Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Possibility of Separation of Deuterium from Natural Hydrogen by a Palladium Particle Bed

Satoshi Fukada[a]; Hiroshi Fujiwara[b]
[a] DEPARTMENT OF APPLIED QUANTUM PHYSICS AND NUCLEAR ENGINEERING, GRADUATE SCHOOL OF ENGINEERING, KYUSHU UNIVERSITY, HIGASHI-KU, FUKUOKA, JAPAN [b] DEPARTMENT OF ADVANCED ENERGY ENGINEERING SCIENCES, INTERDISCIPLINARY GRADUATE SCHOOL OF ENGINEERING SCIENCE OF KYUSHU UNIVERSITY, KASUGA-KOEN, KASUGA-SHI, FUKUOKA, JAPAN

To cite this Article Fukada, Satoshi and Fujiwara, Hiroshi(1999) 'Possibility of Separation of Deuterium from Natural Hydrogen by a Palladium Particle Bed', Separation Science and Technology, 34: 11, 2235 — 2242
To link to this Article: DOI: 10.1081/SS-100100768
URL: http://dx.doi.org/10.1081/SS-100100768

SEPARATION SCIENCE AND TECHNOLOGY, **34**(11), pp. 2235–2242, 1999

Possibility of Separation of Deuterium from Natural Hydrogen by a Palladium Particle Bed

SATOSHI FUKADA*
DEPARTMENT OF APPLIED QUANTUM PHYSICS AND NUCLEAR ENGINEERING
GRADUATE SCHOOL OF ENGINEERING
KYUSHU UNIVERSITY
6-10-1, HAKOZAKI, HIGASHI-KU, FUKUOKA 812-8581, JAPAN

HIROSHI FUJIWARA
DEPARTMENT OF ADVANCED ENERGY ENGINEERING SCIENCES
INTERDISCIPLINARY GRADUATE SCHOOL OF ENGINEERING SCIENCE OF KYUSHU UNIVERSITY
KASUGA-KOEN, KASUGA-SHI, FUKUOKA 816-8580, JAPAN

ABSTRACT

Deuterium in natural hydrogen can be successfully concentrated by means of frontal chromatography using a Pd particle bed at room temperature. The deuterium concentration at the outlet reaches a maximum immediately after hydrogen breaks through the bed. The outlet concentration curve is correlated to a unified profile based on the plate model regardless of the gaseous flow rate and the inlet deuterium concentration. The height equivalent to a theoretical plate, HETP, decreases from 7.6 to 4.7 mm with an increase of the flow rate from 15 to 87 mL(NTP)/min.

INTRODUCTION

Technologies currently used to separate or extract deuterium (or tritium) from hydrogen isotope mixtures are isotopic exchange between H_2O and H_2 or H_2S, cryogenic distillation, and electrolysis (1). Processes which need a special catalyst or sophisticated equipment are predominantly designed for large-scale isotope separation. With a particle bed of Pd or a Pd alloy it is possible to attain a high degree of concentration with a small-scale, simple appa-

---

* To whom correspondence should be addressed. E-mail: s2858tne@mbox.nc.kyushu-u.ac.jp

www.dekker.com

ratus in batch operation. Some previous investigations of this type of the isotope separation process with beds of Pd or a Pd alloy were conducted using gas mixtures of comparatively high or moderate deuterium concentration in protium (2–9). The isotopic effect of hydrogen-absorbing alloys was also investigated in a comparatively high deuterium concentration (10–13). However, no research has been carried out using natural hydrogen. We investigated a Pd or Pd-alloy bed system for the separation of deuterium from natural hydrogen. In the present study a chromatographic separation using a Pd bed was tested to develop a small-scale, highly efficient procedure. Frontal chromatography was adopted as a separation technique because of its simplicity in operation. The effects of the gas flow rate and the inlet deuterium concentration on the separation behavior are discussed. The deuterium concentration profile in the bed at a low deuterium concentration is compared with that at a high deuterium concentration.

EXPERIMENTAL

Palladium particles between 32 and 48 mesh were packed in a stainless-steel column of 6.35 mm inner diameter and 29.1 cm height. The weight of packed material was 24.58 g. The BET specific surface area measured with nitrogen gas at 77 K was 0.45 m^2/g. The void ratio in the bed was 0.772.

Deuterium separation was experimentally carried out by means of frontal chromatography. The frontal chromatography process comprises three steps; out-gassing all hydrogen from the bed, filling the bed with inert gas, and supplying it with a hydrogen isotope mixture. The inert gas filling process is needed only to avoid a reversal of flow or an air leak. Therefore, it is independent of the overall separation behavior. The Pd bed continues to be supplied with the hydrogen mixture before and after hydrogen breaks through the bed. Immediately after the breakthrough, high-concentration deuterium gas flows out of the bed due to the difference in affinity of Pd for protium and deuterium.

The present experiment was conducted by using two types of gas mixtures: natural hydrogen ($x_{\mathrm{D,in}} = 0.00015$ inlet deuterium atomic fraction), supplied from a methanol steam-reforming plant, and an isotope mixture of moderate deuterium concentration in protium ($x_{\mathrm{D,in}} = 0.05$ inlet deuterium atomic fraction). The two gas mixtures were at isotopic equilibrium, and their stated purity was 99.999%. These gases were further purified with a cold trap at 77 K. The outlet deuterium concentration was detected by gas chromatography. Temperature was measured with a thermocouple inserted into the bed. The temperature of the bed was maintained at 30°C with water circulated through the outside of the column in order to eliminate absorption heat from the bed. The gas flow rate, W, is a variable parameter in the present study.

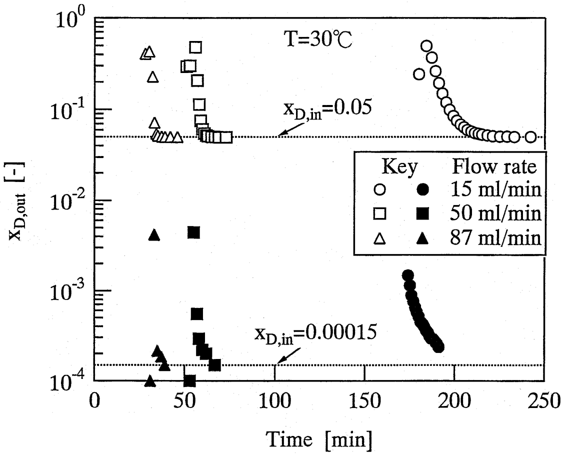

FIG. 1 Variations of outlet deuterium atomic fraction with time after breakthrough. The open symbols are for $x_{D,in} = 0.05$; the filled symbols are for $x_{D,in} = 0.00015$.

RESULTS AND DISCUSSION

Figure 1 shows variations of the deuterium atomic molar fraction at the bed outlet, $x_{D,out}$, with time for $x_{D,in} = 0.05$ and $x_{D,in} = 0.00015$ after hydrogen breaks through the bed. Before the hydrogen breakthrough, the total hydrogen concentration (protium and deuterium) is zero. The respective $x_{D,in}$ values are shown by the two dotted lines in the figure. Although not used in the present experiment, natural hydrogen originating from a soda plant is found to have a deuterium content lower than $x_{D,in} = 0.00015$. As seen in the figure, deuterium for $x_{D,in} = 0.00015$ can be concentrated by the Pd bed in a similar way to that for $x_{D,in} = 0.05$. Maximally, a 10 to 30 times higher concentration of deuterium is obtained immediately after the breakthrough, regardless of the differences in $x_{D,in}$ and W.

The enrichment of deuterium is attained by the following process: The protium and deuterium initially supplied to the bed are absorbed in the inlet zone of the bed. Since the affinity of Pd for protium is higher than that for deuterium, the latter is comparatively less absorbed in the Pd particles. Therefore, the remaining deuterium moves through the preabsorbed Pd bed as long as the bed continues to be supplied with the hydrogen mixture. When it reaches a nonabsorbed Pd zone, it is itself absorbed in the Pd particles. The location where hydrogen absorption predominantly occurs is called the hydrogen-absorbing zone. Thus, high enrichment is attained in the tail end of the hydrogen-absorbing zone in the flow direction. When the tail end of the absorption region reaches the bed outlet, the high-concentration deuterium starts to break through.

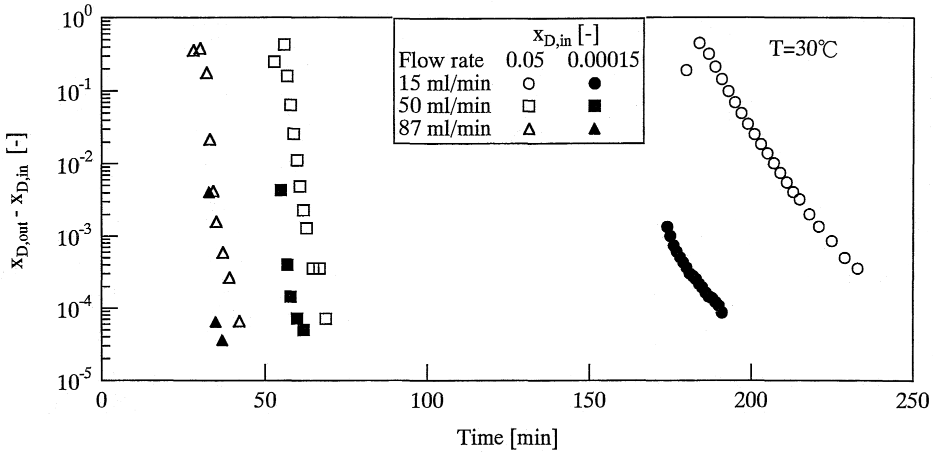

FIG. 2 Logarithmic plot of $x_{D,out} - x_{D,in}$ versus time.

Figure 2 shows a semilogarithmic plot of $x_{D,out} - x_{D,in}$ versus time for the six runs shown in Fig. 1. The data on the ordinate may be correlated to an almost linear function for the respective runs, and the slope was found to be related to the volume of hydrogen absorbed in the Pd particles in an equivalent cell based on the plate theory given in the Appendix. Figure 3 shows a comparison between the plate model calculated and the experimental data. The hydrogen volume absorbed in the unit cell is 70 mL(NTP) for $W = 15$ mL(NTP)/min regardless of the difference in $x_{D,in}$. Then, HETP is 7.6 mm. From similar experiments, the volume and the HETP value for $W = 50$ mL(NTP)/min were determined to be 50 mL(NTP) and 5.4 mm and for 87

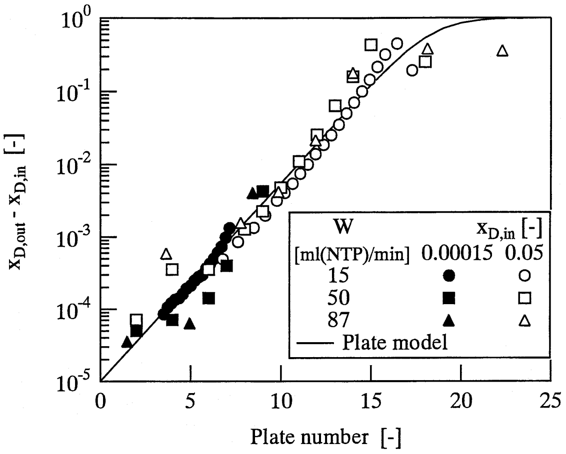

FIG. 3 Comparison of the reduced outlet deuterium atomic fraction and the plate model.

mL(NTP)/min were 42 mL(NTP) and 4.7 mm, respectively. The volume was found to be constant for different $x_{\mathrm{D,in}}$. The HETP value decreases with the gaseous flow rate and was almost the same as in our previous research on the elution chromatography of deuterium and protium (5). Judging from these results, it is concluded that frontal chromatography using a Pd bed is effective for the separation of deuterium from natural hydrogen.

Using the data of the isotope separation factor and the HETP determined with the low or moderate deuterium concentration in protium, an isotope separation system to enrich deuterium in natural hydrogen can be designed. If a single Pd bed with a 29.1-cm bed height concentrates deuterium around 25 times higher, at least three beds with different cross sections in series are necessary to enrich deuterium from natural hydrogen ($x_{\mathrm{D}} = 0.00015$) to a highly purified state ($x_{\mathrm{D}} \fallingdotseq 1$). When all of the beds are operated at the same linear velocity, the inner diameter of the first bed should be five times larger than that of the second one. The second bed also should be five times larger than the third one.

CONCLUSION

Deuterium was successfully concentrated from natural hydrogen by means of frontal chromatography using a Pd particle bed at room temperature by procedures developed for a comparatively higher deuterium concentration. While the HETP based on the plate model was found to be constant regardless of the inlet deuterium concentration, its value decreased from 7.6 to 4.7 mm with an increase in W from 15 to 87 mL/min. The HETP value was almost the same as that obtained in the previous research on elution chromatography with an isotopic mixture of moderate deuterium concentration.

APPENDIX

Plate Model

The separation of deuterium from protium by frontal chromatography is analyzed by the plate theory. In frontal chromatography a hydrogen isotope mixture is continuously fed to a stationary bed which is initially desorbed completely. Then a hydrogen-absorbing region or a mass-transfer zone, in chemical engineering terminology, develops in the bed. The atomic deuterium concentration profile in the mass-transfer zone is described using coordinate system moving at the same propagation velocity as the mass-transfer zone. Then the material balance of atomic deuterium in the volume of a hypothetical cell, V, is expressed by the following equation:

$$\gamma V \frac{dq_{\mathrm{D,J}}}{dt} + \varepsilon V \frac{dc_{\mathrm{D,J}}}{dt} = W_{\mathrm{J}-1} c_{\mathrm{D,J}-1} + \gamma w_{\mathrm{J}+1} q_{\mathrm{D,J}+1} - W_{\mathrm{J}} c_{\mathrm{D,J}} - \gamma w_{\mathrm{J}} q_{\mathrm{D,J}} \tag{A–1}$$

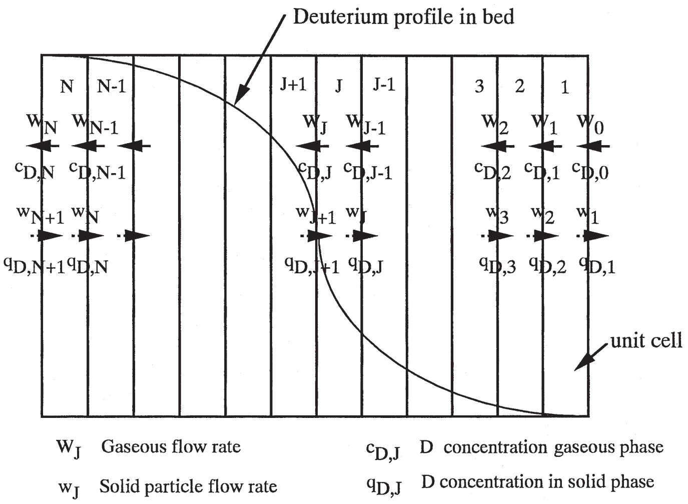

FIG. A1 Plate model under constant pattern.

The notations are given in Fig. A1 and in the Nomenclature section. In a steady-state plate model, the atomic deuterium concentration in the gaseous phase, $c_{D,J}$, which flows out of the cell is in equilibrium with that of the solid phase in the cell, $q_{D,J}$. This means that the following relation holds:

$$\alpha_{H-D} = \frac{c_{D,J} q_{H,J}}{c_{H,J} q_{D,J}} \tag{A–2}$$

From the literatures (5, 6) it is known that the separation factor, α_{H-D}, depends on $q_{D,J}$ according to

$$\alpha_{H-D} = \frac{q_{H,J} + q_{D,J}\alpha_{HD-D_2}}{q_{H,J} + q_{D,J}\alpha_{H_2-HD}}\,\alpha_{H_2-HD} \tag{A–3}$$

where $\alpha_{H_2\text{-}HD}$ and $\alpha_{HD\text{-}D_2}$ are the isotopic equilibrium constants of the following two isotopic exchange reactions, respectively:

$$H_2 + D\text{—}Pd = HD + H\text{—}Pd \tag{A–4}$$

$$HD + D\text{—}Pd = D_2 + H\text{—}Pd \tag{A–5}$$

A constant pattern approximation is applied to the material balance equation. Based upon the experimental fact that the outlet deuterium concentration profiles are very similar regardless of W and $x_{D,in}$ (see in Fig. 1), the concentration profile should be described by a unique one if a proper cell volume is selected. When a constant pattern is established in the mass-transfer zone, the deuterium atomic molar fraction in the upstream cell approaches $x_{D,in}$ and that in the downstream cell approaches unity. Applying the constant pattern approximation to Eq. (A–1), the following equations are approximately valid:

$$\gamma w_{J+1}\,(q_{D,J+1} - q_{D,in}) = W_J(c_{D,J} - c_{D,in}) \tag{A–6}$$

$$\gamma w_{J+1} q_t = W_J c_t \tag{A–7}$$

and the following equation can be deduced from Eqs. (A–2), (A–6), and (A–7):

$$\frac{x_{D,J+1}}{\alpha_{H-D} - (\alpha_{H-D} - 1)x_{D,J+1}} = x_{D,J} - \frac{(\alpha_{H-D,in} - 1)(1 - x_{D,in})x_{D,in}}{\alpha_{H-D,in} - (\alpha_{H-D,in} - 1)x_{D,in}} \tag{A–8}$$

Here, $\alpha_{H-D,in}$ is the value of α_{H-D} for $x_D = x_{D,in}$. Thus, $x_{D,J}$ can be calculated stepwise from any arbitrary $x_{D,1}$ value. If $x_{D,in}$ is much smaller than 1, $\alpha_{H-D,in}$ is equal to α_{H_2-HD}. Then Eq. (A–8) can be simplified to the relation

$$x_{D,J+1} - x_{D,in} = \alpha_{H_2\text{-}HD}(x_{D,J} - x_{D,in})$$

This simplification leads to the result that $\log(x_{D,out} - x_{D,in})$ is proportional to the plate number (see Fig. 3).

The passing time of the unit cell, Δt, is defined as the time interval during which the hydrogen-absorbing region passes through one unit cell. Then the product $Wc_t\Delta t$ is equal to the total hydrogen capacity of the unit cell:

$$(\varepsilon c_s + \gamma q_t)V = Wc_t\Delta t \tag{A–9}$$

The first term in the parentheses on the left-hand side is negligibly small compared to the second term.

NOMENCLATURE

$c_{D,J}$	atomic deuterium concentration in gas phase of cell number J (mol/m^3)
c_t	total atomic hydrogen concentration in gas phase (mol/m^3)
$q_{D,J}$	atomic deuterium concentration in the solid phase of cell number J (D/Pd)
q_t	total atomic hydrogen concentration in the solid phase in a hypothetical cell [(H + D)/Pd]
T	temperature (K)
V	cell volume (m^3)
W	volumetric flow rate at the bed inlet (m^3/s)
W_J	volumetric flow rate across a hypothetical cell (m^3/s)
w_J	solid flow rate across a hypothetical cell (m^3/s)
$x_{D,in}$	inlet deuterium atomic molar fraction in the gas phase (—)
$x_{D,J}$	deuterium atomic molar fraction in the gas phase in a hypothetical cell (—)
$x_{D,out}$	outlet deuterium atomic molar fraction in the gas phase (—)

Greek

α_{H-D}	isotope separation factor between H and D (—)
α_{H_2-HD}	isotope separation factor between H_2 and HD (—)
α_{HD-D_2}	isotope separation factor between HD and H_2 (—)
γ	molar packed density (mol/m^3)
ε	void ratio (—)

REFERENCES

1. H. K. Rae, *Separation of Hydrogen Isotopes* (ACS Symposium Series), American Chemical Society, Washington, DC, 1977.
2. E. Glueckauf and G. P. Kitt, *Proceedings of the International Symposium on Isotope Separation*, 1957, pp. 210–215.
3. F. Botter, J. Menes, S. Tistchenko, and G. Dirian, *Bull. Soc. Chim. Fr.*, *11*, 3374–3382 (1965).
4. A. S. Horen and M. W. Lee, *Fus. Technol.*, *21*, 282–286 (1992).
5. S. Fukada, K. Fuchinoue, and M. Nishikawa, *J. Nucl. Mater.*, *226*, 311–318 (1995).
6. S. Fukada, K. Fuchinoue, and M. Nishikawa, *J. Nucl. Sci. Technol.*, *32*, 556–564 (1995).
7. S. Fukada, K. Fuchinoue, and M. Nishikawa, *Fus. Technol.*, *28*, 608–613 (1995).
8. K. Watanabe, M. Matsuyama, T. Kobayashi, and S. Taguchi, *J. Alloys Compos.*, *257*, 278–284 (1997).
9. S. Fukada and H. Fujiwara, in *Proceedings of the 6th Workshop on Separation Phenomena in Liquids and Gases*, 1998.
10. F. T. Aldridge, *J. Less-Common Met.*, *108*, 131–150 (1985).
11. W. M. Rutherford, *Mater. Sci. Forum*, *31*, 19–38 (1988).
12. L. K. Heung, R. S. Tran, and K. J. Stoner, *J. Less-Common Met.*, *172/174*, 1313–1319 (1991).
13. B. M. Andreev, E. P. Magomedbekov, and G. H. Sicking, *Springer Tracts Mod. Phys.*, *132*, 172 (1996).

Received by editor July 8, 1998
Revision received November 1998

Downloaded At: 11:08 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100100768