Development of PSA Technology for the Separation of Carbon Dioxide from Blast Furnace Gas†

SAIMA Hitoshi[*1] MOGI Yasuhiro[*2] HARAOKA Takashi[*3]

Abstract:

Emission of carbon dioxide from steel makers accounts for 15% in Japan. Blast furnace gas is the main origin of carbon dioxide exhaustion. To reduce its exhausting amount, the pressure swing adsorption (PSA) separation technology is currently under development in JFE Steel. Based on the laboratory experiments, the bench scale plant with 3 tons per day capacity, which is called "ASCOA-3," was constructed in West Japan Works (Fukuyama) and the separation test with actual blast furnace gas was conducted in various conditions. The concept of gas separation technology utilizing PSA with unusually enormous scale was constructed base on these experimental results.

1. Introduction

Global warming caused by emissions of carbon dioxide (CO_2) is truly a problem that affects the entire planet. In responding to this problem, judgment must not waver due to temporary social conditions or temperature changes. Emissions of CO_2 in Japan are trending at 1.1–1.3 billion tons/year [1]. Of this amount, about 200 million tons, or 15%, is emitted by the iron and steel industry. The Japan Iron and Steel Federation is developing an environment-friendly steel manufacturing technology which will reduce CO_2 emissions by 30% by the year 2050 (abbreviated name: COURSE50, CO_2 Ultimate Reduction in Steel-making Process by Innovative Technology for Cool Earth 50) [2] with the support of New Energy and Industrial Technology Development Organization (NEDO) in Japan. As part of this effort, JFE Steel is engaged in research and development on a technology for separation of carbon dioxide from blast furnace gas in the steel works by the pressure swing adsorption (PSA) method.

The PSA method is a method in which a designated component in a pressurized mixed gas is selectively adsorbed using an adsorbent with high adsorptive power for a certain gas in mixed gas, and the designated component in the mixed gas is then recovered by reducing the gas pressure.

The PSA method is widely used as a process for producing high purity gases from mixed gases. In the JFE Group, it is applied to production of hydrogen from coke oven gas, production of carbon monoxide from converter gas, etc. However, these PSA processes are plants that produce high purity gases with high added value on a small to medium scale. Due to the high price of the gases produced by such processes, priority is given to product purity, and the costs of separation and recovery are not a major issue. Moreover, because demand for the product gases is limited, only medium-scale equipment of several 1 000 m^3/h class is constructed. On the other hand, if the purpose is to reduce emissions of CO_2, it is necessary to reduce costs as much as possible, as the separated and recovered CO_2 itself does not have any large value. For example, in order to separate/recover 20% of the CO_2 contained in blast furnace gas, gas separation/recovery equipment of 1 million m^3/h class (feedstock gas base) is necessary. A plant of this scale would be the world's largest PSA plant.

Based on many such issues, a PSA technology for the separation of CO_2 from blast furnace gas was developed. This report describes the history of development of this technology.

†Originally published in *JFE GIHO* No. 32 (Aug. 2013), p. 44–49

[*1]Dr. Eng.,
Senior Researcher General Manager,
Environmental Process Res. Dept.,
Steel Res. Lab.,
JFE Steel

[*2]Senior Researcher Manager,
Environmental Process Res. Dept.,
Steel Res. Lab.,
JFE Steel

[*3]Senior Researcher Deputy Manager,
Environmental Process Res. Dept.,
Steel Res. Lab.,
JFE Steel

Table 1 Evaluation of adsorbent with indexes

Adsorbent		Index A	Index B
Zeolite	ZEOLUM F-9HA (NaX)	29	8.8
	Mizuka Sieve (NaX)	15	1.6
	HSZ640NAD (Na-Mordenite)	11	0.7
Active carbon	Kurare Coal 2GA	15	1.8
	Turumi Coal HC-6	14	1.6
	NORIT RB4	14	1.7
	Seika Fine CO_2X	13	1.6
	NORIT R4	13	1.7
	Kurare Coal 2GG	12	1.8
	DARCOVAPURE	11	1.6
	Turumi Coal 4GM	10	1.7
	Turumi Coal AX	10	2.6
	HYDRODARCO	10	1.8

2. Laboratory-Scale Study

2.1 Selection of Adsorbent

In the PSA method, an important point is the quality of the adsorbent used. Therefore, as the first step in development, 11 types of adsorbents which were thought to be effective for separating CO_2 were selected from among adsorbents on the market. The adsorption isotherms for each of the four main components (carbon dioxide, carbon monoxide, nitrogen, hydrogen) of blast furnace gas were measured, and the following two indexes were calculated and evaluated. Index A is defined as the difference between the amount of CO_2 adsorbed in the PSA adsorption process and the amount remaining in the adsorbent in the desorption process; this index is called the "working capacity". Index B is an index showing the selectivity of the adsorbent by the ratio of Index A and the amount of adsorption of the gases other than CO_2 (i.e., nitrogen, carbon monoxide, and hydrogen). **Table 1** shows the calculated results of these two indexes for various adsorbents. As is clear from Table 1, among these adsorbents, ZEOLUM F-9HA is the most suitable adsorbent in both indexes.

Therefore, PSA tests were conducted at the laboratory scale using ZEOLUM F-9HA.

2.2 Laboratory-Scale PSA Test

The laboratory-scale PSA test apparatus is shown in **Photo 1**. The inner diameter of the adsorption tower is 40 mm, and its length is 500 mm. Approximately 400 g of adsorbent was filled up in the adsorption tower, and a separation test was conducted by supplying a gas simulating blast furnace gas to the test apparatus. The simulated gas was a mixed gas consisting of pure gases of CO_2 (22%), carbon monoxide (21%), nitrogen (54%), and hydrogen (3%).

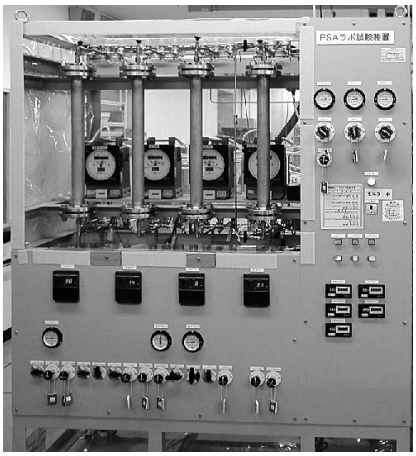

Photo 1 Laboratory pressure swing adsorption (PSA) apparatus

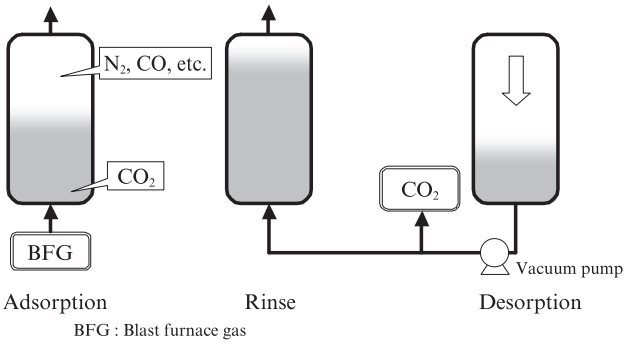

Fig. 1 Separation process with pressure swing adsorption (PSA)

In the laboratory-scale PSA test, as shown in **Fig. 1**, the gas was separated by three processes, namely, an adsorption process, rinsing process, and desorption process. In the adsorption process, the above-mentioned simulated gas was passed through the tower at the specified pressure and adsorbed. In this stage, the CO_2 in the adsorption tower is only concentrated to about 70%. In the following rinsing process, the pressure is released to normal pressure, and high purity CO_2 is passed through the tower. This increases the purity of the carbon dioxide gas in the adsorption tower by purging impurities such as nitrogen, etc. In the final desorption process, the adsorption tower is evacuated, and high purity CO_2 is recovered. Some of this gas is also used in the rinsing process.

The key points here are the pressure in the adsorption process, the rinsing time in the rinsing process, the degree of depressurization in the desorption process, and the time of the total process (hereinafter, referred to as "cycle time"). **Figure 2** shows the results of a gas separation test with the laboratory-scale PSA apparatus at an adsorption pressure of 200 kPa, desorption pressure of 7 kPa, and cycle time of 630 s. In Fig. 2, the relationship between the CO_2 recovery rate and CO_2 purity was investigated by changing the rinsing time. The CO_2 recovery rate is defined as the value obtained by divid-

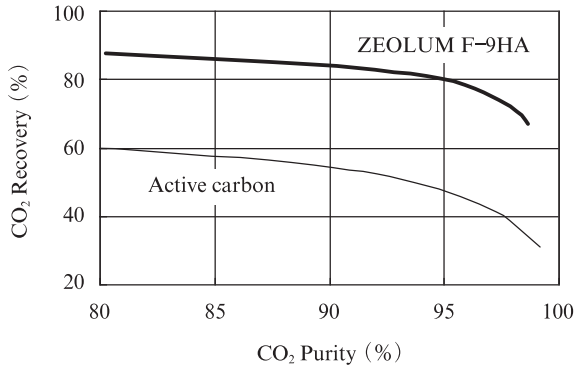

Fig. 2 Results of separation test

ing the amount of recovered CO_2 by the amount of CO_2 in the raw gas.

The target of the project is a CO_2 recovery rate of 80% or higher and CO_2 purity of 90% or higher. It can be understood that the results of the laboratory PSA using the ZEOLUM F-9HA achieved this target in all cases.

Figure 2 also shows the results of a separation test using active carbon. ZEOLUM F-9HA demonstrated higher separation performance.

Based on the results of the laboratory-scale PSA test, it was found that CO_2 can be separated and recovered with high purity.

On the other hand, the cost of CO_2 recovery by the process described above was estimated at approximately ¥ 4 000 per 1 t of CO_2. The target for the recovery cost was ¥ 2 000 per 1 t of CO_2 (guideline of Ministry of Economy, Trade and Industry). Therefore, a study was carried out with the aim of reducing this cost.

2.3 Study on Reduction of CO_2 Recovery Cost

The above-mentioned cycle time (630 s) was presumably set on the long side in order to obtain high purity gas stably with a purity of 99.9%–99.999%. However, as the target of the present research, a high purity product gas is not necessary. Therefore, shortening of the cycle time was studied. **Figure 3** shows the results of separation with cycle times of 300–720 s. Absolutely no difference in separation performance could be observed with cycle times in the range of 450–720 s. When the cycle time was shortened to 300 s, separation performance decreased slightly. In Fig. 3, the difference in separation performance is more emphasized because the minimum scale for purity was expanded to 1%. Therefore, the separation performance at 300 s is not considered to differ greatly from the other results. On the other hand, if the cycle time is shortened from 630 s to 300 s, more than twice as much gas can be separated with the same scale plant. Assuming there are no other effects, this means that the construction cost per unit of CO_2 recovery can be reduced by more than half.

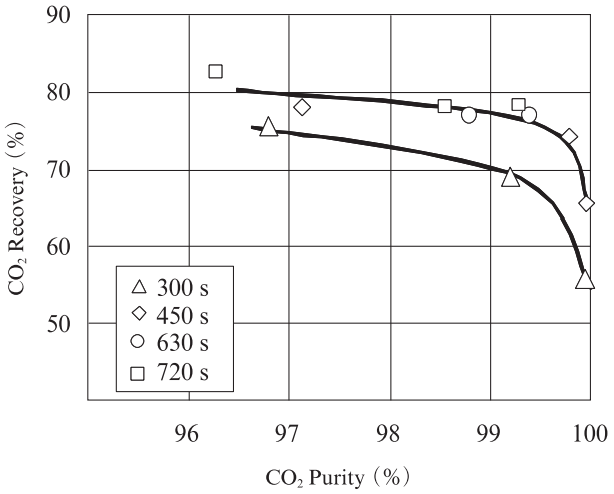

Fig. 3 Effect of cycle time

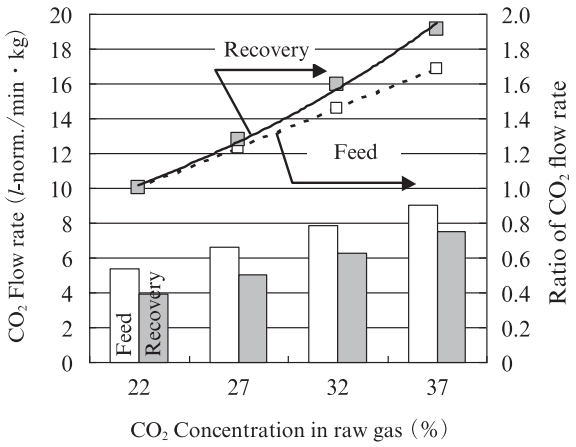

Fig. 4 Effect of CO_2 concentration

Up to this point, the tests were performed assuming the concentration of CO_2 in blast furnace gas is 22%. However, it is predicted that the concentration of CO_2 will be higher in 2050, when COURSE50 technology is to be applied. Therefore, the effect of the CO_2 concentration was also investigated. **Figure 4** shows the test results. Because the total feed amount of raw gas is constant, the feed amount of CO_2 increases with CO_2 concentration. Accompanying this, the amount of recovered CO_2 also increases. The right-hand axis in Fig. 4 shows the amounts of CO_2 feed and recovery at various CO_2 concentrations, where feed and recovery at a concentration of 22% are each 1. For example, in case the concentration of CO_2 in the raw gas is 32%, the CO_2 feed increases by more than 1.4 times, and CO_2 recovery increases by approximately 1.6 times. Moreover, if the concentration of CO_2 in the raw gas rises to 37%, CO_2 recovery increases to approximately twice.

The cost of recovering CO_2 was calculated based on these results, and the result proved to be quite close to the target. Therefore, a bench-scale plant was constructed, and a further study was conducted.

3. Study with "ASCOA-3"

3.1 Outline of "ASCOA-3"

As a bench-scale plant which provides an image of a large-scale plant, "ASCOA-3" (Advanced Separation System by Carbon Oxides Adsorption 3 Tons/Day) with a CO_2 recovery capacity of 3 tons/day was constructed at JFE Steel's West Japan Works (Fukuyama). A bird view of "ASCOA-3" is shown in **Photo 2**, and a flow diagram is shown in **Fig. 5**. The actual blast furnace gas introduced into the "ASCOA-3" is first pressurized by the compressor, after which the moisture content is reduced by cooling in a gas cooler. It is possible to dry the gas to a dew point of –60°C by using the dehumidifier, which is packed with silica gel and alumina gel. This dried gas is then introduced into the CO_2 adsorption tower, which is the heart of the system. The CO_2 adsorption tower, as shown in **Photo 3**, comprises 3 towers with an inner diameter of 750 mm and height of 1 200 mm. Each of the towers repeatedly performs the sequence of processes of adsorption, rinsing, and desorption. The off-gas from the adsorption process and rinsing process (i.e., gas discharged from the adsorption tower) is stored in an intermediate tank (buffer tank), and is sent to the carbon monoxide adsorption tower, which was constructed for the purpose of recovering flammable gas (for use as fuel gas). On the other hand, the amount and purity of the CO_2 recovered in the desorption process are measured at the CO_2 tank. The separated gas is then mixed again at the mixing tank and returned to the blast furnace gas main. Among the CO_2 adsorption towers, one tower (Tower A) is equipped with 11 resistance thermometers, as can be seen in Photo 3, making it possible to determine the detailed temperature distribution and swing condition.

Photo 2 Bird view of "ASCOA-3"

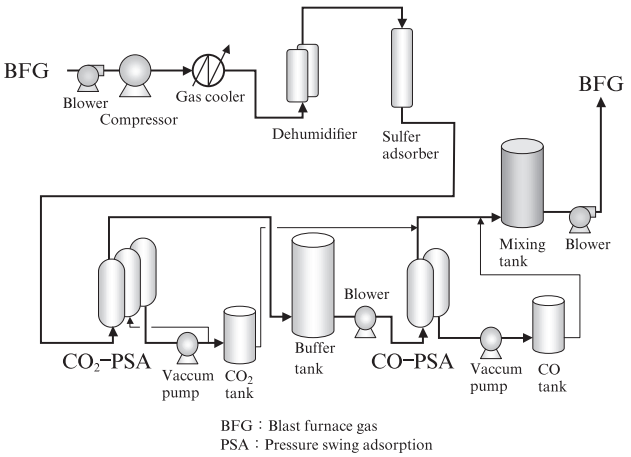

Fig. 5 Flow diagram of "ASCOA-3"

Photo 3 Adsorption Towers of "ASCOA-3"

3.2 Unit Trial Operation of "ASCOA-3"

"ASCOA-3" was completed in February 2011, and test operation was carried out over a period of about one month. The test operation results are shown in **Fig. 6**. Smooth trends were observed in the amount of CO_2 recovery, CO_2 recovery rate, and CO_2 purity, and all targets were achieved, demonstrating that "ASCOA-3" is a system with an ample CO_2 separation/recovery capacity.

3.3 Study of Separation Conditions with "ASCOA-3"

In PSA, electric power is the largest variable cost factor. In particular, in CO_2 PSA systems which use a vacuum pump in the desorption process, the unit power

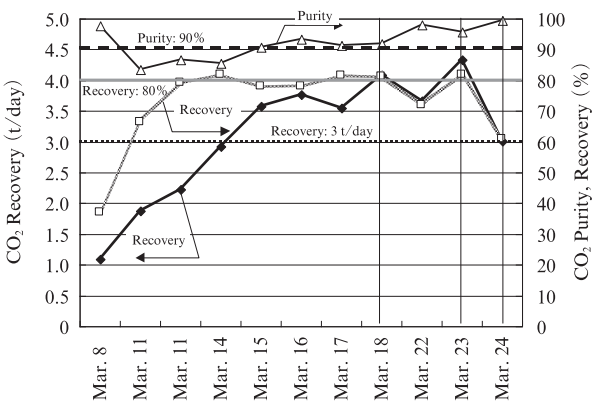

Fig. 6 Test operation results of "ASCOA-3"

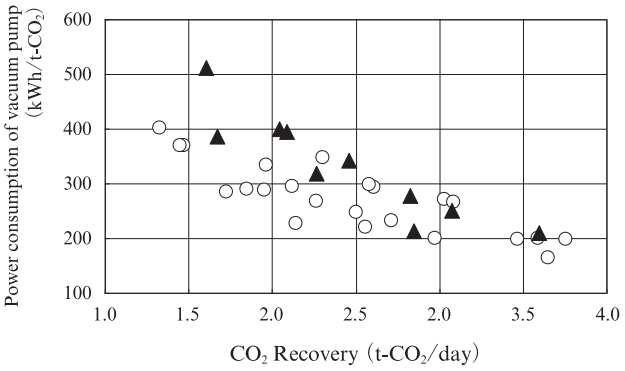

Fig. 7 Power consumption of vacuum pump

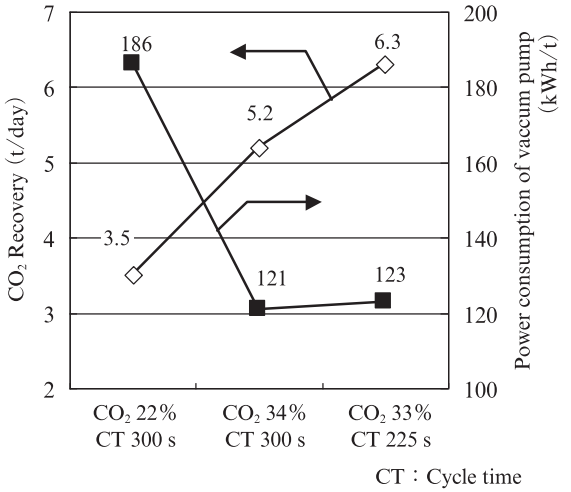

Fig. 8 CO_2 Recovery and power consumption

consumption of the vacuum pump affects the total cost. Therefore, a wattmeter was installed on the vacuum pump in "ASCOA-3" and the unit power consumption of the pump was investigated under various separation conditions. The results are shown in **Fig. 7**. Although Fig. 7 includes the results for various conditions, it became clear that the unit power consumption of the vacuum pump decreases when the amount of CO_2 recovery is large. The plots shown by black triangles (▲) in Fig. 7 are for a condition of low adsorption pressure (50 kPa). However, in this case as well, it can be understood that unit power consumption by the vacuum pump can be held to a low level by increasing the amount of CO_2 recovery. In case the adsorption pressure is reduced to 50 kPa, it becomes possible to use a low power consumption blower to increase the pressure of the raw gas. It is estimated that a further cost reduction can be achieved by this method.

The tests up to this point were carried out with blast furnace gas of the as-delivered gas composition. However, as discussed previously, the concentration of CO_2 in blast furnace gas will presumably increase in the future. Therefore, separation tests were also carried out with blast furnace gas with the CO_2 concentration

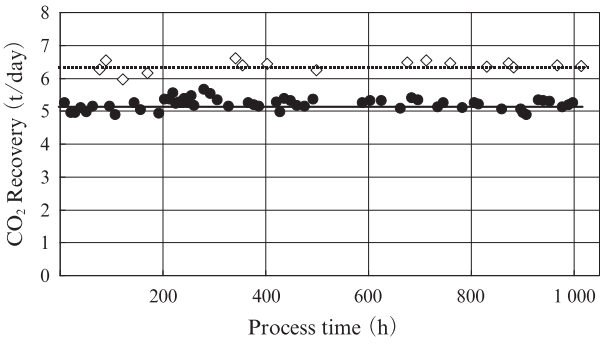

Fig. 9 Life time test

enriched to 33–35% by recirculating/mixing recovered CO_2 in the raw blast furnace gas. The results are shown in **Fig. 8**. When the CO_2 concentration was increased to 33%, the amount of CO_2 recovery increased to 5.2 t/day, and as a result, the unit power consumption of the vacuum pump decreased substantially, from the previous 180 kWh/t-CO_2 to 120 kWh/t-CO_2. Here, when the cycle time was shortened to 225 s, the unit power consumption of the vacuum pump was basically the same, but it was found the amount of CO_2 recovery increased to 6.3 t/day.

3.4 Life Time Test of "ASCOA-3" under Optimum Conditions

With "ASCOA-3," the raw blast furnace gas is dehumidified to the dew point of –60°C. This is done because the zeolite absorbent has poor resistance to water. In a preliminary laboratory test, it was found that the performance of the adsorbent does not deteriorate within the order of 24 hours, if the dew point of the raw gas is 0°C or lower. Therefore, a 1 000 hours life time test was carried out with "ASCOA-3" with the dew point of the raw gas raised to –30°C. As conditions in this test, the CO_2 concentration of the blast furnace gas was adjusted to 33–35%, the adsorption pressure has held constant at 50 kPa, and the two cycle time conditions were used alternately, these being 300 s (5 t/day condition) and 225 s (6 t/day condition). The results are shown in **Fig. 9**. As is clear from this figure, the amount of CO_2 recovery was stable under both conditions, and a life time of 1 000 hours was achieved.

4. Construction of Image of Actual System

4.1 Study of Adsorption Tower

An image of an actual system was constructed based on the results obtained with "ASCOA-3." As discussed in Section 3.1, "ASCOA-3" was equipped with a large number of resistance thermometers, which were used to measure the temperature distribution in an adsorption tower. Among these resistance thermometers, it was

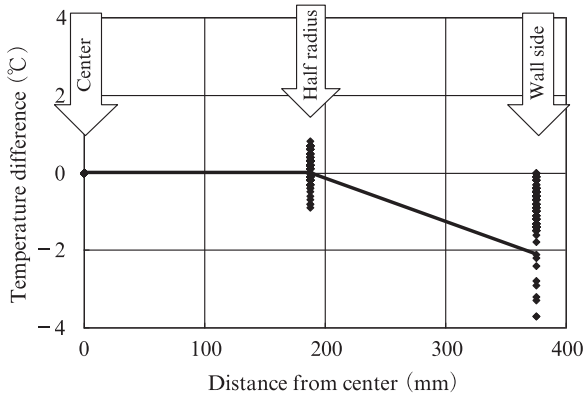

Fig. 10 Temperature difference

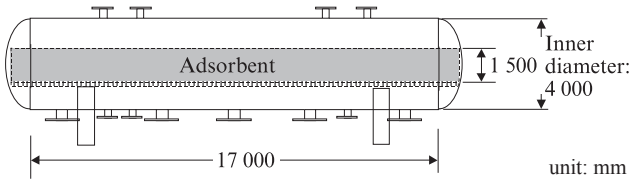

Fig. 11 Design of commercial adsorption tower

found that the temperature in the horizontal direction is approximately consistent, as shown in **Fig. 10**. Because the temperature in the adsorption tower shows the adsorption and desorption behavior of the carbon dioxide, the fact that the temperature is basically uniform in the horizontal direction indicates that the adsorption and desorption behavior of CO_2 is also the same in a horizontal plane. In other words, even if the adsorption tower is greatly up-scaled in the horizontal direction, the larger unit will display the same CO_2 adsorption/desorption behavior, and uniform performance can be maintained. Therefore, as an actual adsorption tower, a bullet tank-shaped adsorption tower was designed, as shown in **Fig. 11**. Considering future improvements, the height of the adsorbent layer was set at 1.5 m, which is slightly larger than that of "ASCOA-3." The ratio of feed gas and adsorbent was the same as in "ASCOA-3." As a result, the adsorption tower is a bullet tank-shaped structure having a diameter of 4 m and a length of 17 m, and one unit is filled with 65 t of adsorbent. Based on the test results with "ASCOA-3," 500 000 t/year-CO_2 can be recovered.

4.2 Construction of Image of Total Process

The image of the total process of a commercial PSA system was studied. The results are shown in **Fig. 12**. The supplied blast furnace gas (270 000 m^3-norm./h on dry gas base) is dedusted and cooled with cold water, and moisture is removed to a dew point of –30°C by a rotary-type desiccant dehumidifier. The gas is then sent

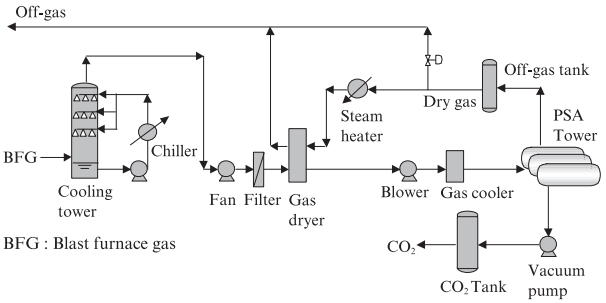

Fig. 12 Flow diagram of commercial plant

to the adsorption tower (PSA unit). Carbon dioxide is recovered by means of a vacuum pump and temporarily stored in a buffer tank. Part of the adsorbed off-gas and rinsed off-gas is used in the desiccant regeneration process, taking advantage of the low dew point of these gases. Because these off-gases have a higher heating value than blast furnace gas, effective utilization as fuel gas is possible.

The CO_2 recovery cost was estimated based on the test results with "ASCOA-3" and the results of construction of the image of the actual system to this point. From rough estimates for each equipment item, the construction cost for a 1-million-tons/year plant (equivalent to 2 PSA lines) was estimated at ¥ 7 billion. The power consumption of the vacuum pump and other equipment and steam for regeneration of the desiccant dehumidifier were also estimated from the image outlined above, and it was found that the target of ¥ 2 000 per 1 t of CO_2 can be achieved.

5. Conclusion

Initially, it appeared to be very difficult to achieve the CO_2 recovery cost target. However, as a result of repeated research and development, it was possible to achieve the original target. When this paper is published, the next phase of this project will already have begun, and the plan will be in the period of research and development aiming at practical use. Although the ultimate target of the COURSE50 Project is practical application by 2050, the authors hope to further accelerate research and development of the PSA separation technology for blast furnace gas so as to enable earlier practical use.

References

1) Center for Global Environmental Research. National Institute for Environmental Studies, Japan. National Greenhouse Gas Inventory Report of Japan. 2012-04.
2) The Japan Iron and Steel Federation. http://www.jisf.or.jp/course50/index_en.html