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The downsizing of a TSA system for an air purification unit using a high flow rate method

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Abstract A high flow rate type air purification unit to reduce the size of adsorption vessel was developed. The setting area of air purification unit and the cost of adsorption vessel were reduced to 65% and 70% respectively. The downsizing was achieved by the way that a mass transfer zone (MTZ) was formed in the whole region of adsorbent layer and by the development of adsorbent for the high flow rate process. As regards the adsorbent, the adsorption performance to realize the process was investigated. Then the adsorbent which has larger size and higher adsorption performance was developed and TSA process experiment was carried out. As the result, the realization of the high flow rate process was made sure experimentally.

Keywords Adsorption · TSA · MTZ · Air · Purification · NaX · Carbon dioxide

1 Introduction

The air purification unit to remove impurities such as water vapor (H_2O) and carbon dioxide (CO_2) included in atmosphere is essential in a cryogenic air separation plant. The industrial gases such as oxygen, nitrogen and argon are produced by the plant and these gases are separated from air by distillation of liquid air. Before distillation, feed air is cooled to low temperature and liquefied. However, if feed air is cooled without air purification, the impurities solidify and plug the passages in equipments. Therefore, before cooling feed air an air purification unit is widely installed. In most case, Thermal Swing Adsorption (TSA) process is used as an air purification method. In a typical air purification TSA unit, the adsorption vessel is packed with layers of two different adsorbents, with activated alumina to remove H_2O in the upstream side of the adsorption vessel, and NaX type zeolite to remove CO_2 in the downstream side of the adsorption vessel. There are a large number of reports on a layered bed process (Kumar et al. 2003; Fujita and Nakamura 1997; Ahn and Lee 2003).

In this study, a high flow rate type air purification unit to reduce the size of an adsorption vessel was developed using a new process and adsorbent developed for the process. Recently, downsizing of the plant has become necessary with increasing of demand for a large scale cryogenic air separation plant. The setting area of an air purification unit becomes larger with increasing of the volume of feed air. Then the downsizing of an air purification unit is strongly required. In order to downsize an adsorption vessel, improvement of an amount of CO_2 adsorption was studied by many researchers. Although the improvement can make shorter the height of adsorbent layer, it doesn't lead to decrease cross-sectional area of an adsorption vessel. Another way to downsize an adsorption vessel is to adopt short cycle time method, it is to make amount of feed air per cycle decreased and packed amount of an adsorbent decreased. But this method doesn't also lead to decrease cross-sectional area of an adsorption vessel.

2 Theory

2.1 Process for high flow rate

In order to downsize cross-sectional area of an adsorption vessel, higher flow rate was the first consideration. The

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higher flow rate can make smaller vessel diameter. But it also means that length z_a of a MTZ extends so as to be clear from (1) (Takeuchi 2003) and height of adsorbent layer increases. This leads to increase of amount of adsorbent and amount of heat for regeneration. As a result, it leads to increase of initial cost and running cost.

$$z_a = \frac{u}{K_F a_V} \times \int_{C_B}^{C_E} \frac{dc}{(C - C^*)} \tag{1}$$

where z_a is length of MTZ, u is flow rate, $K_F a_V$ is overall mass transfer coefficient, and C is concentration. Therefore, to solve the problem the application of the following method was studied.

Application of short cycle time. Although amount of feed air per time increased by the high flow rate process, it becomes possible to decrease amount of feed air per cycle by short cycle time. Then decrease of amount of adsorbent was planned.

Application of new adsorption operation method. Conventional adsorption vessel is designed by the way of thinking that CO_2 adsorption distribution in the vessel consists of an adsorption equilibrium part and a MTZ part. To make shorter height of adsorbent layer, short MTZ and higher effective utilization rate of adsorbent layer are important ideas. However, in high flow rate process, an adsorption equilibrium part may not always exist on the assumption that MTZ must become long. In short the adsorption operation method that whole height of adsorbent layer becomes MTZ was applied.

2.2 Adsorbent for a high flow rate process

It is hard to realize a high flow rate system by means of the change of process only. So, adsorbent for exclusive use of a high flow rate process was produced. Beforehand, adsorption characteristics necessary for realization of the process were examined, and the adsorbent was produced according to the result.

Large particle diameter adsorbent. In case that a high flow rate process is applied using conventional adsorbent, fluidization of adsorbent is worrying. Therefore it is necessary to make particle diameter of adsorbent larger in order to prevent the fluidization. However, it is important to choose proper diameter within the range of no fluidization, because an increase of particle diameter causes deterioration of kinetic performance.

So the diameter of adsorbent within the range of no fluidization was evaluated. A fluidization of adsorbent in packed bed begin when a value of a pressure drop of adsorbent layer $\Delta P/L$ becomes equivalent to the packed density of adsorbent γ. By using this equation, relationship between flow rate and fluidization particle diameter can be calculated. Here, the calculation of a pressure drop of adsorbent layer used the Ergun's equation (2) (Ergun 1952).

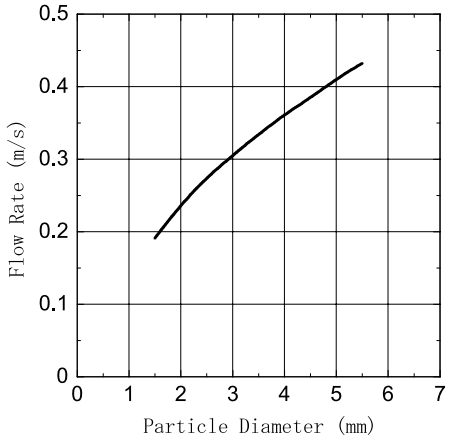

Fig. 1 Relation of particle diameter of adsorbent and flow rate to prevent fluidization

$$\frac{\Delta P}{L} = 150 \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} \cdot \frac{\mu \cdot u}{d_p^2} + 1.75 \cdot \frac{1-\varepsilon}{\varepsilon^3} \cdot \frac{\rho \cdot u^2}{d_p} \tag{2}$$

where ΔP is pressure drop, L is a length of adsorbent layer, ε is bed void fraction, μ is viscosity, u is flow rate, d_p is particle diameter, and ρ is density. In this calculation, bed void fraction ε of 0.4 and packed density of adsorbent γ of 630 kg/m^3 was used. The relationship between particle diameter of adsorbent and fluidization starting flow rate is shown Fig. 1. From this result, in case that flow rate of 0.4 m/s is selected, it turns out that it is necessary to make particle diameter of adsorbent more than 4.5 mm.

Improvement of adsorbent performance. A regeneration process includes a depressurizing step, a heating step, a cooling step and a pressurizing step. In case that a large amount of adsorbent is used, it is difficult to finish these steps within short cycle time. Therefore, it is necessary to improve the following adsorption performance in order that the amount of adsorbent become below some value.

1. By the application of the adsorption operation method in which a MTZ is formed in the whole region of adsorbent layer, the ratio of region contributed to CO_2 adsorption becomes smaller than that of conventional design. In the conventional design, adsorption layer consists of an adsorption equilibrium part and a MTZ part. Since it leads the increase of amount of adsorbent, it is necessary to increase CO_2 adsorption capacity.
2. As mentioned-above, the length of MTZ extends by a high flow rate method. Moreover, it also extends by making particle diameter of adsorbent larger. Because, according to (3) and (4) (Takeuchi 2003), value of intra-particle mass transfer coefficient and over all mass transfer coefficient decrease by making particle diameter of

adsorbent larger. An increase of over all mass transfer coefficient causes extension of MTZ by (1).

$$\frac{1}{K_F a_V} = \frac{1}{k_F a_V} + \frac{1}{\beta k_S a_V} \tag{3}$$

$$\beta k_S a_V = \frac{15 D_e (1-\varepsilon_p)}{r^2} \tag{4}$$

where $\beta k_S a_V$ is intraparticle mass transfer coefficient, $k_F a_V$ is fluid film mass transfer coefficient, D_e is effective diffusion coefficient, ε_p is porosity of adsorbent particle, and r is radius of adsorbent particle. Since the extension of MTZ leads to an increase of height of adsorbent layer, it is necessary to improve adsorption rate to make MTZ shorter.

Next, necessary adsorption performance was examined specifically. First of all, TSA having two layers of activated alumina and zeolite was considered. The following were assumed as an operating condition: an air flow rate: 0.4 m/s, a cycle time: 2 hour, an adsorption temperature: 298 K, an adsorption pressure: 550 kPaA, a CO_2 concentration: 400 ppm, a regeneration temperature: 323 K, amount of regeneration gas: 20% (ratio to feed air). Under the condition, a minimum amount of adsorbent with which the regeneration step finish within the cycle time was estimated by using the TSA process simulator, which developed on the basis of liner driving force model. As a result, in order to finish regeneration step within the cycle time, it is necessary to limit a height of adsorbent layer to be below about 1.0 m. Furthermore, necessary adsorption performances to realize high flow rate process were examined under the condition above mentioned. Equation (1) is transformed to (5) by assuming that the whole region of adsorbent layer Z becomes MTZ ($z_a = Z$).

$$Z = \frac{u}{K_F a_V} \times N_{OF} \tag{5}$$

$$N_{OF} = \int_{C_B}^{C_E} \frac{dc}{(C - C^*)} \tag{6}$$

where Z is height of adsorbent layer and N_{OF} is number of transfer units. A value of N_{OF} can be calculated from CO_2 adsorption isotherm in air (Takeuchi 2003). A value of $K_F a_V$ can be calculated from the result of break through experiment. As mentioned above, when it is assumed that height of adsorbent layer Z is less than 1.0 m and flow rate u is 0.4 m/s, adsorbent performance need to satisfy the condition of (7) to realize high flow rate process.

$$\frac{N_{OF}}{K_F a_V} < 2.5 \tag{7}$$

3 Experiments

The adsorbent for exclusive use of the high flow rate process, which is large size zeolite with spherical shape, was produced based on the above adsorption performance and the adsorption characteristic was evaluated. After that, TSA process examination is carried out and the realization of high flow rate process was made sure.

Adsorption isotherm for single component gases of CO_2 and N_2 was measured by the volumetric method. Measurements were performed in the pressure range of 0–2 kPaA and 0–1 MPaA, at 283 K, 293 K and 303 K. Prior to each measurement, the adsorbent was heated at 623 K for 2 hours in vacuum. From these results, amount of adsorption in binary mixture was estimated.

Break through curve was measured using a stainless column whose inner diameter and length were 0.0175 m and 1.0 m respectively. Measurement was performed under the condition of an adsorption temperature: 283 K, an adsorption pressure: 550 kPaA and a flow rate: 0.4 m/s. The feed gas, an air contained CO_2 of 400 ppm, which made by adding a small amount of CO_2 to a purification air from which H_2O and CO_2 were removed, was prepared. Prior to measurement, the adsorbent was heated at 623 K for 2 hours in a purification air flowing at 5 liters/min under atmospheric pressure. The CO_2 concentration of outlet gas was measured by an infrared CO_2 analyzer (Fuji Electric systems, Japan). By these result, adsorption amount and length of MTZ of CO_2 in gas mixture was estimated.

TSA process experiment was performed under the condition of flow rate: 0.4 m/s, adsorption pressure: 550 kPaA, adsorption temperature: 283 K, regeneration temperature: 323 K and amount of regeneration gas (product air): 20% (ratio to feed air). Bed diameter was 0.108 m, activated alumina for H_2O removal was packed 0.4 m at air inlet side and the newly developed zeolite for CO_2 removal was packed 0.9 m at the latter part. Packed height of the zeolite was decided on the basis of the result of break through measurement. Cyclic sequence is shown in Fig. 2.

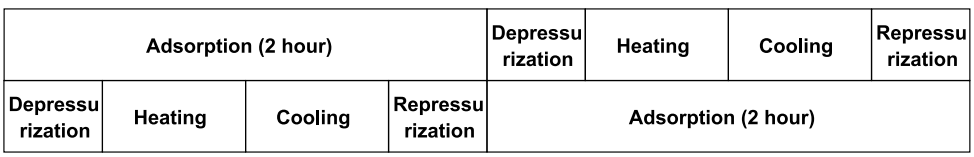

Fig. 2 Cyclic sequence in TSA process experimental

Fig. 3 Pictures of new adsorbent (*left*) and common 1/16 pellet adsorbent (*right*)

Table 1 DSL parameters in binary gas of CO_2 and N_2 on the adsorbent for high flow rate process

		CO_2	N_2
m_b	(mol/kg)	1.858	1.858
b_0	(1/kPa)	2.253×10^{-7}	2.588×10^{-7}
Q_b	(J/mol/K)	35579	20600
m_d	(mol/kg)	1.810	1.810
d_0	(1/kPa)	1.676×10^{-7}	7.175×10^{-7}
Q_d	(J/mol/K)	45754	18614

4 Results

4.1 characterization of the adsorbent

Picture of the adsorbent for a high flow rate process (large size zeolite) is shown in Fig. 3. For comparison, an adsorbent of general use (NaX) is also shown together. Particle diameter of adsorbent has distribution. Therefore, average particle diameter was calculated by measuring particle diameter of a thousand adsorbent at random sampling. The result was 4.7 mm. It was made sure to be satisfied the above condition, which particle diameter of adsorbent must be more than 4.5 mm.

In order to calculate value of N_{OF}, it is necessary to estimate an amount of CO_2 adsorption in air. So Dual-Site Langmuir (DSL) model shown by (8) was applied to the estimation (Mathias et al. 1996).

$$q_i = \frac{m_b b_i P y_i}{1 + \sum_{j=1}^{2} b_j P y_j} + \frac{m_d d_i P y_i}{1 + \sum_{j=1}^{2} d_j P y_j}$$
$$b_i = b_0 \exp\left(\frac{Q_b}{RT}\right), \qquad d_i = d_0 \exp\left(\frac{Q_d}{RT}\right) \tag{8}$$

Those parameters could be obtained from adsorption isotherms of single gas. The DSL parameters on the adsorbent are shown in Table 1. In this case, binary gas of CO_2 and N_2 was assumed. The experimental results of adsorption isotherms for single gas of CO_2 and the estimation result of CO_2 adsorption isotherm in binary gas of CO_2 and N_2 at 283 K are shown in Fig. 4. Adsorption isotherm for CO_2 on typical NaX type zeolite is also shown in Fig. 4. From the result, adsorption amount of CO_2 on the adsorbent for high flow rate process is much larger than that on typical NaX, and adsorption amount of CO_2 in mixed gas reduce under the influence of N_2. A calculation of N_{OF} was carried out using the estimation result of CO_2 adsorption isotherm in binary gas and (6). As the result, the value of N_{OF} became 9.4.

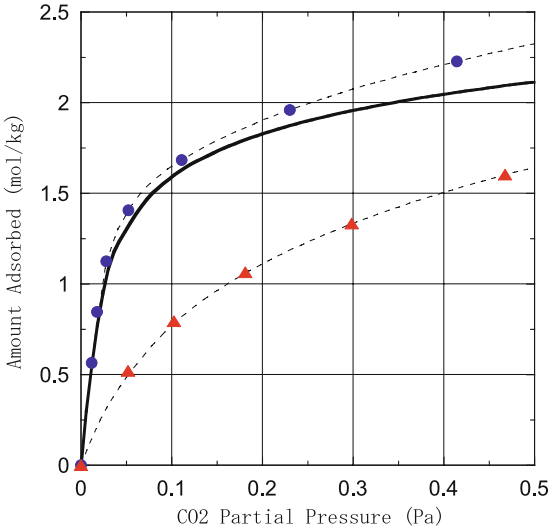

Fig. 4 CO_2 adsorption isotherms at 283 K; (●) single gas component on the new adsorbent; (*solid line*) mixed gas prediction on the new adsorbent by DSL model with the parameter given in Table 1; (▲) single gas component on typical NaX type zeolite

Table 2 The result of breakthrough measurement

t_b (min)	t_e (min)	z_a (m)	$K_F a_V$ (1/s)
251	654	0.89	4.2

Breakthrough curve measurement result of the adsorbent for a high flow rate process is shown in Table 2. Here, (9) was used in calculation of z_a (Takeuchi 2003).

$$z_a = Z \times \frac{t_E - t_B}{t_E - 0.5 \times (t_E - t_B)} \tag{9}$$

where t_E and t_B are breakthrough time and adsorption equilibrium time respectively. From this result, the value of z_a became 0.89. Moreover, the value of $K_F a_V$ was calculated using (1). The result became 4.2 ($u = 0.4$, $N_{OF} = 9.4$, $z_a = 0.89$).

Next, the condition of (7) was calculated using the above result. The result became 2.2 and it was made sure that it was satisfied the condition of (7).

4.2 Kinetic performance of the adsorbent for a high flow rate process

From (4), when a particle diameter of adsorbent becomes large, intraparticle mass transfer coefficient $\beta k_S a_V$ become small. However, the adsorbent doesn't cause extreme deterioration of mass transfer resistance. It seems that performance of effective diffusion coefficient D_e is improvement. Two factors can be considered for this. D_e is expressed (10).

$$D_e = D_p + \rho_s D_s \frac{\partial q}{\partial C} \tag{10}$$

where D_p is intraparticle pore diffusion coefficient, D_s is surface diffusion coefficient and ρ_s is adsorbent particle density. The right side first term of (10) is related to pore diffusion. Furthermore, in case of X type zeolite, D_p is expressed in the sum of molecular diffusion coefficient D_{AB} and Knudsen diffusion coefficient D_{KA} (Takeuchi 2003). D_{AB} don't depend on a sort of adsorbent. That is decided by adsorption condition. D_{KA} depend on pore diameter of adsorbent. Therefore, it seems that large pore diameter of the adsorbent is one of the reason of improvement of D_{KA}, namely D_e. The right side second term of (10) is related to amount of adsorption. As shown in Fig. 4, the amount of CO_2 adsorption of the adsorbent for high flow rate process is larger than that of general NaX. Therefore, it also seems that increasing of amount of CO_2 adsorption contributes improvement of D_e.

4.3 TSA process experiment

CO_2 concentration distribution of gas phase in adsorption bed was measured at the end of adsorption step in cyclic steady state. The result is shown in Fig. 5. A breakthrough of CO_2 wasn't detected in the top of bed within adsorption step.

Therefore it was made sure that high flow rate process realized. Moreover, the whole region of adsorbent layer became MTZ. From this result, it was made sure that the first prediction was valid.

4.4 The efficiency of high flow rate type TSA system

The efficiency of the high flow rate system was estimated on the basis of conventional air purification unit using a normal flow rate (∼0.2 m/s) and common NaX. Firstly, air purification unit of feed air 25 000 Nm^3/h was assumed. The vessel diameter in conventional design method is 3.1 m. By the application of high flow rate system, it has been possible to make double flow rate (∼0.4 m/s). As the result, the vessel diameter becomes 2.2 m, and then the cost of adsorption vessel is reduced to 70% compared with conventional one. Cross sectional area of adsorption vessel decrease to half by double flow rate. From this effect, the setting area of the TSA system including valve and pipe is reduced to 65% compared with conventional TSA system using a normal flow rate.

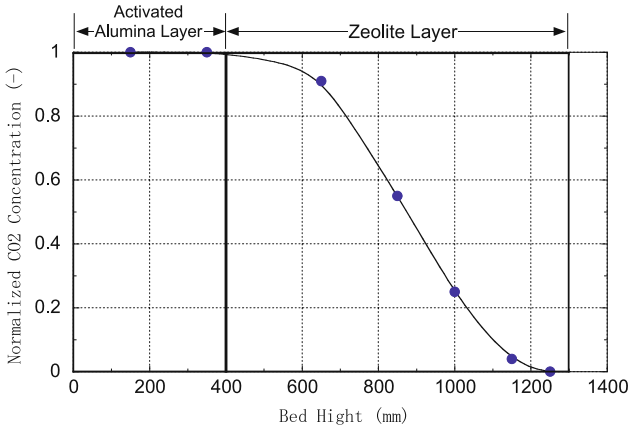

Fig. 5 CO_2 concentration distribution of gas phase in adsorption bed at the end of adsorption step

5 Conclusion

In this work, a high flow rate type air purification unit to reduce the size of adsorption vessel was developed. The efficiency of the new process was estimated. As the result, the setting area of air purification unit and the cost of adsorption vessel were reduced to 65% and 70% respectively. Thus, the downsizing of an air purification unit was achieved. It became possible by means of short cycle time, by the design method in which a MTZ is formed in the whole region of adsorbent layer, by the large diameter adsorbent and by the improvement of adsorbent performance. Thus it was possible to decrease cross-sectional area of an adsorption vessel.

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