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# Tritium trapping capacity on metal surface

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## Abstract

It is well known by experience that tritium is apt to stick to the surface of various materials. If the amount of tritium trapped to the surface is not small enough compared to the amount of tritium introduced to the system, interactions of tritium with the system materials affect the behavior of tritium in a manner peculiar to the system. This phenomenon has been named as the system effect of tritium by the present authors and the way to quantify this effect using the serial reactors model, connection of perfect mixed type reactors and plug flow type reactors, also has been proposed. The tritium trapping capacity on the surface of stainless steel, copper or aluminum is quantified in this study considering that the surface water consists of physically adsorbed water, chemically adsorbed water and structural water. It is observed in this study that the amount of surface water on each material in this study gives non-negligible tritium trapping capacity and that the structural water controls the tritium trapping capacity when the vapor pressure is low or when temperature is high. Further phenomenal discussion from the viewpoint of material science is required because the interaction of tritium with material surface is observed to be highly dependent on the surface condition. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

It is well known by experience that tritium is apt to stick to the surface of various materials in the course of tritium handling using a certain tritium-processing system. If the amount of tritium trapped to the surface is not small enough compared to the amount of tritium introduced to the system, interactions of tritium in the gas stream with the surfaces of the system materials affect the behavior of tritium in the system. Then, the transitional response of tritium concentration at the outlet of the system changes in a manner peculiar to the system in accordance with system constitution and construction materials. The local tritium inventory, tritium in gas stream and tritium trapped to the construction material in the system, also change with time. This phenomenon has been named as the system effect of tritium by the present authors in the previous paper [1] and the way to quantify the system effect using the serial reactors model, connection of perfect mixed type reactors and plug flow type reactors, also has been proposed in the paper. The memory effect of an ionization chamber or a proportional counter can also be explained as a kind of system effect because it has arisen from trapping behavior of tritium on the electrode surface of a monitor [2]. We also have found that non-negligible amount of water exists on the surface of various piping materials such as stainless steel, copper and aluminum, and that this water on the surface plays an important role in trapping of tritium through such reactions as adsorption and isotope exchange reactions [3,4].

The amount of water on the surface of 304 stainless steel (304 SS), copper or aluminum is quantified in this work considering that the water on the surface can be classified into physically adsorbed water, chemically

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adsorbed water and structural water, though only the over-all amount of adsorbed water was discussed in the previous paper [4].

## 2. Preparatory consideration

It is commonly known by experience that not a small amount of tritium is trapped to the surface of various piping and construction materials. However, qualitative and quantitative analysis on this phenomenon has not been performed yet.

It is considered by the present authors that some amount of water or —OH bases exist on the surface of various materials and they are named as the surface water as a whole. Then, tritium is taken to the surface water through such reactions as adsorption and isotope exchange reactions. Accordingly the amount of the surface water means the tritium trapping capacity of the surface.

It is considered in this report that the surface water consists of physically adsorbed water, chemically adsorbed water and structural water. Each type of water is defined as follows.

The amount of physically adsorbed water $q_{\mathrm{ad,C}}$ (mol/m$^2$) changes reversibly with the vapor pressure in the gas phase at the given temperature, and it is considered that the amount of adsorption is represented by the Lagmuir equation

$$q_{\mathrm{ad,p}} = b\exp(-Q_{\mathrm{ad,p}}/RT)P/(1+aP), \tag{1}$$

where $a$ (1/Pa) and $b$ (mol/m$^2$ Pa) are the Langmuir constants and $Q$ (J/mol), $T$ (K) and $P$ (Pa) are heat of adsorption, temperature and vapor pressure, respectively.

The amount of chemically adsorbed water $q_{\mathrm{ad,C}}$ cannot be desorbed by the purging operation with dry gas at the same temperature as it is adsorbed. In other words, heating is required to desorb chemically adsorbed water, and the amount of adsorption is represented by

$$q_{\mathrm{ad,C}} = c\exp(-Q_{\mathrm{ad,C}}/RT)P^{1/2}, \tag{2}$$

where dissociative adsorption is considered and $c$ (mol/m$^2$ Pa$^{1/2}$) is the constant.

The structural water represents any chemically adsorbed water, crystal water and some chemical groups containing hydrogen such as —OH bases which are strongly connected with the surface, and tritium is exchanged with hydrogen in the structural water through the isotope exchange reactions. Accordingly, the amount of structural water $q_{\mathrm{str}}$ (mol/m$^2$) does not depend on the vapor pressure in the gas phase as

$$q_{\mathrm{str}} = d\,f(T), \tag{3}$$

where $d$ (mol/m$^2$) is the constant.

Then, the amount of the surface water $q_{\mathrm{s}}$ is given by

$$q_{\mathrm{s}} = q_{\mathrm{ad,p}} + q_{\mathrm{ad,c}} + q_{\mathrm{str}}. \tag{4}$$

Fig. 1 shows a schematic diagram to compare the condition of the surface water under various conditions.

It must be noted that the purging operation with dry gas at the same temperature can reduce only the amount of physically adsorbed water, and that some amount of chemically adsorbed water and structural water remaines on the surface even after drying at elevated temperature. As stated later, drying at temperature above 400 K can reduce the chemically adsorbed water to such an extent that it can be neglected, though rather small reduction is observed in the amount of structural water.

When the molecular form of tritium (HT or $T_2$) is present in the gas stream, the isotope exchange reaction between tritium in the gas phase and water on the surface (named as the isotope exchange reaction 1 by the present authors) supplies tritium to the surface water till the T/H ratio in the surface water becomes the same as the T/H ratio in the gas stream.

$$\begin{aligned}&\mathrm{HT(gas\ phase)} + \mathrm{H_2O(surface)}\\&\quad = \mathrm{H_2(gas\ phase)} + \mathrm{HTO(surface)}.\end{aligned} \tag{5}$$

When tritiated water (HTO or $T_2O$) is present in the gas stream, tritium is trapped to the surface as the physically or chemically adsorbed water at first and then, the isotope exchange reaction between tritiated water in the gas phase and water on the surface (named as the isotope exchange reaction 2) supplies tritium to the surface till the T/H ratio in the surface water becomes the same as the T/H ratio in the gas phase.

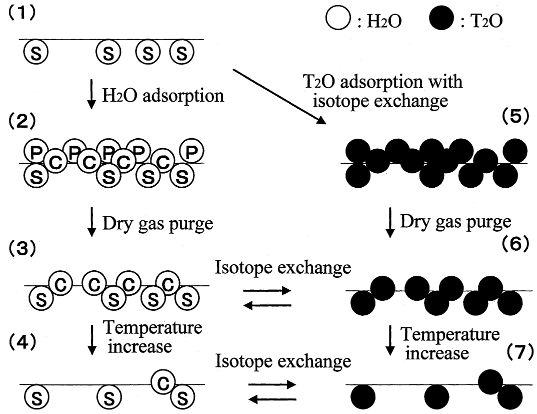

Fig. 1. Schematic diagram to compare the condition of the surface water. (P, C and S in this figure mean physically adsorbed water, chemically adsorbed water and structural water, respectively.)

$$\mathrm{HTO(gas\ phase)} + \mathrm{H_2O(surface)} = \mathrm{H_2O(gas\ phase)} + \mathrm{HTO(surface)}. \quad (6)$$

A similar way has been applied by the present authors successfully in estimation of the tritium inventory in a solid breeder blanket [5,6].

## 3. Experimental

### 3.1. Way to evaluate the amount of surface water

The total amount of surface water was evaluated from the amount of tritium trapped to the surface in the adsorption experiments using tritiated water. In this evaluation, the isotope effect was assumed to be negligible.

The amount of physically adsorbed water was evaluated from the amount of water or tritium that was released from the surface during the purging procedure by a dry gas performed following the adsorption of water or tritiated water at the same experimental temperature. This procedure corresponds to the condition change from case (2) to case (3) in Fig. 1.

The amount of chemically adsorbed water was evaluated using the amount of water or tritium released from the surface when the temperature was elevated after the procedure to drive away the physically adsorbed water by a dry purging gas. This procedure corresponds to the condition change from case (3) to case (4) or that from case (6) to case (7) in Fig. 1. The water released at this procedure includes water both from chemically adsorbed water and structural water. Accordingly, the dissociative adsorption is assumed in formularization of adsorption isotherm of the chemically adsorbed water.

The amount of structural water was evaluated by reducing the amounts of physically adsorbed water and chemically adsorbed water from the amount of surface water.

The sample bed or the sample pipe was pre-dried at 423 or 473 K for several hours to release physically and chemically adsorbed residual water before each run consulting the experimental results of this work. The dry gas with a small amount of water vapor below 1Pa was introduced for more than 6 h to recover structural water at room temperature after this pre-drying procedure.

### 3.2. Experimental apparatus

The same experimental apparatus as those used in the previous studies were also used in this study [1–3]. Details about the experimental apparatus and procedures were stated in the previous papers.

### 3.3. Sample preparation

#### 3.3.1. Piping tube type sample

The test piping tubes used in this study were 304 stainless steel (304 SS) tube (JIS SUS304 TP S-C; stainless steel cold worked seamless pipe), copper tube (JIS A 1100 TD; oxygen-free copper seamless pipe), and aluminum tube (JIS A 1100 TD; aluminum welded pipe). The inner diameter of these tubes was 4.0 mm. The piping tubes 2–3 m in length were used in tritium experiments, and tubes 10–20 m in length were used in water adsorption experiments. The test piping tubes, articles of commerce, were degreased by acetone wash before each experiment.

#### 3.3.2. Particle type sample

The aluminum pellets 2.0 mm in diameter and 2.5 mm in length were used in tritium experiments. They were made from aluminum wire (99.99% purity) from NILACO. The aluminum pellets were subsequently washed with 10% sodium hydroxide solution at 343 K and 15% nitric acid solution at room temperature. After the alkali and acid wash, the aluminum pellets were washed in distilled water and then dried in the room air.

The 304 SS spherical particles 2.0 mm in diameter with mirror-finished surface from Amatsuji Koukyu Seisakusho were also used in tritium experiments. Some 304 SS spheres were used in some tritium trapping experiments after only the acetone wash and others were used after oxidation at 973 K in the air following acetone wash.

## 4. Results and discussion

### 4.1. Physically adsorbed water

Example of the amount of physically adsorbed water is shown in Figs. 2–4 for copper, 304 SS and aluminum tubes. These figures imply that the amount of tritium adsorbed onto the piping surface is not negligible at consideration of the tritium behavior in a tritium processing system because about 10 Ci of physically adsorbed tritium is expected on a square meter of the metal surface when it is placed in the atmosphere where vapor pressure of tritiated water is about 10 Pa. The observed amount of physically adsorbed water on 304 SS, aluminum or copper surface is well represented by the Langmuir type adsorption isotherm as shown in these figures. The Langmuir equations obtained in this study are compared in Table 1.

In the case of stainless steel, however, it is observed in this study that difference in pre-treatment of the sample surface gives strong effect on the trapping capacity of tritium as discussed later.

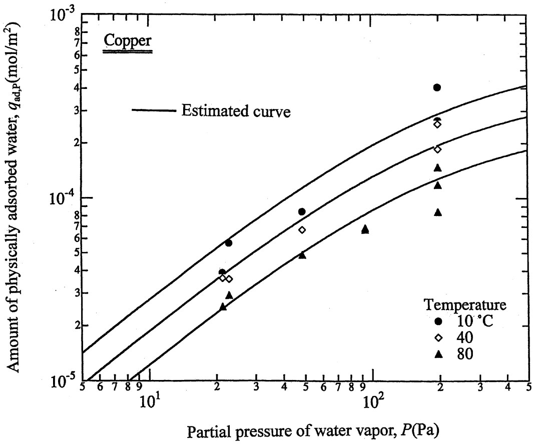

Fig. 2. Amount of physically adsorbed water on copper surface.

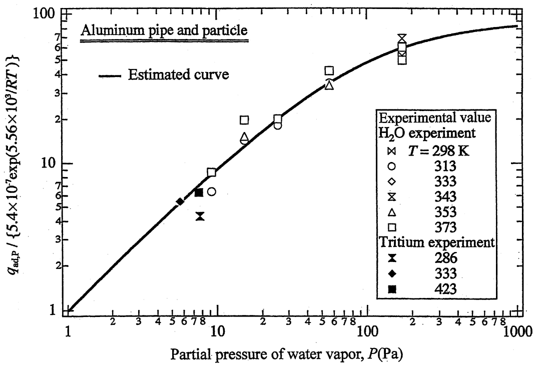

Fig. 3. Amount of physically adsorbed water on aluminum surface.

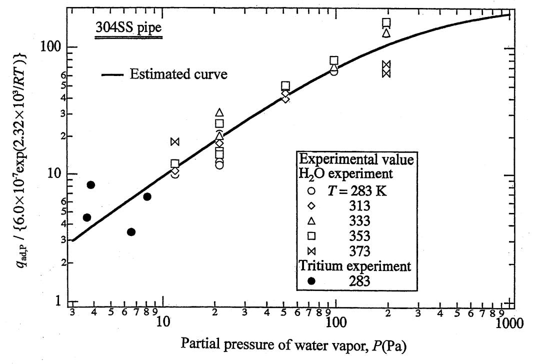

Fig. 4. Amount of physically adsorbed water on surface of stainless steel tube.

### 4.2. Chemically adsorbed water

The observed values of the amount of chemically adsorbed water is shown in Fig. 5 for aluminum where observed values for $q'_{ad,C}$ are compared with the correlated values, here $q'_{ad,C}$ represents the amount of water released from the surface when the temperature is elevated to 373 K following the purging operation to drive out the physically adsorbed water.

$$q'_{ad,C} = (q_{ad,C} - q_{ad,C\ at\ 373\,K}) + (q_{str} - q_{str\ at\ 373\,K}). \tag{7}$$

This figure is made considering that it is better to compare the observed data itself with estimated values because increase of temperature after desorption of the physically adsorbed water gives simultaneous change both in the amount of structural water and that of chemically adsorbed water.

The chemically adsorbed water on aluminum or stainless steel is rather smaller than the physically adsorbed water judging from the results of this work, and almost no chemically adsorbed water is observed on the copper surface.

The adsorption equation of the chemically adsorbed water is represented by the adsorption isotherm considering the dissociative adsorption, and the adsorption constant and heat of adsorption observed in this study. These are also compared in Table 1.

In the case of stainless steel, the surface condition gives a similar effect on chemically adsorbed water as in the case of physically adsorbed water.

The experimental results of this study show that the amount of chemically adsorbed water becomes negligible after purging with dry gas at the higher temperature than 373 K.

### 4.3. Structural water

The amount of structural water is shown in Fig. 6 for an aluminum tube and the 304 SS particle with

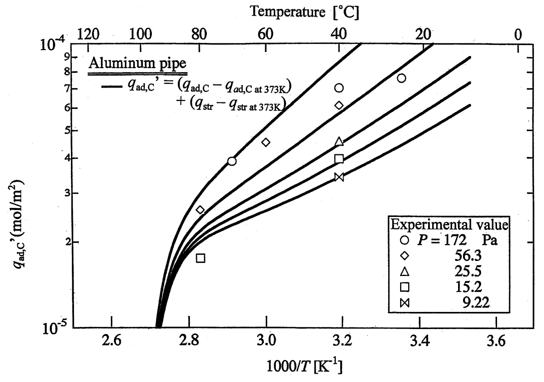

Fig. 5. Comparison of $q'_{ad,C}$ on aluminum surface.

Table 1
Equations obtained for water of various type on metal surface

| | | |
|---|---|---|
| Aluminum | Physical adsorption | $q_{\mathrm{ad,p}} = \dfrac{5.4\times10^{-7}P\exp(5.56\ \mathrm{kJ}/RT)}{1+1.1\times10^{-2}P}$ |
| | Chemical adsorption | $q_{\mathrm{ad,C}} = 4.15\times10^{-9}P^{1/2}\exp(\dfrac{19.5\ \mathrm{kJ}}{RT})$ |
| | Structural water | $q_{\mathrm{str}} = 6.2\times10^{-5} + \dfrac{3.9\times10^{-30}\exp(180\ \mathrm{kJ}/RT)}{1+8.9\times10^{-26}\exp(180\ \mathrm{kJ}/RT)}$ |
| Copper | Physical adsorption | $q_{\mathrm{ad,p}} = \dfrac{4.72\times10^{-8}P\exp(9.7\ \mathrm{kJ}/RT)}{1+5.0\times10^{-3}P}$ |
| | Chemical adsorption | $q_{\mathrm{ad,C}} = 0$ |
| | Structural water | $q_{\mathrm{str}} = \dfrac{2.1\times10^{-10}\exp(35\ \mathrm{kJ}/RT)}{1+8.0\times10^{-6}\exp(35\ \mathrm{kJ}/RT)}$ |
| 304SS | Physical adsorption | $q_{\mathrm{ad,p}} = \dfrac{2.82\times10^{-6}P\exp(2.32\ \mathrm{kJ}/RT)}{1+4.5\times10^{-3}P}\alpha_{\mathrm{f}}$ |
| | Chemical adsorption | $q_{\mathrm{ad,C}} = \dfrac{1.93\times10^{-23}P^{1/2}\exp(121\ \mathrm{kJ}/RT)}{1+8.2\times10^{-19}\exp(121\ \mathrm{kJ}/RT)}\alpha_{\mathrm{f}}$ |
| | Structural water | $q_{\mathrm{str}} = \dfrac{3.06\times10^{-8}\exp(27\ \mathrm{kJ}/RT)}{1+3.6\times10^{-4}\exp(27\ \mathrm{kJ}/RT)}\alpha_{\mathrm{f}}$ |

mirror-finished surface. It is known from this figure that an nonnegligible amount of the tritium trapping capacity remains even after chemically adsorbed water is taken away by the drying operation at the elevated temperature. The correlated equations for structural water obtained in this study are compared in Table 1.

On the fresh aluminum surface exposed to the room air, a thin oxide layer called bayerite (β-$Al_2O_3{\cdot}3H_2O$) is rapidly formed, and heating above 363 K changes the bayrite layer to the oxide layer of boehmite (α-$Al_2O_3{\cdot}H_2O$). Rather sudden change of structural water on the aluminum surface at around 373 K corresponds to the change in the nature of the oxide layer.

### *4.4. Surface condition factor of stainless steel*

It is observed in this study that the amount of surface water on stainless steel is different by ways of pretreatment. For instance, sorption capacity of water to the mirror-finished surface is about five times larger than that to the surface of the commercial tube. The reported values of the tritium trapping capacity onto the 304 SS plate are about three to five times larger than that to the mirror-finished surface, where the plate is left in the room air for more than one year after acetone wash. It is supposed in this study that the sorption behavior varies with surface condition and that sorption amount of each type of water on surface is proportional to the surface condition factor $\alpha_{\mathrm{f}}$ where it is considered by the present authors that the amount of surface water varies with thickness and chemical composition of the oxide layer though physical meaning of the surface condition factor

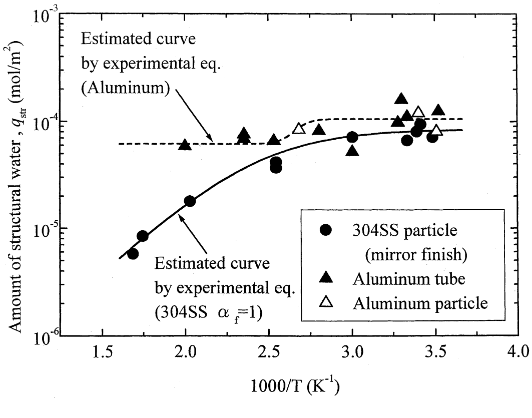

Fig. 6. Amount of structural water on aluminum and 304 SS with mirror-finished surface.

Table 2
Comparison of surface condition factor

| | |
|---|---|
| 304 SS plate or pipe (more than 1 year in room air) [2] | $\alpha_f = 3 \sim 5$ |
| 304 SS particle with mirror-finished surface | $\alpha_f = 1.0$ (taken as standard) |
| 304 SS particle oxidized in air at 973 K | $\alpha_f = 0.74$ |
| 304 SS commercial tube(acetone washed) | $\alpha_f = 0.21$ |
| 316 SS polished plate [7] | $\alpha_f \sim 1$ |
| 304 SS plate [8] | $\alpha_f = 2 \sim 4$ |

is rather obscure at present. The value of $\alpha_f$ obtained in this study are listed in Table 2. As shown in Fig. 7, the correlative equations obtained in this way represent well the observed values of tritium trapping capacity on the surface of 304 SS pre-treated in various ways. It is supposed by the present authors that the tritium trapping capacity estimated from the data by Hirabayashi and Saeki [7] is almost the same as that obtained for the 304 SS particle with mirror-finished surface because their data show linear increase in tritium amount on the polished 316 SS surface with time even after 36 days. The value of $\alpha_f$ for the stainless steel plate used by Dickson and Miller [8] seems to be around 4 as compared in this figure.

In the case when the anode oxidation method is applied to the aluminum surface, a thick and porous oxide layer is formed. Then, the large tritium trapping on the aluminum surface as 1000 Ci/m$^2$ reported by Walthers et al. [9] can be explained using the surface condition factor also on aluminum.

Further discussion about the effect of the surface condition on tritium trapping performances from the viewpoint of material science is required though a simple value is given to $\alpha_f$ in this study because the purpose of this study is to know if the tritium trapping capacity on piping materials used in the construction of a tritium processing system is large enough or not to cause the system effect of tritium.

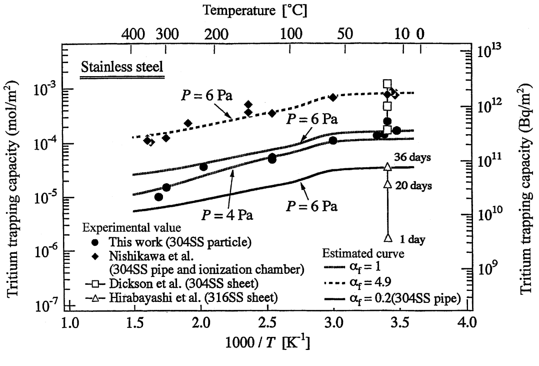

Fig. 7. Tritium trapping capacity on various surfaces of stainless steel.

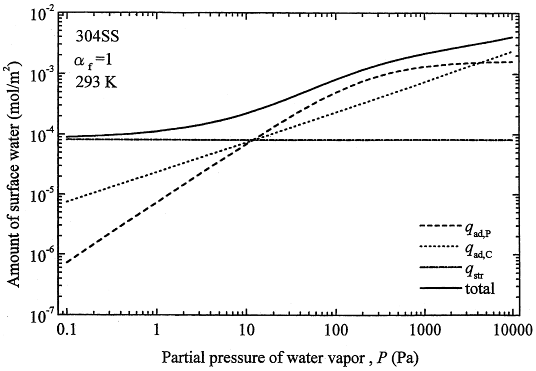

Fig. 8. Contribution of physically adsorbed water, chemically adsorbed water and structural water to tritium trapping capacity of stainless steel at 293 K.

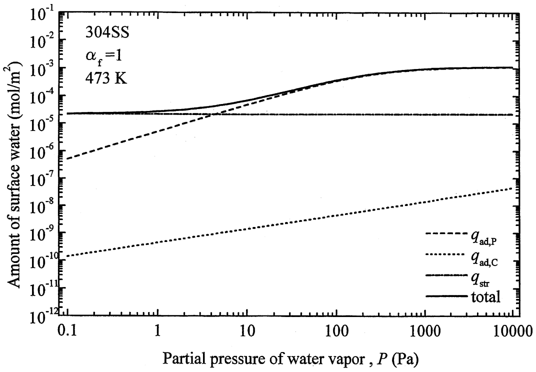

Fig. 9. Contribution of physically adsorbed water, chemically adsorbed water and structural water to tritium trapping capacity of stainless steel at 473 K.

The contribution of physically adsorbed water, chemically adsorbed water and structural water to the tritium trapping capacity is compared in Figs. 8 and 9 taking the mirror-finished 304 SS as example. The physically and chemically adsorbed water control the tritium trapping capacity when the vapor pressure of water including tritiated water is above several tens of pascals at room temperature, though structural water decides the tritium trapping capacity when the vapor pressure is below several pascals. The contribution of chemically adsorbed water becomes negligible when the temperature is above 373 K. It is also known from these figures that the tritium trapping capacity of about 10 Ci/m$^2$ remains on the mirror-finished 304 SS surface after the purging operation using dry gas following the contact with inert gas having water of 10 Pa at room temperature. Even after the purging operation with 473 K dry gas, structural water corresponding to the trapping capacity of 1.5 Ci/m$^2$ is retained. These values cannot be ignored in estimation

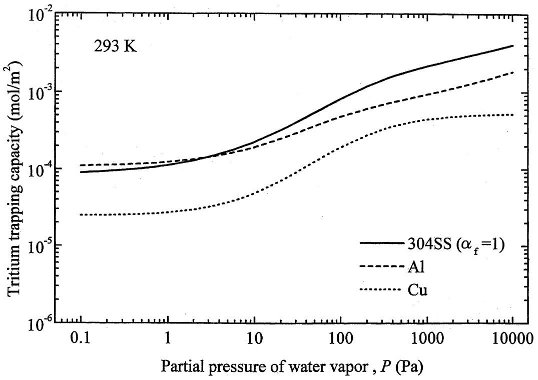

Fig. 10. Comparison of tritium trapping capacity at 293 K.

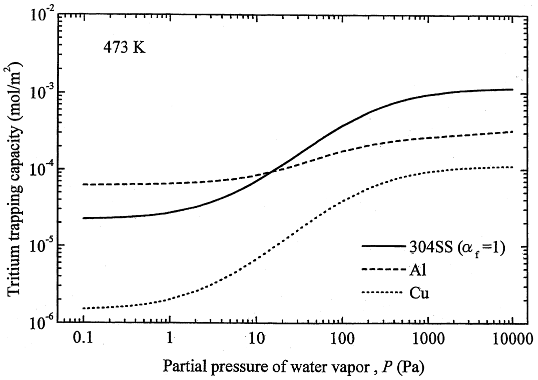

Fig. 11. Comparison of tritium trapping capacity at 473 K.

of the system effect of tritium in the case when not so much amount of tritium, in molecular or oxide form is handled.

The tritium trapping capacity is compared for 304 SS with mirror-finished surface, aluminum and copper in Figs. 10 and 11. Almost the same amount of tritium is trapped to the 304 SS with mirror-finished surface and aluminum when the vapor pressure is below several tens of pascals at the room temperature, though 304 SS traps about two times more tritium at the higher vapor pressure than 100 Pa. The amount of tritium trapped to the copper surface is only one-fifth of the tritium trapped to the surface of aluminum or mirror-finished 304 SS at room temperature. Also at an elevated temperature more tritium is trapped to the 304 SS with mirror-finished surface than tritium to aluminum when vapor pressure is larger than several tens of pascals because of the contribution from physically adsorbed water. Though two to three times more tritium is trapped to the aluminum surface than to the 304 SS with mirror-finished surface at the lower vapor pressure because of the difference in the amount of structural water. Among three materials examined in this study, copper gives the smallest trapping capacity even at an elevated temperature.

## 5. Conclusion

The amount of water on the surface of 304 stainless steel, copper and aluminum is quantified in this study where water on the surface is classified into physically adsorbed water, chemically adsorbed water and structural water. The conclusions are as follows.

1. The amount of surface water on each material examined in this study gives non-negligible tritium trapping capacity in estimation of the system effect of tritium.
2. Copper gives the smallest tritium trapping capacity among three materials examined in this study.
3. The tritium trapping capacity onto stainless steel varies with ways of surface pre-treatment, and the surface condition factor is introduced to express the difference.

Further phenomenal discussion from the viewpoint of material science is expected because the results of this study show that interaction of tritium with the surface of construction or piping materials gives large effect on the behavior of tritium, and that the trapping phenomena of tritium is largely dependent on the surface condition of the materials.

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