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PRESSURE–TEMPERATURE-SWING PROCESS USING THREE ABSORPTION BEDS FOR HYDROGEN ISOTOPE SEPARATION

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ABSTRACT

Pressure–temperature-swing (PTS) process was comparatively investigated using one, two, or three columns packed with palladium particles. In the PTS process using the one or two columns, product was withdrawn from the system discontinuously. The deuterium enrichment ratio was lower in the one-column PTS process. In the three-column PTS process, a highly enriched product was recovered continuously. Back-filling another column and making pressure equilibrium with part of an exhaust that was slightly enriched in deuterium could enhance the enrichment ratio and recovery ratio of deuterium compared with the case of no back-filling or pressure-equilibrium operation.

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Key Words: Deuterium; Hydrogen isotope; Isotope separation; Palladium; Pressure-swing process; Temperature-swing process; Absorption; Tritium

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INTRODUCTION

Palladium dissociates molecules of hydrogen isotopes, i.e., protium, deuterium, and tritium and absorbs atoms of the hydrogen isotopes. When the hydrogen pressure is higher than a plateau pressure, it forms hydrides of PdH_x, PdD_x, and PdT_x ($x = 0.7-0.8$). The equilibrium isotope separation factor of the Pd hydride between protium and deuterium defined as $(D/H)_{gas}/(D/H)_{solid}$ is 1.9 at 303K and that between protium and tritium defined as $(T/H)_{gas}/(T/H)_{solid}$ is 2.7 at 303K.[1] Although the isotope separation factor of Pd is the maximum among all hydrogen-absorbing metals and alloys, there were few industrial applications to hydrogen isotope separation.

Natural hydrogen includes around 150 ppm deuterium. Commercial deuterium has been separated from the natural hydrogen by isotopic exchange reaction between water and hydrogen or hydrogen sulfide gas or from distillation of water or liquid hydrogen.[2] Any of these methods, however, was effectively operated only on a large scale, needed special catalysis, or cooling apparatus, and therefore, consumed large energy. Deuterium and tritium have been widely used as tracers in chemical or biotic experiments including NMR measurement or radiochemical analysis. Deuterium is also a coolant or moderator of heavy-water nuclear reactors operated worldwide. Recently, the two hydrogen isotopes are expected as the fuel of a fusion nuclear reactor. Consequently, there is still high demand on a laboratory scale of a hydrogen isotope separation apparatus.

We have investigated alternatives for the isotope-separation system using Pd or other metal hydrides, such as elution chromatography,[3] H_2-displacement chromatography,[4,5] self-displacement chromatography,[6] frontal chromatography,[7] simulated moving bed,[8] and interruptedly counter-current-extraction method.[9] These separation systems using metal hydrides have the following advantages of operation at around room temperature and normal pressure: (i) no use of corrosive gas such as hydrogen sulfide, therefore safe and easy to operate, (ii) a comparatively high hydrogen-isotope separation factor, (iii) no need of catalyst and a small apparatus.

Pressure-swing-adsorption (PSA) process using adsorbents is one of the most popular separation systems that have been utilized for gas separation in chemical industry, such as oxygen separation from air or recovery of hydrogen or methane from steam-reforming gas.[10–12] The hydrogen isotope separation by

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the pressure-swing (PS) process was also investigated using Pd[13] and V.[14,15] There was no difference in operation procedure between the PSA and the PS process. The only difference between the two was that hydrogen isotopes are not adsorbed on Pd but are absorbed in it. Unfortunately, some of the previous PS experiments showed that the enrichment ratio of deuterium or tritium in product was small compared with previous chromatographic methods or simulated moving-bed method.[4–8] This might be so because hydrogen is hardly desorbed only by reducing pressure under an isothermal or heatless condition. This means that the pressure-composition isotherm of the Pd-hydrogen and the Pd-deuterium systems are much preferable for hydrogen absorption around at room temperature that will be seen in the first figure in the next section. However, the PSA cycle still kept high interest because of the advantages of continuous separation and easy operation using a few columns. In the present study, we investigated the enrichment of deuterium in the product stream by means of a pressure–temperature-swing (PTS) process using one, two, or three columns packed with Pd particles. The column was back-filled with part of the exhaust gas in order to improve the recovery ratio and the enrichment ratio of deuterium.

PRESSURE–TEMPERATURE-SWING PROCESS

In the PS process, desorption of hydrogen from hydrogen-absorbing metals is made by reducing the column pressure from p_{abs} to p_{des} under a heatless condition or an isothermal condition. In the temperature-swing (TS) process, desorption can be accomplished by elevating the column temperature from T_{abs} to T_{des} under an isobaric condition. The PTS process is the combination of the PS and the TS processes, and desorption is performed by changing the column condition from (p_{abs}, T_{abs}) of higher pressure and lower temperature to (p_{des}, T_{des}) of lower pressure and higher temperature. Figure 1 shows the pressure-composition (P-C) isotherm of the Pd-hydrogen system. The P-C isotherm was much different from adsorption isotherms of zeolite or silica gel. Characteristics of the P-C isotherm are that there is a wide plateau region, i.e., pressure constant region, and the isotherm is much preferable for hydrogen absorption at lower temperature. On the contrary, the equilibrium isotope separation factor between protium and deuterium decreased with an increase in temperature.[1] Therefore, the PTS process of absorption at lower temperature and desorption at higher temperature was selected for the hydrogen-isotope separation in the present study. An advantage of PTS is potentially higher enrichment in product because sufficient desorption can be made by heating columns and reducing pressure. One disadvantage is that desorption by heating consumes more time and energy than the PS process. In order to perform PTS effectively, a separation system using three columns was investigated here.

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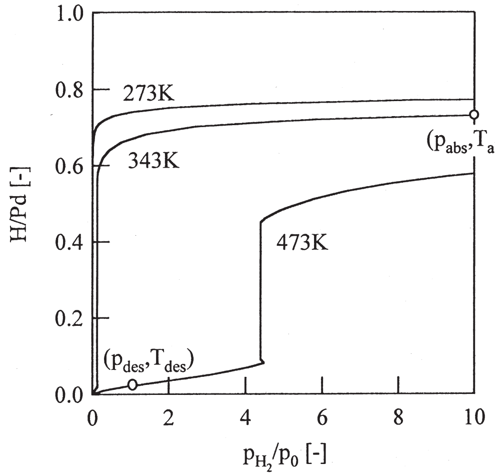

Figure 1. Pressure–composition isotherm of the Pd-hydrogen system. p_{H_2} is hydrogen pressure, p_0 is atmospheric pressure, and H/Pd is the atomic ratio of H to Pd.

One cycle of the present PTS process using three columns comprises five steps of pressurization, product-withdraw, back-filling, pressure equilibrium, and desorption by heating and cool-down. These steps are shown in Fig. 2. Each of the steps was performed as follows:

(a) *Pressurization step*: The column pressure is raised from p_{des} to p_{abs} by supply of process gas through the bottom-end valve under a constant flow rate. Two exhausts from another column in the back-filling step and the pressure-equilibrium step are used for pressurization. The column temperature is kept almost constant at T_{abs} throughout this step. Temperature rise by absorption heat was negligibly small in the present study.

(b) *Product-withdraw step*: When the column pressure has reached p_{abs}, the top-end valve is opened and a product gas is withdrawn from the top. The time of the product-withdraw step is $t_{product}$.

(c) *Back-fill step*: When time reached $t_{product}$, part of the product gas is used to back-fill another column keeping a constant flow rate of feed gas. This is because the deuterium concentration in the exhaust after the product-withdraw step is slightly higher than that of the feed gas. The time of the back-fill step is $t_{backfill}$. The direction of the flow in the back-fill step will be discussed later. The pressure of the back-fill gas is atmospheric one.

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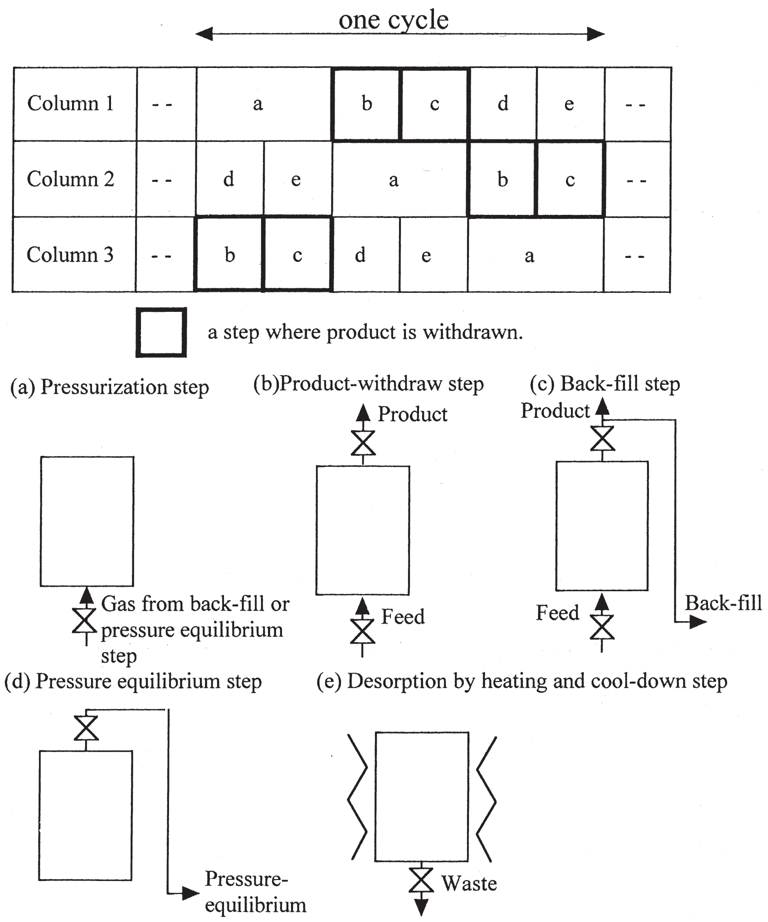

Figure 2. Operation program for three-column PTS process.

(d) *Pressure-equilibrium step*: While keeping open the top-end valve after stopping the feed from the bottom, hydrogen isotopes remaining in the column and absorbed in Pd are partly exhausted by blow-down from p_{abs} to equilibrium pressure. The exhausted gas is supplied to pressurize another column. The equilibrium pressure depends on the material balance of hydrogen isotopes between the connected two columns. The column temperature is still T_{abs}.

(e) *Desorption by heating and cool-down step*: The column is heated up to specified desorption temperature (T_{des}) under vacuum or

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atmospheric pressure (p_0) to desorb hydrogen isotopes still remaining in the column. The desorbed gas is exhausted as a waste. After the desorption, all valves are closed, and the column temperature is cooled down from T_{des} to T_{abs}. The time of desorption by heating and cool-down step is t_{waste}.

In the three-column PTS process, any one of the columns is always fed with a hydrogen-isotope mixture to be separated, and a product is withdrawn from another column continuously.

EXPERIMENTAL

Apparatus

Figure 3 shows a schematic diagram of the experimental apparatus for the three-column PTS process. The apparatus consists of three mass-flow controllers, two pressure gauges, three columns, a rotary pump, a hydrogen–deuterium gas cylinder, and a thermal conduction detector (TCD). The mass-flow controllers could regulate a flow to a constant flow rate between 5 and 500 mL (NTP)/min. The accuracy of the flow rate was ±1%. The two pressure gauges in different ranges could measure the pressure at the column outlet within ±1%. The columns were made of SUS 304, 700 mm in height and 3.00 mm in inner diameter. The packed amount of Pd particles per each column was 10.00 g. The average diameter of the Pd particles was 350 μm. The rotary pump was used to evacuate the column during Pd activation before the PTS experiment. The deuterium composition of the feed gas was 0.050 in atomic molar fraction, and the rest (0.950) is balance gas of protium. The atomic molar fraction is defined as follows:

$$x_D = \frac{2p_{D_2} + p_{HD}}{2p_{H_2} + p_{HD} + 2p_{D_2}} \tag{1}$$

where, x_D: deuterium atomic molar fraction; p_i: hydrogen isotope partial pressure ($i = H_2$, HD, D_2).

Since the gas mixture after passing the Pd column was always under the isotopic equilibrium of $H_2 + D_2 = 2HD$ in a similar way to our previous studies,[16,17] the outlet deuterium concentration was correlated in terms of the atomic molar fraction throughout our present study. This means that the hydrogen absorption rate was very fast and the hydrogen isotope separation was always under the equilibrium condition. The TCD was used to detect the deuterium concentration in the product stream continuously.

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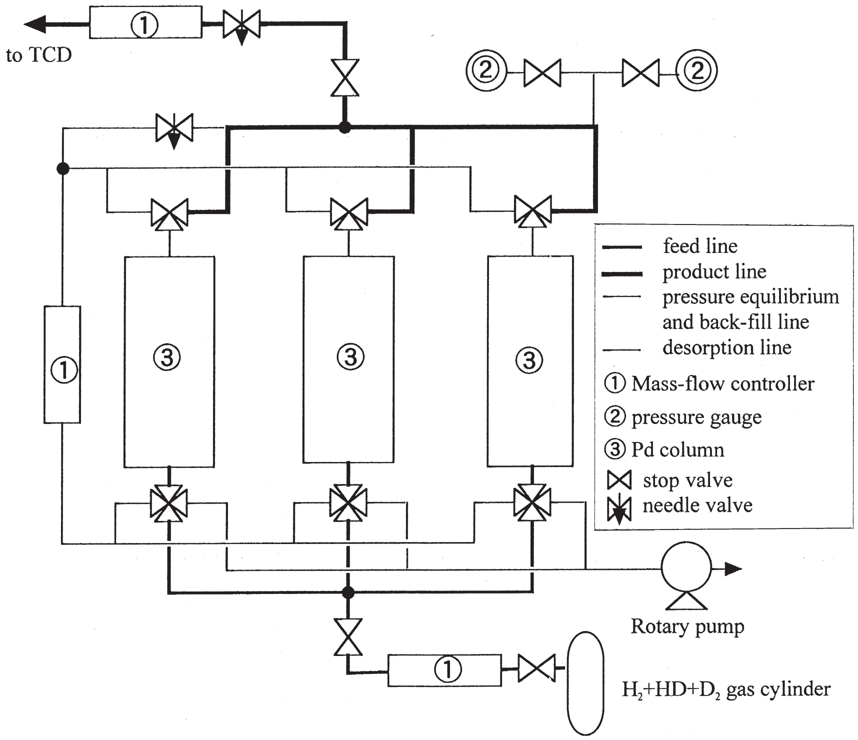

Figure 3. A schematic diagram of the experimental apparatus for three-column PTS process.

Activation

Before the enrichment experiment, the columns were heated up to 473K by the electric furnace under vacuum to desorb all impurities and hydrogen isotopes in particles. The columns were then cooled down to a specified experimental absorbing temperature, and the temperature was kept constant for about an hour. After the column temperature became a steady state, the PTS cycle was performed in the order of the pressurization, product-withdraw, back-fill, pressure-equilibrium, and desorption by heating and cool-down steps. The cycle was repeated.

Experimental Conditions

Optimum conditions of the temperature and pressure, the cycle time and the flow rate were determined by preliminary experiment using one-column PS and

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PTS processes. Temperature at absorption or desorption was a key factor for deuterium enrichment. For the hydrogen desorption, it was necessary to heat the Pd particles over the plateau pressures of the Pd hydride. So, the desorption temperature of 473K was selected. The preliminary experiment for several different absorption temperatures showed a slight decrease in the enrichment behavior under the conditions of 303, 323, and 343K. From the viewpoint of short operating time, therefore, 343K was selected. The absorption pressure was 1.0 MPa from the regulations of the Japanese law in handling high-pressure gas, and that at the desorption was atmospheric pressure judging from the operation time and enrichment performance. This was because there was no change in the enrichment behavior between desorption down to 0.1 MPa and down to 100 Pa by using a rotary pump.

Thus, the conditions of $T_{\mathrm{abs}} = 343\mathrm{K}$, $p_{\mathrm{abs}} = 1.0\,\mathrm{MPa}$, $T_{\mathrm{des}} = 473\mathrm{K}$,, and $p_{\mathrm{des}} = 0.1\,\mathrm{MPa}$ were selected as optimum ones. Any of the three columns was continuously supplied with the feed gas of 0.05 in deuterium atomic molar fraction under a constant flow rate. The feed flow rate was 77.2 mL (NTP)/min except for the one-column PS and PTS experiment where two feed flow rates (77.2 and 279 mL (NTP)/min) were tested. The flow rate was selected in such a way that the HETP value of the Pd bed becomes the minimum.[16] The hydrogen desorption rate was limited by diffusion of hydrogen in Pd particles in a similar way to our previous experiments.[16] Therefore, it took 7 min to desorb hydrogen from Pd particles at 473K. So, the values of t_{product} and t_{waste} were 3 and 7 min, respectively. The t_{backfill} was the same as t_{waste}.

EXPERIMENTAL RESULTS

Result of Three-Column Pressure–Temperature-Swing Process

An example of the experimental results of the three-column PTS process is shown in Fig. 4. As shown in the figure, the high-enrichment deuterium product was obtained at the column outlet repeatedly. The outlet deuterium concentration curves showed characteristics of a steep peek immediately after initiating the withdrawal of the product and then gradual tailing. Since a deuterium concentration history after two cycles was almost the same as the next one, it was considered that steady-state separation could be achieved real fast. Since part of the product gas was recycled for back-filling another column, the product gas was continuously withdrawn from the outlet. The exhaust gas was withdrawn as a product flow when the difference in deuterium concentration between the outlet and the feed is over 5% higher than the maximum concentration difference as

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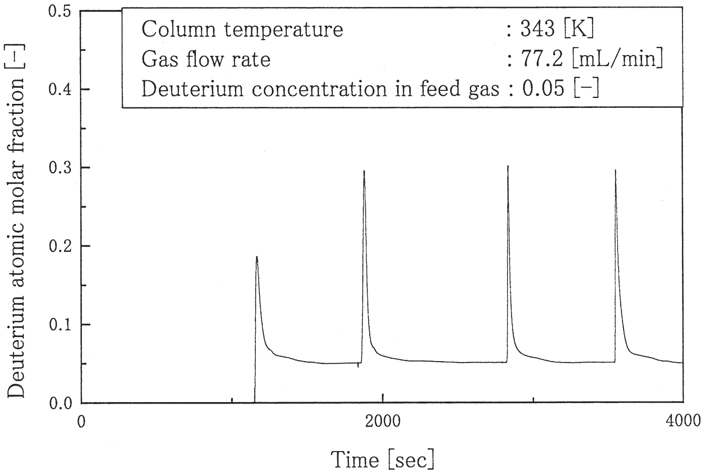

Figure 4. Deuterium concentration at column outlet for three-column PTS process.

follows:

$$\frac{x_{D,out} - x_{D,in}}{(x_{D,out})_{max} - x_{D,in}} \geq 0.05 \qquad (2)$$

where, $x_{D,in}$ is deuterium atomic molar fraction in feed flow; $x_{D,out}$ is deuterium atomic molar fraction in product flow; and $(x_{D,out})_{max}$ is maximum deuterium atomic molar fraction in product flow.

Results of One-Column and Two-Column Pressure–Temperature-Swing Processes and One-Column PS Process

For comparison, one-column PTS, one-column PS, and two-column PTS processes were investigated using the columns 1 and 2. The operation procedures are shown in Fig. 5. There is no back-fill step in the two-column PTS process, and there is a blank process where any feed or exhaust was imposed on the column. This was because $t_{product}$ was different from t_{waste}. There is no back-fill or pressure-equilibrium step in the one-column PTS and PS processes. In the PS process, (insufficient) desorption of hydrogen was carried out by depressurization under the isothermal condition of 343K.

Figure 6 shows an example for the results of the two-column PTS process. In the two-column PTS process, the feed gas was supplied to either of the two columns continuously, and the product was withdrawn intermittently. A similar

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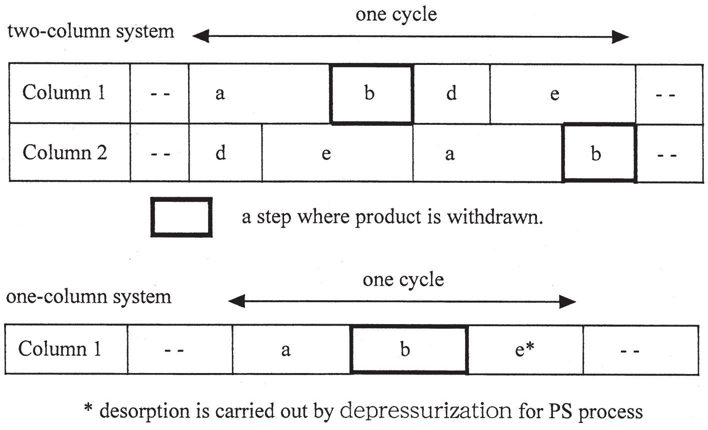

Figure 5. Operation program for two-column and three-column PTS process.

steep peak and broad tailing in the deuterium concentration history curve were observed in a similar way to the three-column system. In the one-column PTS and PS processes, the feed gas was supplied to the column intermittently and the product was withdrawn intermittently.

Figure 7 shows a comparison of variations of the deuterium concentration history in the product flow under a steady-state operation for the one-, two- and three-column PTS processes and the one-column PS process. Table 1 shows

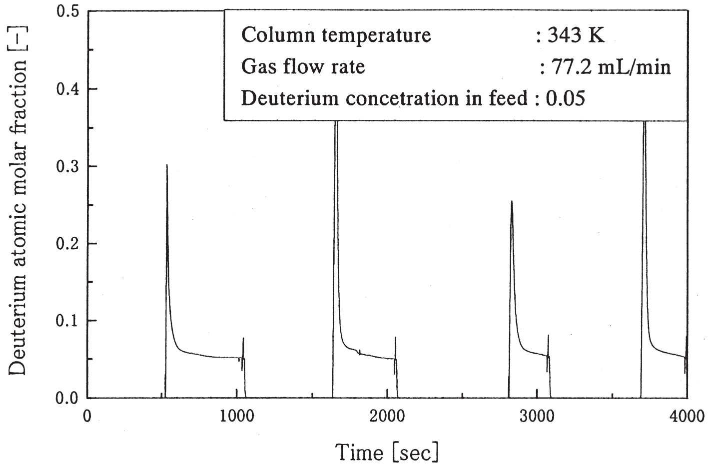

Figure 6. Deuterium concentration at column outlet for two-column PTS process.

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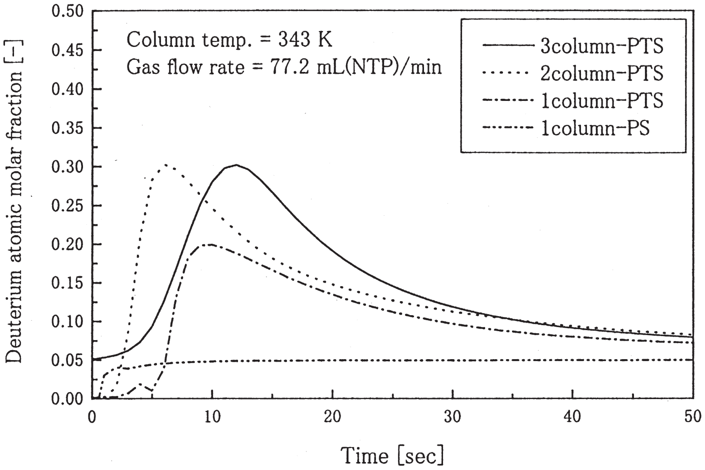

Figure 7. Comparison of deuterium concentration in product among one-, two-, three-column PTS processes and one-column PS process.

comparison in the enrichment ratio, the recovery ratio of deuterium and the product cut among the one-, two-, three-column PTS processes and the one-column PS process. The deuterium enrichment ratio (E_D), the deuterium recovery ratio (R_D) and the product cut (θ) are defined as follows:

$$E_D = \frac{(x_{D,out})_{ave}}{x_{D,in}} \tag{3}$$

$$R_D = \frac{\int_0^{t_{product}+t_{backfill}} P x_{D,out} dt}{\int_0^{t_{product}+t_{backfill}} F x_{D,in} dt} \tag{4}$$

Table 1. Comparison of One-, Two-, Three-Column Pressure–Temperature-Swing Processes and One-Column Pressure-Swing Process

System	Temperature (abs/des) [K]	Flow Rate [mL (NTP)/min]	$(X_{D,out})_{max}$	$(X_{D,out})_{ave}$	E_D	R_D	θ
1-column PS	343/343	77.2	0.0543	0.0537	1.07	0.139	0.13
	343/343	278.6	0.0536	0.0532	1.06	0.129	0.12
1-column PTS	343/473	77.2	0.199	0.0895	1.79	0.232	0.13
	343/473	278.6	0.275	0.104	2.08	0.218	0.11
2-column PTS	343/473	77.2	0.315	0.172	3.43	0.494	0.14
3-column PTS	343/473	77.2	0.317	0.179	3.57	0.486	0.14

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$$\theta = \frac{\int_0^{t_{\text{product}}+t_{\text{backfill}}} P\text{d}t}{\int_0^{t_{\text{product}}+t_{\text{backfill}}} F\text{d}t} \tag{5}$$

where, $(x_{\text{D,out}})_{\text{ave}}$ is average deuterium atomic molar fraction in product flow; F is feed flow rate; and P is product flow rate.

DISCUSSION

The following things were found from comparison of different processes in Figs. 2, 4–7, and Table 1.

(a) The deuterium enrichment was poor in the one-column PS process. This was because sufficient desorption could not be performed under the heatless condition judging from Fig. 1.

(b) The E_{D} value was the largest in the three-column PTS. It was a similar value in the two-column PTS processes and the next in the one-column PTS process. The PS process was the worst. This was because sufficient desorption was performed in the PTS processes.

(c) Heating up to 473K under the atmospheric pressure was sufficient for hydrogen desorption. Evacuation by a pump was not necessary except for activation of Pd. So, hydrogen desorption under atmospheric pressure was sufficient.

(d) The R_{D} value was the largest in the three-column and two-column PTS processes. It was the next in the one-column PTS process and the smallest in the one-column PS process. Thus, the back-fill and pressure-equilibrium step could enhance the R_{D} value. The pressure-equilibrium step would be more effective for enhancement of the R_{D} and E_{D}. This might be because more gas was recycled to the column in the pressure-equilibrium step than in the back-fill step.

(e) The values of E_{D} and R_{D} in the PS and PTS processes were almost independent of the gas flow rate. This might be because the isotopic enrichment was achieved by the equilibrium separation process. In other words, the deuterium enrichment behavior was less affected by the rate process.

(f) The θ value in the two-column and three-column PTS processes was slightly increased by addition of a column. This was because part of gas fed to the system could be recycled to another column in the back-fill and pressure-equilibrium steps.

(g) There was a blank time where no feed or exhaust was imposed to a column in the two-column PTS process. The blank time might be avoided by adopting $t_{\text{product}} = t_{\text{waste}}$. However, it was possible only

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under the condition where the flow rate is low, because it took at least 7 min to desorb hydrogen in Pd sufficiently. The two-column PTS process was allowed to be operated within a limited flow rate under the condition of $t_{\text{product}} = t_{\text{waste}}$. If the flow rate is over the limit, the deuterium concentration will breakthrough the column. On the other hand, there is no limitation of the flow rate in the three-column PTS process. Thus, it was proved experimentally that the three-column PTS process has advantages of the higher deuterium enrichment ratio, deuterium recovery ratio and product cut.

(h) The direction of gas flow was always the same among the steps of pressurization, product-withdraw, back-fill, and pressure equilibrium. In conventional PSA processes, part of product is used for desorption of another column in the blow-down step. The direction of the blow-down flow was reversal to the product flow, because desorption could be effectively performed by depressurization. In the present process, on the other hand, the flow in the steps of the back-fill and pressure equilibrium was in the same direction as the feed or product flow. This was because hydrogen was hardly desorbed by blow down under the isotherm condition and the deuterium concentration during the two steps was very near to the feed one. Therefore, the deuterium mixing might hardly occur in the column, and it resulted in higher enrichment.

(i) The direction of the gas flow in the desorption step was different from that in other steps. The enrichment behavior did not change even when desorption was carried out from the top of the columns where the direction of the gas flow in desorption was the same, although not shown in the present paper. This might be because almost all hydrogen absorbed in Pd was desorbed by heating up to 473K.

(j) The value of E_D was around 3.5 for the three-column PTS process. Unfortunately, it was lower than that of the simulated-moving bed using Pd particles.[8] The latter method needs complicated arrangement of columns under isobaric condition and needs many times of hydrogen passing through columns in series until the steady-state deuterium enrichment was achieved. The degradation of E_D might occur because of drastic, intermittent change of the column condition between absorption under a higher-pressure and lower-temperature condition and desorption under a lower-pressure and higher temperature. There would be still improvements in operating the PTS process.

It is known that particles of hydrogen-absorbing metals and alloys tend to crack in the course of absorption–desorption cycle. So, the pressure drop through the Pd column also increased in the present study. In order to avoid the defect of

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Pd cracking, we developed a pellet of Pd mixed with Al_2O_3 that has no effect on hydrogen absorption. The absorption–desorption cycle of the Pd–Al_2O_3 pellets was repeated up to maximally 1000 cycles[18,19] using commercial-grade hydrogen without further purification. No change was observed on the capacity and rate of hydrogen absorption as well as the pellet shape. It also indicated that Pd was not affected by a small amount of impurities of oxygen or water vapor included in feed gas.

Uniform heating and cooling of a large bed may be difficult. Therefore, there may be a problem for scale-up of the present PTS process in order to apply to separation of deuterium from natural hydrogen. In the present system, the rate-controlling step of the hydrogen absorption and desorption rates was diffusion in Pd in a similar way to our previous study.[16] So, we used very small particles of 0.35 mm in diameter in the experiment in order to get fast absorption rates. From these things, the present PTS system may be useful for isotope separation systems on a laboratory scale. The present PTS process will be applicable to tritium enrichment in laboratories.

CONCLUSIONS

The deuterium enrichment and continuous product recovery could be achieved by the three-column PTS process that comprises five steps of pressurization, product-withdraw, back-fill, pressure equilibrium, and desorption by heating and cool-down. The steady-state enrichment was readily achieved within two or three cycles. The value of E_D for the three-column PTS process was around 3.5. The back-fill and pressure-equilibrium steps could enhance the deuterium enrichment and recovery.

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