

研究報告

Adsorption Characteristics of Water Vapor on Gear-Pellet and Honeycomb-Pellet Types of Adsorbents Containing A-type Zeolite

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Abstract

It is necessary to recover or detritiate tritiated species that are extensively coexistent in nuclear fusion installations. A conventional way to recover tritium release to atmosphere is catalytic oxidation of tritiated species and adsorption of tritiated water vapor on adsorbents with high surface areas. However, pressure loss would become more serious with increase in the size of adsorbent beds, which could lead to greater power needs. Therefore, new adsorbents with low pressure loss and surface areas need to be developed and utilized for such large-scale adsorption systems. Thus, the authors tested new types of adsorbents, which are gear-type and honeycomb-type pellet adsorbents.

It was found that the gear-type pellet adsorbents have larger adsorption capacity than the honeycomb-type pellet adsorbent. Furthermore, it was also found that the gear-type MS4A adsorbent possesses larger adsorption capacity than other adsorbents tested in this work. Among the new adsorbents studied in this work, the gear-type MS4A adsorbent appears to be most promising for the application to the adsorption systems in terms of adsorption capacity and adsorption rate.

1. Introduction

A large amount of tritium would be handled as fuel in nuclear fusion power plants. Tritium is the radioisotope of protium, and is easily taken into human body. Thus the behavior of tritium accidentally released in fusion power plants should be studied for the safety design and radioprotection of workers. For this reason, recovery or detritiation of tritiated species is indispensable. A fusion research facility and a power plant will be require a large detritiation system to prevent the tritium release and to recover the tritiated water vapor. Tritium released should be recovered as efficiently as possible. A conventional way is to oxidize tritiated species and make them be adsorbed on adsorbents with high surface areas. Thus, reliable adsorption systems of tritiated water vapor are required, which would be large-scale adsorption systems. Some studies have been done for this purpose^{(1),(2)}. However, pressure loss would become more serious with increase in the size of adsorption beds, which could lead to greater power needs with regard to blowers, pumps and so forth. The adsorbents used in the system need to

possess greater surface area for better adsorption rate and low pressure loss when they are packed as adsorption beds.

In this study, attention was focused on new adsorbents, which are gear-type pellet MS5A adsorbent, gear-type pellet MS4A adsorbent and honeycomb-type pellet MS5A adsorbent. The adsorption characteristics of the new adsorbent were comparatively studied with conventional type of adsorbents (pellet-type MS5A adsorbent, pebble-type MS5A adsorbent), in terms of adsorption capacity, pressure loss and adsorption rate.

2. Experimental

2.1 Adsorbent

In this work, new adsorbents such as gear-type pellet adsorbents and honeycomb-type pellet adsorbent. These are produced by Nagamine Manufacturing Corporation, of which major component is zeolite-5A or zeolite-4A. The photographic views of the adsorbents are shown in Fig.1. As shown in Fig.1 (a) and (b), appearance of the gear-type pellet adsorbents (both of zeolite-5A and zeolite-4A are produced) is like small gear wheels, which could result in greater surface areas to be contacted with process gases including water vapor. According to information given by the manufacturer, pressure loss of the bed packed with gear-type pellet adsorbents is smaller than that of

Received July 22, 2013

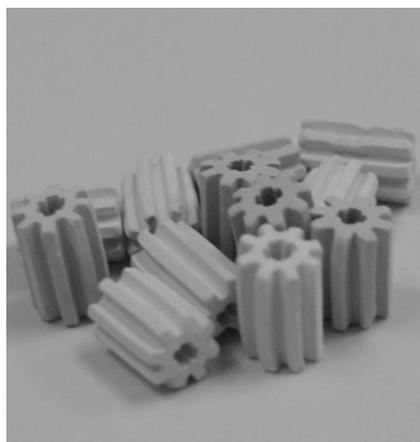
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usual pellet-type adsorbents. Figure 1 (c) shows the photographic views of honeycomb-type pellet adsorbent (zeolite-5A), indicating that appearance of the honeycomb-type pellet adsorbent is just as honeycomb-type adsorbents. However, the adsorbent is not used as usual honeycomb stacks but used as



(a) Gear-type 5A adsorbent



(b) Gear-type 4A adsorbent



(c) Honeycomb-type 5A adsorbent

Fig.1 Picture of (a) gear-type 5A (b) gear-type 4A and (c) honeycomb-type 5A adsorbent.

packed beds, which could result in greater surface areas to be contacted with process gases including water vapor. According to information given by the manufacturer, pressure loss of the bed packed with honeycomb-type pellet adsorbents is also smaller than that of usual pellet-type adsorbents. Advancement in manufacturing technology has enabled manufacturing of the above adsorbents with complicated shapes.

For comparison, the authors also examined two conventional pellet-type (Molecular Sieves 5A) adsorbents and pebble-type (Molecular Sieves 5A) adsorbents, manufactured by UNION-SHOWA Co. and ALDRICH Inc., respectively. The average sizes of pellet-type and pebble-type adsorbents were 3 mm (ϕ) \times 7 mm (length) and 3 mm (ϕ), respectively. The photographic views of the pellet-type and the pebble-type adsorbents are shown in Fig.2.



(a) Pellet-type 5A adsorbent



(b) Pebble-type 5A adsorbent

Fig.2 Picture of (a) cylinder-type 5A and (b) pebble-type 5A adsorbent.

2.2 Water adsorption

The experiments were conducted by the breakthrough method, in terms of adsorption capacity and adsorption rate. Figure 3 shows a flow diagram of the experimental apparatus used in this study. Sample adsorbents were packed in a tubular reactor made of quartz, and water adsorption experiments were carried out using fixed beds of the adsorbents. The adsorbents were dried under the flow of dry Ar gas at 350 °C for 8 h and water vapor adsorbed was desorbed from the adsorbents in each experiment. H₂/Ar gases were first passed through the cold trap packed with a molecular sieves 3A adsorbent dipped in ice water at 273K to remove water vapor contained in mixture gases supplied from gas cylinders. Then, water vapor (converted from H₂ to H₂O completely) was generated in the mixture gases by introducing the H₂/Ar mixture gases to a copper oxide bed held at the temperature of 623 K. Then, the H₂O/Ar gases generated with the CuO bed were passed through the sample bed (packed with the adsorbents), of which temperature was maintained at experimental temperatures (283K, 303K, 323K) with a constant-temperature water bath. The water vapor concentrations in the process gas (Ar) were measured with a hygrometer. Breakthrough curves obtained in this way were analyzed, and the amounts of adsorbed water or adsorption rates were discussed.

3. Results and discussion

3.1 Experimental isotherms on adsorbents

Figure 4 shows the amounts of water adsorbed

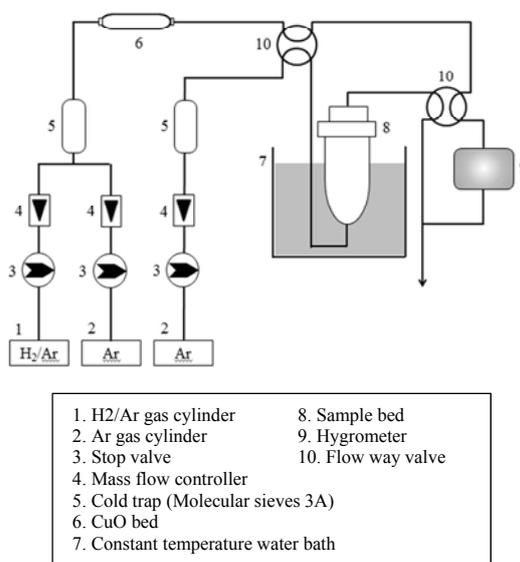
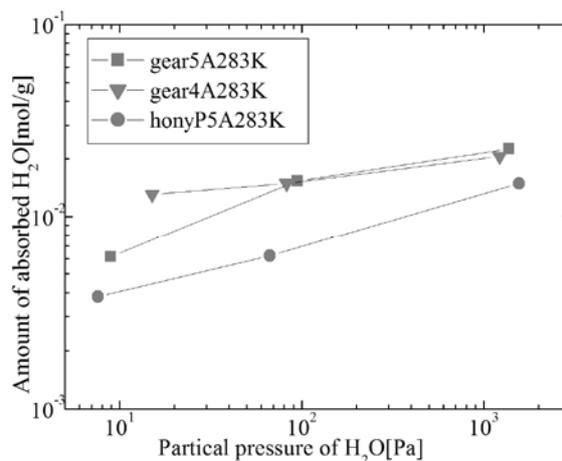
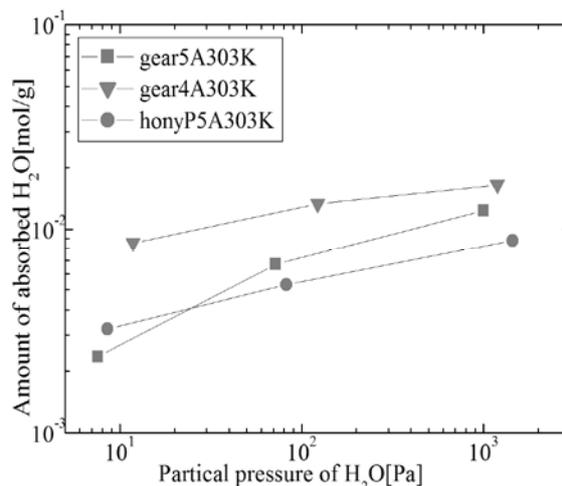


Fig.3 Experimental apparatus for water adsorption.

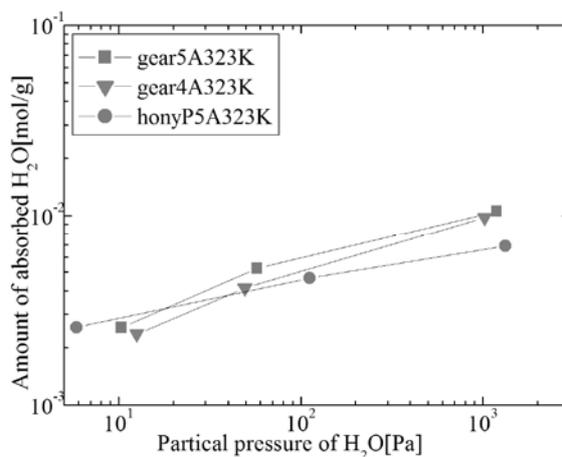
on gear-type 5A, gear-type 4A and honeycomb 5A adsorbents at 283K, 303K and 323K as functions of



(a) Amount of water adsorbed at 283K



(b) Amount of water adsorbed at 303K



(c) Amount of water adsorbed at 323K

Fig.4 Amount of water adsorbed on various adsorbents at (a) 283K (b) 303K (c) 323K

partial pressure of water vapor. The adsorption amounts of water on the adsorbents were investigated in the partial pressure range of 10-1000 Pa. The experimental results indicate that the adsorption capacity of water on the honeycomb-type adsorbent is lower than that of the gear-type adsorbents, while the gear-type 4A adsorbent possesses the highest adsorption capacity among the adsorbents tested in this work. The content of zeolite 5A was 70% in the gear-type 5A and honeycomb-type adsorbents, but it was 80% in the gear-type 4A adsorbent. This is probably a chief reason for greater adsorption capacity of the gear-type 4A adsorbent. Therefore, in terms of adsorption capacity, the gear-type 4A adsorbent could be also used as an adsorbent for adsorption of water like zeolite 5A-based adsorbents that are usually used for adsorption systems in the fusion reactor facility. The effect of pore size attributed to the zeolite structure on the adsorption capacity of water appears to be small.

3.2 Analysis of experimental adsorption isotherms for adsorbents

The authors analyzed the adsorption isotherms of water vapor on the gear-type 5A, gear-type 4A, and honeycomb-type 5A adsorbents at the temperatures of 283, 303 and 323K. First, the Langmuir model was tested for correlation of the isotherm. The result of correlation is also shown as lines in Fig.5, which indicates that Langmuir equation cannot properly reproduce the experimental isotherm data. Therefore, other adsorption isotherm models were tested for correlation of the experimental isotherms. Then, the authors tested the Langmuir-Freundlich (L-F) equation, which is expressed as:

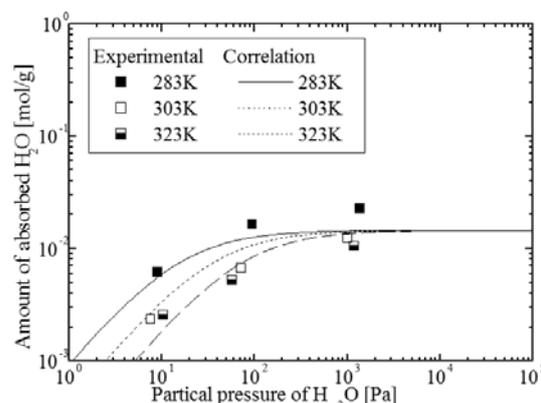
$$q = \frac{q_s k p^u}{1 + k p^u} \quad (1)$$

$$k = k_0 \exp\left(\frac{E}{RT}\right) \quad (2)$$

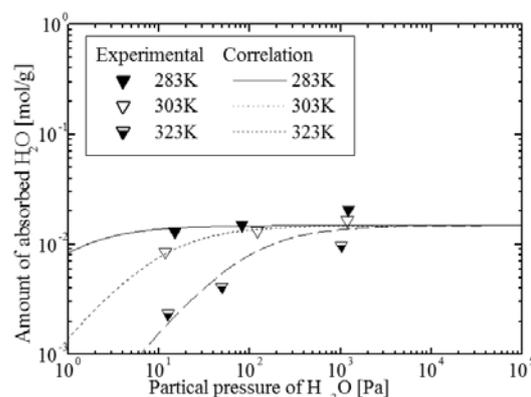
The results of correlation with the above equations are shown in Fig.6. The Langmuir-Freundlich equation rather well reproduced the experimental isotherms on the gear-type 4A or 5A honeycomb-type adsorbents in spite of its mathematical simplicity. However, experimental isotherms of the gear-type 5A adsorbent could not be properly reproduced. Thus, the authors tested more complicated model that can be called a 2-site Langmuir-Freundlich equation:

$$q = \frac{q_{s_1} k_1 p^{u_1}}{1 + k_1 p^{u_1}} + \frac{q_{s_2} k_2 p^{u_2}}{1 + k_2 p^{u_2}} \quad (3)$$

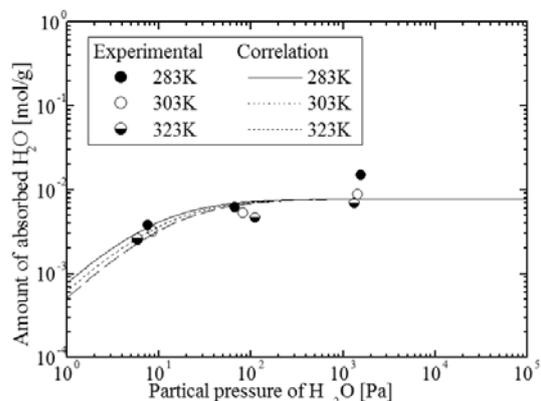
$$k_i = k_{0,i} \exp\left(\frac{E_i}{RT}\right) \quad (4)$$



(a) Gear-type 5A



(b) Gear-type 4A



(c) Honeycomb-type 5A

Fig.5 Adsorption isotherms of water vapor on (a) gear-type 5A (b) gear-type 4A and (c) honeycomb-type correlated with Langmuir equation.

Figure 7 shows the results of correlation of the experimental isotherms obtained by using the 2-site Langmuir-Freundlich equation, which suggests that the 2-site Langmuir-Freundlich equation better correlates the experimental isotherms.

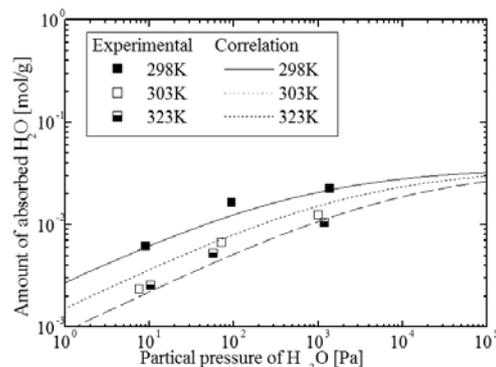
3.3 Breakthrough profiles

Adsorption performance for the water vapor was also investigated by observing the breakthrough behavior. Figure 8 compares the breakthrough curves for a water vapor adsorption on gear-type, honeycomb-type, pellet-type and pebble-type adsorbent with the almost same size (~3 mm). The break through curves indicate that the adsorption capacities (based on the bed volume) of water vapor of the new types of adsorbents are smaller than conventional adsorbents. The breakthrough period on gear-type and honeycomb-type adsorbent (300-500 min) is shorter than on cylinder-type and pebble-type adsorbent (500-1000 min). This is because the bed densities of the gear-type and honeycomb-type adsorbents are smaller than that of conventional pellet or pebble adsorbents.

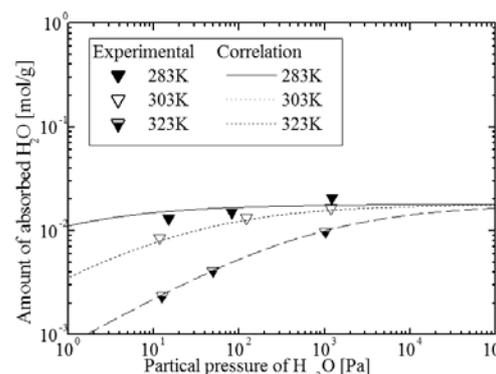
Figure 9 compares breakthrough curves at the initial stages of breakthrough for water vapor adsorption on gear-type, pellet-type and pebble-type adsorptions. The adsorption rates (represented by the slope of the breakthrough curves) of water vapor on the pellet-type adsorbent appears to be greater than that of the gear-type and pebble-type adsorbents. The breakthrough curves on the gear-type and pebble-type adsorbents at the initial stage of breakthrough exhibit almost the same slopes. As mentioned above, the bulk bed densities of gear-type and honeycomb-type are lower than that of pellet-type and pebble-type adsorbents. Thus, it is considered that the adsorption capacities and adsorption rate for water vapor could be improved if the higher bulk densities of gear-type and honeycomb-type adsorbents are achieved by more advancement in fabrication technologies of such adsorbents. The honeycomb-type adsorbent produced in the industry at the present stage is not as effective as the gear-type adsorbents for adsorption of tritiated water vapor.

Figure 10 also compares the breakthrough curves for water vapor adsorption on the gear-type adsorbents containing 5A or 4A zeolite. This result indicates that the gear-type 4A adsorbent offers a higher adsorption rate than the gear-type 5A adsorbent. One reason is possibly the difference in zeolite contents between the two adsorbents; the gear-type 4A adsorbent possesses higher water

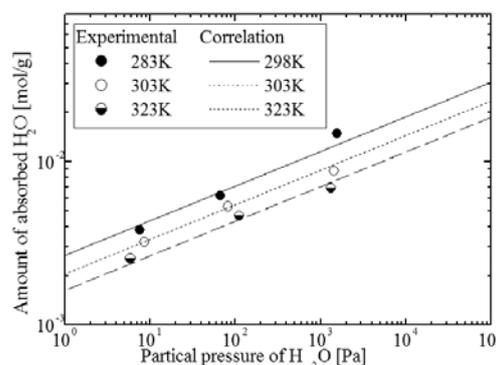
adsorption capacity than the gear-type 5A adsorbent. As mentioned above, the zeolite contents are 70% in the gear-type 5A and 80% in gear-type 4A, respectively. It seems that difference in micro-pore sizes of 4A and 5A gives less effect on adsorption rates.



(a) Gear-type 5A



(b) Gear-type 4A



(c) Honeycomb-type 5A

Fig.6 Adsorption isotherms of water vapor on (a) gear-type 5A (b) gear-type 4A and (c) honeycomb-type correlated with Langmuir-Freundlich equation.

Figure 11 shows the breakthrough curves for water vapor adsorption on gear-type 4A at various flow rates. As expected, breakthrough time is shortened with increasing flow rates of process gas. In order to analyze these adsorption breakthrough curves and to quantify adsorption rates, we are now

in the process of developing a numerical calculation model. More detailed data on experimental adsorption isotherms are necessary to more accurate adsorption isotherm equations, as well.

4. Conclusion

To develop a high performance adsorbent system for tritiated water vapor, the properties of new types of adsorbents such as gear-type adsorbents and honeycomb-type adsorbent were experimentally studied and the results were summarized as follows:

- (1) Adsorption characteristics of gear-type and honeycomb-type adsorbent were investigated by the breakthrough method.
- (2) Various adsorption models were tested to correlate the experimental isotherms. It is found that the Langmuir-Freundlich model could properly correlate the experimental adsorption isotherms.
- (3) It was found that the adsorption capacity of water vapor on the gear-type adsorbents is

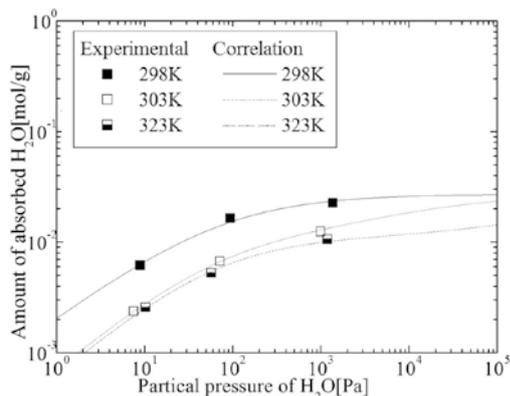


Fig.7 Adsorption isotherms of water vapor on Gear-type 5A correlated with Langmuir-Freundlich 2site model.

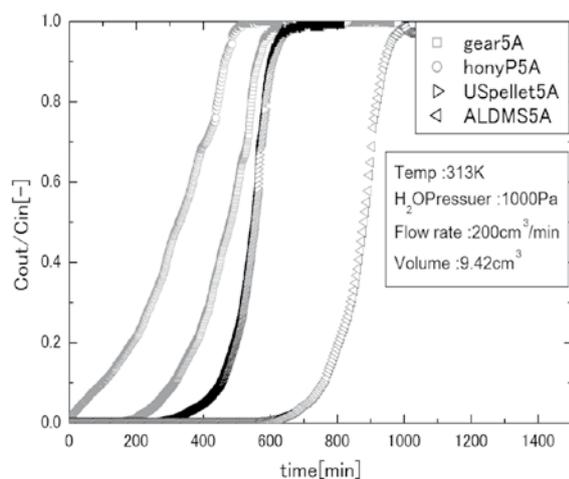


Fig.8 Breakthrough curves for water vapor adsorption on various adsorbents.

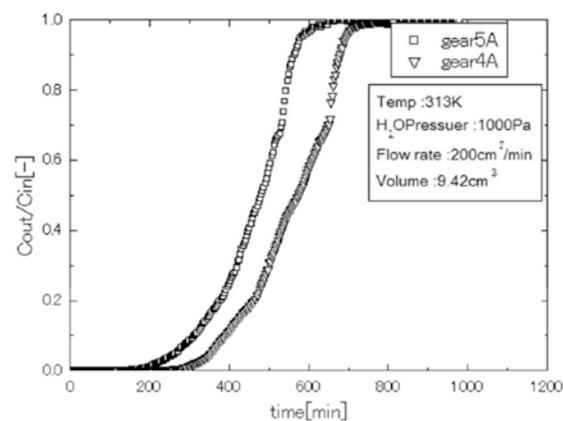


Fig.10 Breakthrough curves for water vapor adsorption on gear-type containing 5A and 4A.

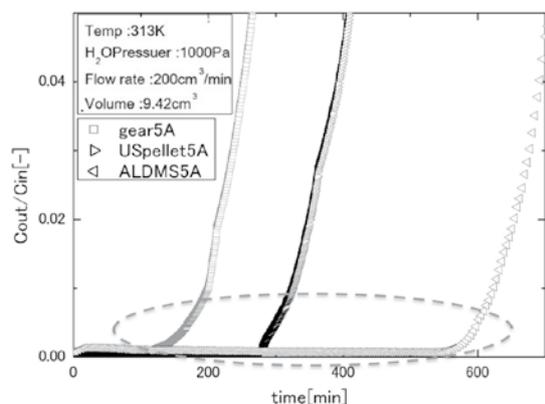


Fig.9 Break through curves for water vapor adsorption on various adsorbents at beginning sites.

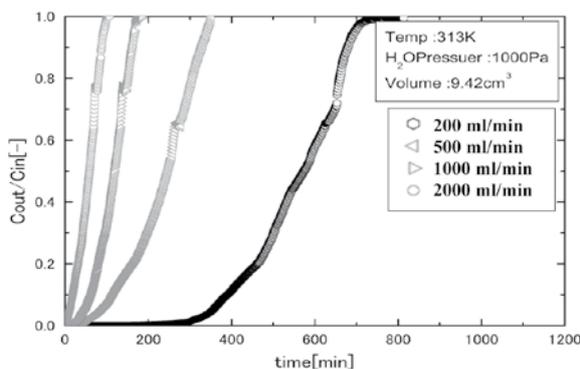


Fig.11 Breakthrough curves for water vapor adsorption on gear-type 4A at various flow rate.

higher than that on a honeycomb-type adsorbent.

- (4) The experimental breakthrough curves indicate that the adsorption rates of water vapor on gear-type and honeycomb-type adsorbents are smaller than that on conventional type adsorbents. The reason is probably the smaller bulk bed densities of the gear-type and honeycomb-type adsorbents compared with the conventional pellet and pebble types of adsorbents.

Nomenclature

E	energy-related term in Henry's law constant and constant in Freundlich equation [$\text{J} \cdot (\text{molK})^{-1}$]
k	constant in Freundlich equation [arbitrary, depending on the value of u]
k_0	constant in Freundlich equation at beginning state
p	partial pressure of adsorbent [Pa]
q	number of moles in the surface phase [$\text{mol} \cdot \text{g}^{-1}$]
q_s	maximum number of moles of i in the surface phase [$\text{mol} \cdot \text{g}^{-1}$]
R	gas constant ($=8.31$) [$\text{J} \cdot (\text{molK})^{-1}$]
u	constant in Langmuir-Freundlich equation

Subscript

i number of adsorption site in Langmuir or Langmuir-Freundlich models

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Acknowledgments

This work was performed with the support and under the auspices of the NIFS Collaboration Research programs (NIFS 10KOBA023, NIFS13KOBA029).

ゼオライトを含有するギア型・ハニカム型ペレット における水蒸気の吸着特性

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要 旨

核融合装置において、広範囲にわたり存在するトリチウムを回収、脱トリチウム化する方法を確立させることは必要不可欠である。従来の方法では種々トリチウム化した物質を酸化させることにより高い表面積を有する吸着剤で吸着させる方法が主流である。しかし、吸着層の大型化に伴い多大な圧力損失が生じ、より大きなエネルギー動力を必要とする。そのため、大きな表面積を有し、圧力損失が低い新型吸着剤を開発することが必要である。本研究では、新しく開発された吸着材の大規模吸着装置への適用性を検討した。

本研究で用いた、吸着材は、ギア型あるいはハニカム型に成形された、A型のゼオライトを主成分とする新しい吸着材である。検討結果から、ギア型ペレット吸着材はハニカム型ペレット吸着材よりも大きな吸着量を持つことが見いだされた。さらに、ギア型ペレットモレキュラーシーブの4Aタイプの吸着材は、他の吸着材と比較すると、より大きな量のガス吸着処理が出来ることがわかった。新型吸着材を使用した今回の実験では、ギア型モレキュラーシーブ4Aの吸着剤は吸着量、および吸着速度において吸着装置に最適であると考えられた。

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