abstract

Since the 1980s, Kobe Steel has been refining adsorption separation technology and catalytic reaction technology and has continued to contribute to a green society and ensure safety and security in community development and manufacturing through the practical application of distinctive gas separation processes in the steel and chemical industries, as well as environmental conservation in thermal power plants. In recent years, as movements towards carbon neutrality and a circular economy have accelerated, it is believed that these technologies, which involve highly separating substances and transforming substances into valuable entities, will become even more important in realizing a sustainable society with a reduced environmental burden while effectively utilizing previously discarded resources. This article introduces the evolution of both technologies and provides examples of their applications while discussing prospects for the future.

Introduction

Industrial processes and environmental purification processes often require the separation, removal, purification, concentration, and recovery of substances in gases and liquids with many constituents. Adsorptive separation methods using adsorbents are widely used for these operations. Catalysts are often used in chemical synthesis and decomposition to improve the efficiency of the conversion by reducing the activation energy and accelerating the reaction rate. As such, both adsorptive separation and catalytic reaction are widely used as fundamental techniques in industrial processes.

The KOBELCO Group has spent many years cultivating plant engineering services and gas separation equipment. The adsorptive separation gas purification processes developed have been adopted in a variety of industrial applications and are renowned for their superior purification capacity and purified gas recovery rate. We have further amassed extensive knowledge regarding catalytic reaction technology through the design and construction of chemical plants. We use this knowledge to advance engineering technology, environmental conservation, and process equipment. Through these efforts, we have established a wide range of technologies and expertise supporting the development of new products and processes unique to Kobe Steel. Examples include technologies for the evaluation of adsorbents and catalysts, process optimization through laboratory testing and simulation, and plant system design and control.

Alongside various existing products and processes, adsorptive separation and catalytic reaction technologies will become increasingly important in supporting carbon neutrality (CN). This is because such technologies can support the control of greenhouse gas emissions and diffusion, the switch to alternative energy, and environmental conservation. Contributing to a green society and ensuring safety and security in community development and manufacturing are materialities of the KOBELCO Group. As such, the group must advance both aforementioned technologies as core technologies and must continue providing products and processes that are beneficial to society. In this paper, we describe the history of the KOBELCO Group's accomplishments in both technologies, including applicable products and processes, and detail our future outlook.

1. Gas separation and purification process

Kobe Steel's focus on adsorptive separation technology dates back to the 1980s. During this period, argon (Ar) gas was used as the bottom blowing gas in the converter at Kakogawa Works. The issue, however, was that Ar is costly. Carbon monoxide (CO), on the other hand, is economical. The COSORB process was introduced to separate and recover the high proportion of CO in converter byproduct gas (LDG). Plant operation using this wet process (gas-liquid absorption) began in 1985.[1)] We subsequently collaborated with Kansai Coke and Chemicals to develop an adsorbent with a unique composition that uses the chemical constituents of this process to selectively adsorb CO (hereinafter, CO adsorbent). In 1989, we released the CO-PSA process, which is a dry method (gas-solid adsorption) that uses the same adsorbent for advanced separation and purification of CO. The commissioning of a plant at Kakogawa Works marked the beginning of our process plant business centering around adsorptive separation.[2)]

While continuing to cultivate our CO-PSA plant business in the 1990s, we began expanding our testing and evaluation infrastructure and analytical technology for adsorptive separation. It was during this time that we began developing new processes for industrial and environmental purification applications. Since the late 2000s, we have been focused on adsorptive separation processes that reduce environmental burden and foster a sustainable society. Examples include hydrogen purification processes for the future hydrogen society and olefin PSA supporting effective use of petrochemical industry compounds such as ethylene.

1.1 CO-PSA process

As mentioned above, the CO-PSA process uses a unique CO adsorbent for the high-capacity separation and purification of CO. **Fig. 1** shows a basic flow diagram of this process.[3)] The adsorption and desorption method employed is the pressure swing adsorption (PSA) method. This involves the switching of four adsorption columns filled with CO adsorbent between pressurization, adsorption, depressurization, cleaning, and desorption modes for a continuous supply of CO with a purity of at least 99%, and at a high recovery rate of at least 80%.[4)] Cryogenic separation and wet scrubbing are

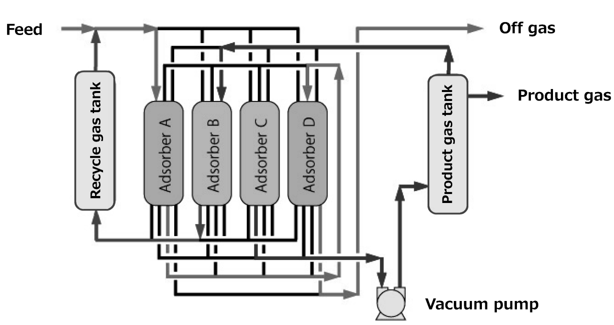


Fig. 1 Process flow of pressure swing adsorption

Fig. 2 Commercial CO-PSA plant installed at Kobe Steel's Kakogawa Works

the industry's primary methods of CO recovery and purification; our method is the only dry CO purification process. Being a dry process gives it the major advantages of using relatively simple equipment and being easy to operate and control. **Fig. 2** shows the first commercial plant, constructed in 1989 at Kakogawa Works for the purification of CO in converter by-product gas. We have delivered eight plants since the 1990s, including an expansion at Kakogawa Works and plants for CO separation and purification in chemical production. Each of these facilities continues to operate smoothly today. KOBELCO E&M Co., Ltd. currently designs, manufactures, and constructs these plants, with new plants having been commissioned in 2019 and 2023.

1.2 Fundamental technologies supporting the process

Developing and designing gas purification processes that use adsorptive separation technology necessitates three types of technologies. Namely, these are (1) technology to accurately evaluate the performance of the adsorbent, (2) process evaluation technology to maximize performance by optimizing adsorption and desorption operations, and (3) process design technology to design a plant that yields the necessary specifications (raw gas composition and volume, product gas purity, throughput, etc.).

Kobe Steel's fundamental technologies and infrastructure for testing and evaluating adsorbent performance and small-scale processes are useful in process development. Next, we describe our performance evaluation and process design methodologies using the CO adsorbent and CO-PSA described above as examples.

Fig. 3 shows the CO adsorbent. The agent comprises a copper compound (CuCl) on the surface of a porous alumina support with a pore structure conducive to CO adsorption. This type of chemical adsorbent selectively traps CO through

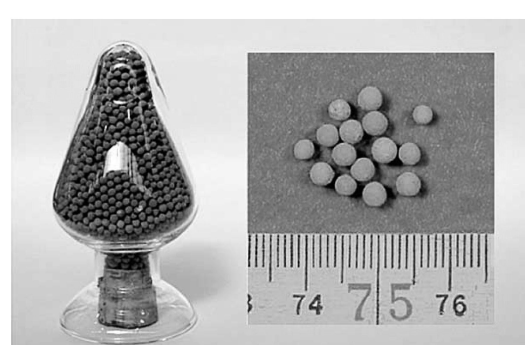


Fig. 3 Proprietary CO adsorbent

the formation of a complex between Cu+ and CO. **Fig. 4** compares the adsorption mechanism of this adsorbent with that of conventional physical adsorbents such as zeolites. **Fig. 5** shows the characteristics of CO adsorbent as revealed by equipment for determining adsorption properties.[5)] CO adsorbent has more than three times the CO adsorption capacity of conventional physical adsorbents such as zeolites in the operating pressure range of PSA. In addition, because physical adsorbents generally have poor selective adsorption properties, they tend to co-adsorb substances other than CO. CO adsorbents, by contrast, adsorb CO with high selectivity even in the presence of N_2 and CO_2. We use our process design method to determine the parameters of a plant based on the performance characteristics of the adsorbent. Kobe Steel's design technology and operational know-how specific to the PSA process is based upon simulations as well as experience with general-purpose single-column adsorption units and a four-column lab-scale PSA test apparatus (see **Fig. 6**). Testing and demonstration using this equipment played a major role in establishing the overall process. Specifically, we optimized operating conditions and the dimensions of the adsorption tower through testing cycles of pressurization → adsorption → depressurization → cleaning → desorption based on an actual plant. Trace components other than CO remaining in the system after adsorption were removed efficiently, and both high purity of the product gas and a high recovery rate were achieved despite being inherently contradictory objectives. Furthermore, we obtained valuable data and know-how from the system, such as an understanding of how adsorbent capacity changes over time based on evaluation during

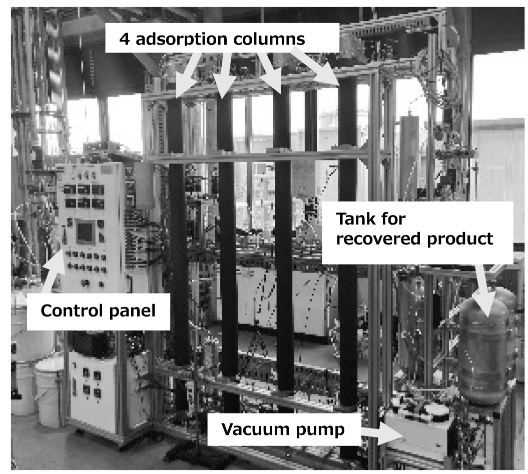
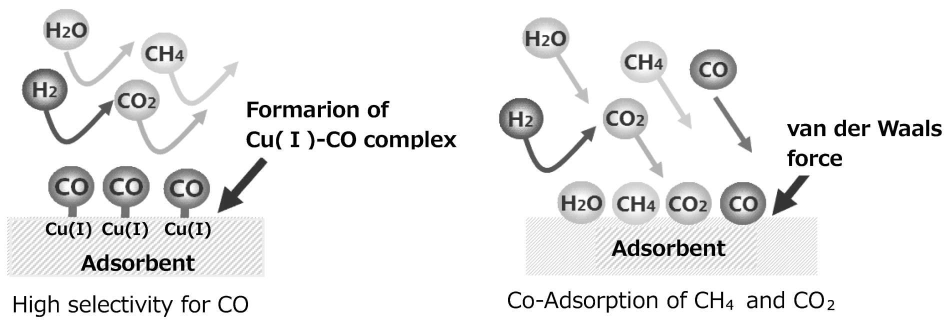


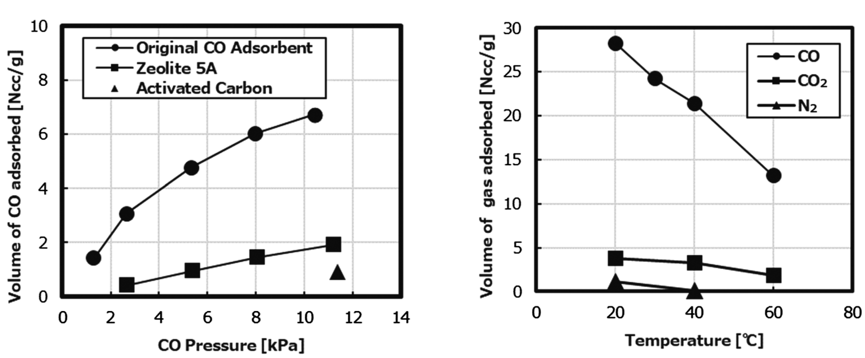
Fig. 6 4-column PSA test apparatus



(a) Original chemical adsorbent

(b) Conventional physical adsorbents such as activated carbon and zeolites

Fig. 4 Schematic of CO adsorption mechanism



(a) Adsorption isotherm for CO (40℃)

(b) Selectivity of Original CO adsorbent (100 kPa)

Fig. 5 Adsorption characteristics of proprietary CO adsorbent continuous operation. We have incorporated this information and expertise into the design of the system, safeguarding the long-term reliability of the process.

1.3 Development of new applications

1.3.1 Hydrogen purification PSA system

In the 2000s, in anticipation of the future hydrogen society, we began developing a hydrogen purification PSA system (H2-PSA) that uses CO adsorbent in support of the production of hydrogen for fuel cells.[5), 6), 7)] The purification of hydrogen for fuel cells from petroleum-derived reforming reaction gas requires highly effective separation and removal of CO, a harmful component in the battery. CO adsorbent has highly selective adsorption capacity for CO even in an atmosphere containing H_2, and the diffusion of CO once captured is extremely low. Therefore, hydrogen supply equipment subjected to DSS (daily start and stop) operation do not need to idle after startup to allow the gas composition to stabilize, as ISO-compliant hydrogen (CO concentration ≤ 0.2 ppm) can be supplied immediately after startup. Another advantage is that less adsorbent is required than with PSA, which uses general-purpose adsorbent. This makes it possible to maintain a high hydrogen recovery rate with a more compact adsorption tower. This PSA system will be used in devices and processes that require hydrogen, such as fuel cells, which are expected to see expanded use in the future. The system will also be useful in the reduction of CO_2 via hydrogen in the CCUS (carbon capture, utilization, and storage) process.

1.3.2 Olefin PSA process

CO adsorbents can also selectively adsorb lower olefins (ethylene, propylene, etc. with double bonds), which are the raw materials of plastics and resins.[8), 9)] Kobe Steel and KOBELCO E&M Co., Ltd. used their technical expertise related to the CO-PSA process to develop an olefin PSA process that can recover residual olefins in reaction off-gas from petrochemical plants with high purity (≥ 99%) and high efficiency (recovery rate ≥ 80%).

Environmental burden is reduced substantially because valuable high-purity olefins can be recovered from mixed gas, which is conventionally treated by combustion. This system is also expected to be used in CCU-related processes such as Fischer-Tropsch synthesis to olefins (FTO).

2. Catalyst life prediction technology

We have amassed extensive knowledge and experience in the engineering, procurement, and construction (EPC) of chemical plants since the 1970s. Specifically, we have partnered with our customers to conclude many projects involving catalytic reaction technology. Although we have since downsized our EPC business, the Technical Development Group has secured fundamental technologies related to catalytic reactions and has expanded its scope of application beyond plant engineering. For instance, group's scope now includes environmental conservation technologies for thermal power plants and the development of new water electrolysis process equipment.

2.1 Advanced deNOx (denitration) and catalyst life prediction at Kobe Power Plant

Kobe Steel's Kobe Power Plant operates a world-class exhaust treatment system to reduce air pollution.[10), 11)] It converts nitrogen oxides (NOx) in gas from coal combustion into harmless N_2 and H_2O. This occurs via a high-temperature reaction with ammonia (NH_3, fed into the system separately) and the catalyst in an exhaust gas deNOx system containing a deNOx catalyst (SCR, selective catalytic reduction). **Fig. 7** shows the exhaust gas treatment flow of a thermal power plant including the deNOx process. DeNOx performance and the rate of catalyst degradation depend on the power plant's specific operating conditions, including the properties of the feedstock coal used for power generation. This concept led Kobe Steel to develop proprietary technology to evaluate the performance and degradation characteristics of deNOx catalysts, enabling highly accurate catalyst life prediction and as well as the continued and stable operation of advanced deNOx systems.

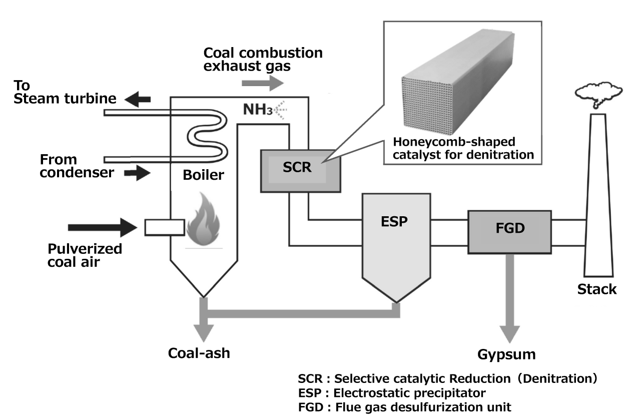


Fig. 7 Process flow of exhaust gas treatment in Kobe Power Plant

2.2 Fundamental technologies supporting the process

As with adsorptive separation, evaluation technologies for catalytic reactions and process design require evaluation of the basic performance and characteristics of the catalyst, laboratory testing of the reaction process, and large-scale performance validation. Only then can the design process for the actual machine commence. **Table 1** details Kobe Steel's evaluation technologies and testing infrastructure for catalytic reactions. Our repository of test equipment is designed to evaluate deNOx catalyst performance, reactions under high temperature and high pressure on the scale of a few grams of catalyst, and the efficiency of electrolysis processes that use catalysts. This equipment collectively helps us understand catalyst performance in support of process design.

Fig. 8 shows the deNOx catalyst test apparatus. This apparatus, an original Kobe Steel design, is specially designed for evaluating a sample with a honeycomb-type catalyst of the same overall length as the actual deNOx catalyst. Our high-precision gas analyzer evaluates catalyst performance in the extremely low NOx concentration range unique to Kobe Steel and helps us optimize the operating conditions of the actual machine.

Catalytic reaction processes generally occur at high temperatures and involve process gas with harmful constituents that cause catalyst degradation (i.e., reduced reactivity). Therefore, catalyst evaluation necessitates spectroscopic analysis and surface observation to achieve an understanding of how catalyst properties change as well as the mechanisms behind deterioration. **Fig. 9** shows SEM (scanning electron microscope) imaging and EDX (energy dispersive X-ray) analysis of a deNOx catalyst whose performance had deteriorated after a period of use in the exhaust gas deNOx system of a thermal power plant.[12)] The surface of the catalyst is covered in a film of SiO_2-based deposits from coal combustion gas. The main cause of reduced performance was that this film inhibited the diffusion of gas from the surface of the catalyst to the interior. We subsequently developed a performance prediction model relating degradation of performance to the progression of deposition with time. **Fig.10** shows the estimated and measured change in the reaction rate coefficient across a given period of catalyst use (number of hours omitted).[12)] The estimated values correlate strongly with the measured values; therefore, this model makes it possible to predict catalyst life (years of use before reaching the lower performance limit). Kobe Steel's catalyst replacement system to identifies the appropriate time for catalyst replacement at the Kobe Power Plant, reducing operating costs and enabling stable deNOx equipment operation.

Table 1 Kobe Steel's evaluation technologies and testing apparatuses for catalytic reactions

Category	Evaluation/Analysis	Apparatus	Application
Catalytic reaction analysis	-Evaluation of low-concentration DeNOx reaction -Modelling of catalyst lifetime Prediction	-Lab-scale test equipment for for selective catalytic reduction -4-column PSA test apparatus	DeNOx for powerplants and industries ・Analysis on effect of types of coal ・Catalyst performance
	-Evaluation of conversion and synthetic Reaction - CO_2 conversion - Hydrogen generation	-high temperature/high pressure catalyst test equipment	CCU (Carbon capture & Utilization) ・Methanation ・Reverse water gas shift reaction
Electrochemical reaction analysis	-Evaluation of electrolysis process efficiency - I-V characteristic - I-R characteristic	-Electrolytic process evaluation equipment	Water electrolysis process ・PEM (Polymer electrolyte membrane) electrolysis ・AEM (Anion exchange membrane) electrolysis

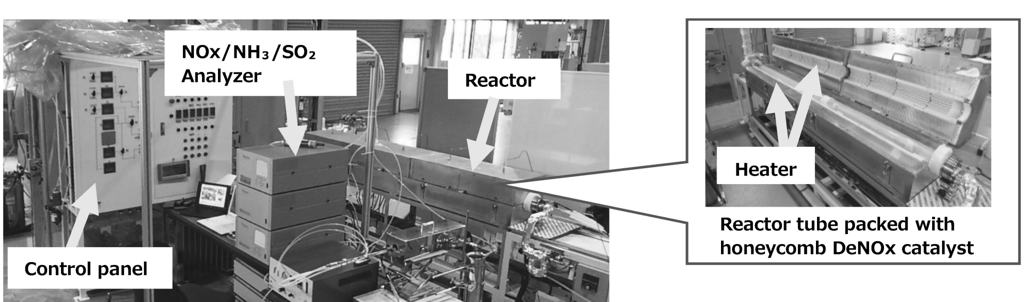


Fig. 8 Test apparatus for deNOx catalytic reaction

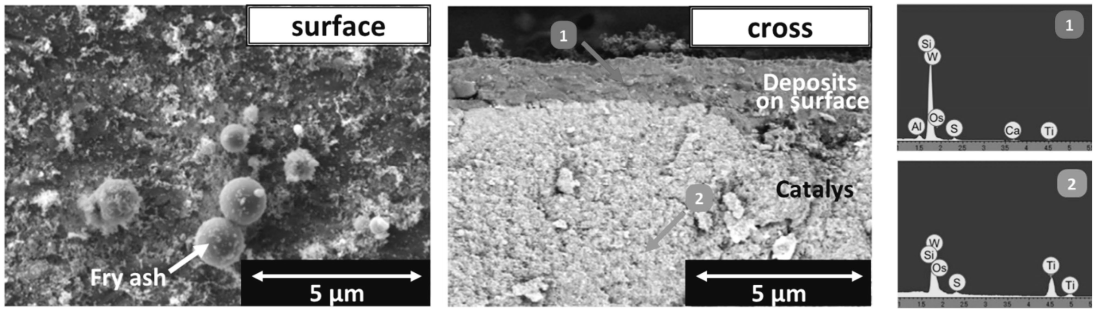


Fig. 9 Example of SEM images and EDX analysis on surface of degraded deNOx catalyst

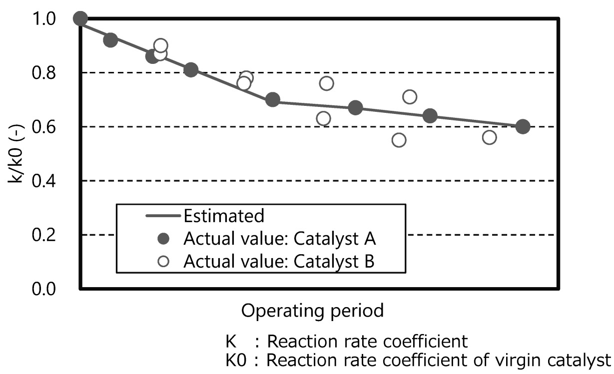


Fig.10 Change of reaction rate coefficient of deNOx catalyst with operating period

3. Future prospects

Adsorptive separation and catalytic reaction technologies will undoubtedly become increasingly important as efforts toward carbon neutrality and the circular economy (CE) accelerate.

Kobe Steel will develop unique products and processes that contribute to CN and CE and will use the foundational concepts and historical operating data related to these technologies to ensure a broad scope of application. In CCU in particular - an area undergoing technological progress all over the world - efficient separation and recovery of target components in the synthesis of C1 compounds (one-carbon; CO, methane, methanol, etc.) and olefins via CO_2 reduction are critical for overall efficiency and economic viability. Therefore, Kobe Steel's PSA technology, which features high purity and high recovery rates, will become even more widely used. In the 1990s, Kobelco Eco-Solutions Co., Ltd. released the number one hydrogen production system in Japan with the High-purity Hydrogen Oxygen Generator (HHOG). The company will use catalytic reaction evaluation technology to improve hydrogen production efficiency and the capacity of the HHOG and will foster development in renewable energy to support the growing need for green hydrogen produced by water electrolysis.[13), 14), 15)]

Even beyond these examples, we will continue to enhance the technologies we have developed in adsorptive separation and catalytic reactions and will seize business opportunities arising from the growing demand accompanying the progression of CN and CE.

Conclusions

The KOBELCO Group has been developing and releasing products and processes based on its core adsorptive separation and catalytic reaction technologies since the 1980s. This paper details only a sample of our endeavors in creating products and processes renowned among our customer base, including successes that occurred despite various changes such as operational restructuring.

As our everyday lives become intertwined with the global movements to recycle resources and reduce CO_2 emissions, it is increasingly apparent that technologies in both of these core areas will help us overcome these challenges and foster a safe, secure, and sustainable society. We will continue fortifying technologies in these areas and establishing products and businesses that will meet the needs of tomorrow.

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