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Study on behavior of tritium in concrete wall

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Abstract

It is required to understand the tritium behavior in concrete for establishment of tritium safety technology of a fusion reactor or a tritium handling facility because the concrete wall is used as the final containment to prevent tritium release to the environment. This paper discusses about the effect of adsorption and diffusion of water and isotope exchange reaction between physically adsorbed water and chemically adsorbed water or structural water. It is known in this study that a large amount of tritium can be trapped to the concrete wall because cement paste has the nature of porous hydrophilic material. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Release of tritium to the environment should be prevented to secure the tritium safety of a fusion reactor. In a tritium handling facility, the multi-containment system is used to recover tritium leaked from the barrier of the primary containment system to prevent the transfer of tritium to the circumferential atmosphere.

The concrete wall is usually used as the barrier of the final containment of a tritium handling facility. Furthermore, a concrete wall will be used to separate a room that may have an atmosphere with high tritium concentration in a fusion reactor system. Accordingly, it is necessary to understand the

transfer behavior of tritium through the concrete materials.

Concrete, which is a porous hydrophilic material, consists of cement paste, water and aggregates such as sands and small stones. The tritium behavior in the cement paste is discussed in this paper because the cement paste is the key material of concrete.

Although there are some reports on the behavior of tritiated water in concrete materials [1–4], the article about the behavior of water vapor particularly on low humidity has been hardly reported. The adsorption isotherm of physically adsorbed water or chemically adsorbed water and diffusion coefficient of water vapor in the cement paste have been reported in the previous paper by the present authors [5].

The over all mass transfer coefficients representing adsorption of water vapor onto the cement surface and that representing isotope exchange reaction in the matrix of cement paste are experimentally obtained in this paper. Behavior of tritium in a

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concrete wall in various conditions is discussed by simulation using properties obtained in this study.

2. Theory

Fig. 1 shows the picture of cement paste obtained using a scanning electric microscope (SEM). As the cement paste is a hydrophilic porous material having nature resembling to adsorbent such as zeolite or silica gel, cement wall must be treated as the huge body of adsorbent. Therefore it is considered by the present authors that the following transfer processes can give contribution to the permeation behavior of tritiated water through the cement paste as:

(a) adsorption of water vapor on cement paste,
(b) diffusion of water through the matrix of cement paste,
(c) isotope exchange reaction among physically adsorbed water, chemically adsorbed water and structural water in cement paste and
(d) desorption of water vapor from cement paste.

The physically adsorbed water, chemically adsorbed water and structural water in various metal surface were defined by Nishikawa et al. [6]. The physically adsorbed water, chemically adsorbed water and structural water also exist in cement paste, and those have been already quantified by the present authors in the previous paper [5] using the packed bed with cement particles. Although the physically adsorbed water and chemically adsorbed water occur the phenomena of
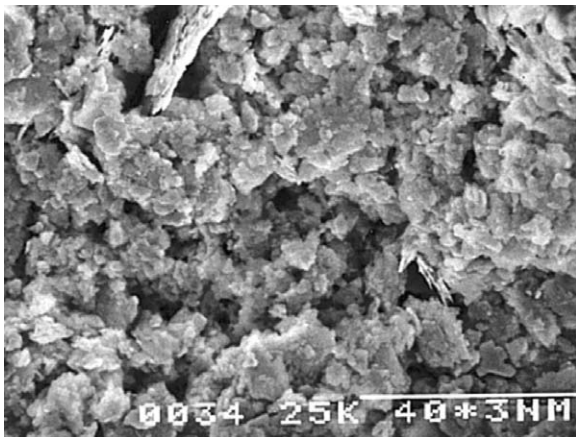

Fig. 1. SEM photograph of cement paste surface.

adsorption and desorption of water vapor essentially, the condition of concrete wall is almost about room temperature. Therefore it is sufficient to adsorb the water vapor in concrete materials due to only physically adsorbed water in this paper. In accordance with this consideration, it is not discriminated between chemically adsorbed water and structural water in this paper, hence it should be discriminated them at high temperature such as over 373 K. Fig. 2 shows the permeation model constructed in this study where tritium permeates through the cement paste wall from the flow with high concentration tritium to the flow with low concentration tritium. Ph., Ch. and St. in Fig. 2 mean physically adsorbed water, chemically adsorbed water and structural water in cement paste, respectively. Another symbols in Fig. 2 were used the same symbol as the equations in this report. Diffusing water in cement paste is physically adsorbed water in this model, because it is considered for diffusivity of water in cement paste that the driving force of diffusivity is the gap of concentration of adsorbed water in cement paste in this study. In the case when H_2O vapor is introduced, the flux of permeation is decided by diffusivity of water in cement paste and the difference of adsorbed amount of H_2O on both sides of the wall. In the case when vapor of tritiated water is introduced, tritium is transferred to chemically adsorbed water and structural water through the isotope exchange reaction. In Fig. 2 and following equations, only water vapor, H_2O, and tritiated water vapor, T_2O, were taken into account for simplification considering that $HTO = 1/2 H_2O + 1/2 T_2O$. It is considered that this consideration was not detrimental to this study because it was not detrimental to Pt-molecular sieve 5A, piping materials and blanket materials [7,8].

The following equations give the mass transfer of H_2O and T_2O between the gas phase and surface layer of cement paste corresponding to the transfer processes listed above as (a) and (d),

$$\frac{\partial q_{H_2O}}{\partial t} = K_{F,ad} \cdot a \cdot X_1 \cdot \left(C_{H_2O} + C_{T_2O} - C^*_{H_2O+T_2O} \right), \quad (1)$$

and

$$\frac{\partial q_{T_2O}}{\partial t} = K_{F,ad} \cdot a \cdot X_2 \cdot \left(C_{H_2O} + C_{T_2O} - C^*_{H_2O+T_2O} \right), \quad (2)$$
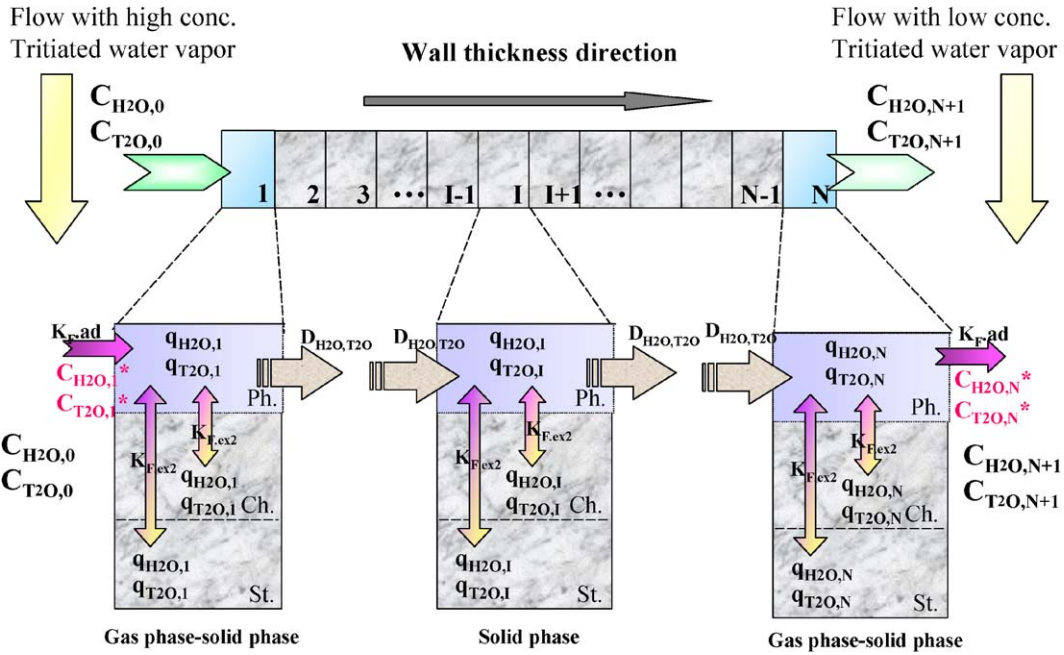
Fig. 2. Permeation model for tritiated water in cement paste.

For $C_{H_2O} + C_{T_2O} - C^*_{H_2O+T_2O} \geqslant 0$,

$$X_1 = \frac{C_{H_2O}}{C_{H_2O} + C_{T_2O}}, \quad X_2 = \frac{C_{T_2O}}{C_{H_2O} + C_{T_2O}}, \quad (3)$$

For $C_{H_2O} + C_{T_2O} - C^*_{H_2O+T_2O} \leqslant 0$,

$$X_1 = \frac{q_{H_2O}}{q_{H_2O} + q_{T_2O}}, \quad X_2 = \frac{q_{T_2O}}{q_{H_2O} + q_{T_2O}}. \quad (4)$$

where q_{H_2O} and q_{T_2O} are the amount of adsorbed water and tritiated water on the volume of cement paste (mol/m³), respectively, $C^*_{H_2O+T_2O}$ is the total concentration of water and tritiated water vapor in the gas phase equilibrated to the amount of water and tritiated water adsorption (mol/m³), $K_{F,ad}$ is the overall mass transfer coefficient representing the adsorption of water vapor (m/s), a is the specific surface area of the cement paste (m²/m³), C_{H_2O} and C_{T_2O} are the concentrations of water vapor and tritiated water vapor in the gas phase (mol/m³), respectively.

Mass balance of physically adsorbed water at a control volume of the cement paste is shown by,

$$\frac{\partial q_{H_2O,P}}{\partial t} = \frac{\partial}{\partial x}\left(D_{H_2O}\frac{\partial q_{H_2O,P}}{\partial x}\right) - \frac{\partial q_{H_2O,C}}{\partial t} - \frac{\partial q_{H_2O,S}}{\partial t}, \quad (5)$$

and

$$\frac{\partial q_{T_2O,P}}{\partial t} = \frac{\partial}{\partial x}\left(D_{T_2O}\frac{\partial q_{T_2O,P}}{\partial x}\right) - \frac{\partial q_{T_2O,C}}{\partial t} - \frac{\partial q_{T_2O,S}}{\partial t}. \quad (6)$$

Mass balance of chemically adsorbed water at a control volume of the cement paste is shown by,

$$\frac{\partial q_{H_2O,C}}{\partial t} = K_{F,ex2} \cdot a \cdot (q_{H_2O,P} + q_{T_2O,P})$$
$$\times \left\{\frac{q_{H_2O,P}}{q_{H_2O,P} + q_{T_2O,P}} - \frac{q_{H_2O,C}}{q_{H_2O,C} + q_{T_2O,C}}\right\}, \quad (7)$$

and

$$\frac{\partial q_{T_2O,C}}{\partial t} = K_{F,ex2} \cdot a \cdot (q_{H_2O,P} + q_{T_2O,P})$$
$$\times \left\{\frac{q_{T_2O,P}}{q_{H_2O,P} + q_{T_2O,P}} - \frac{q_{T_2O,C}}{q_{H_2O,C} + q_{T_2O,C}}\right\}. \quad (8)$$

Mass balance of structural water at a control volume of the cement paste,

$$\frac{\partial q_{H_2O,S}}{\partial t} = K_{F,ex2} \cdot a \cdot (q_{H_2O,P} + q_{T_2O,P})$$
$$\times \left\{\frac{q_{H_2O,P}}{q_{H_2O,P} + q_{T_2O,P}} - \frac{q_{H_2O,S}}{q_{H_2O,S} + q_{T_2O,S}}\right\}, \quad (9)$$

and

$$\frac{\partial q_{T_2O,S}}{\partial t} = K_{F,ex2} \cdot a \cdot (q_{H_2O,P} + q_{T_2O,P})$$

$$\times \left\{ \frac{q_{T_2O,P}}{q_{H_2O,P} + q_{T_2O,P}} - \frac{q_{T_2O,S}}{q_{H_2O,S} + q_{T_2O,S}} \right\}, \quad (10)$$

where $K_{F,ex2}$ is the overall mass transfer coefficient representing the isotope exchange reaction in the cement paste (m/s), D_{H_2O} and D_{T_2O} are the diffusion coefficient of water vapor and tritiated water vapor in the cement paste (m^2/s), and the subscripts P, C and S, in above equations mean physically adsorbed water, chemically adsorbed water and structural water, respectively. The isotope exchange reaction is the phenomenon that occurs among physically adsorbed water and chemically adsorbed water or structural water when there are differences of H/T ratio among physically adsorbed water and chemically adsorbed water or structural water.

Mass balance of H_2O and T_2O in gas phase of the flow channel are given as

$$\frac{\partial C_{H_2O}}{\partial t} + u \frac{\partial C_{H_2O}}{\partial z} + \frac{A}{V_g} Q_{H_2O} = 0, \quad (11)$$

$$\frac{\partial C_{T_2O}}{\partial t} + u \frac{\partial C_{T_2O}}{\partial z} + \frac{A}{V_g} Q_{T_2O} = 0, \quad (12)$$

where u is superficial velocity (m/s), z is the length in the direction of gas flow (m) and A (m^2) is effective permeation area, V_g (m^3) is volume of flow channel and Q (mol/m^{2}s) is the molar flux of mass transfer between gas phase and surface layer of cement paste.

3. Experimental

3.1. Packed bed of cement particles

A packed bed of cement particles was used to quantify $K_{F,ad}$ by using the breakthrough method. Three-months-old ordinary Portland cement paste with a water/cement ratio of 0.6 was used for all experiments. The 12–16 mesh cement particles of 0.5 g were packed in a quartz tube of 8 mm diameter and the height of sample bed was 13 mm. The schematic diagram of the experimental apparatus for water adsorption is shown in Fig. 3. The H_2/N_2 gas was changed to the H_2O/N_2 gas by passing through the CuO bed at 573 K. After drying of the cement sample with the N_2 gas till the water vapor of outlet of sample bed is below 1 Pa, the H_2O/N_2 gas was introduced into the sample bed at the flow rate of 400 cm^3/min. H_2O pressure was
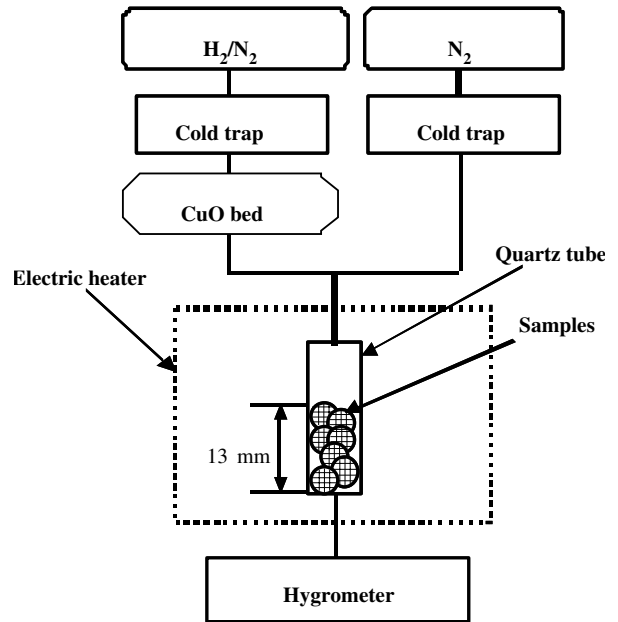

Fig. 3. Experimental apparatus for adsorption of water vapor.

introduced between 40 Pa and 1000 Pa of water vapor. The change of the concentration of water vapor in the exit gas was measured with time by a hygrometer until the adsorption of water vapor on the cement sample came to an equilibrium state. The other experimental data of cement particles sample are shown in Table 1.

3.2. Apparatus to measure permeation rate through cement wall

The permeability of water vapor through cement paste was measured in this study using a tube made of cement paste. The experimental apparatus for permeation is shown in Fig. 4. A reaction tube was a double tube structure, which consists of a quartz tube (outside) and a sample tube (inside). This cement permeation tube had 13 mm outside diameter, 6 mm inside diameter and 42 mm length.

After drying of the cement sample with He gas till the water vapor of outlet of each channel is

Table 1
Experimental condition for adsorption of water vapor

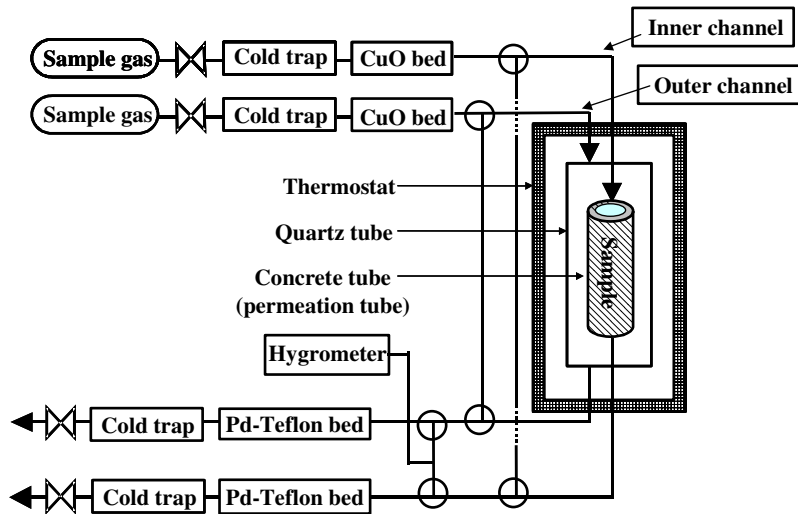|	
Water/cement(W/C)	0.60
Density of cement sample (g/cm^3)	1.60
Flow rate (cm^3/min)	400
Amount of cement particle (g)	0.50
Porosity of packed bed (–)	0.759
Diameter of cement particle (mm)	1.0–1.41

Fig. 4. Experimental apparatus for permeation of heavy water vapor.

Table 2
Experimental condition for permeation of heavy water vapor

Water/cement(W/C)	0.60
Density of cement sample (g/cm^3)	1.60
Thickness of cement sample (g/cm^3)	3.50
Hight of cement sample (mm)	42.0
Inside diameter of cement tube (mm)	6.0
Outside diameter of cement tube (mm)	13.0
Flow rate (cm^3/min)	400.00

below 4 Pa, the D_2O/He gas, which was made by the same way of the adsorption experiment, was provided into the inside path of the sample tube. The change of the concentration of moisture gas at the exit of the sample bed was measured with time. The total amount of H_2O, HDO and D_2O was measured by a hygrometer, and that of HDO and D_2O was measured by a gas chromatograph at liquid N_2-temperature after converting D_2O and HDO to D_2 and HD by passing the sample gas through a packed bed with Pd–Teflon catalyst at 473 K. The permeation experiment using heavy water vapor was continued until the permeation of heavy water vapor through the cement sample came to an equilibrium condition. The other data of cement tube sample are shown Table 2.

4. Results and discussion

4.1. Overall mass transfer coefficient representing adsorption

Fig. 5 shows the breakthrough curve of 40 Pa H_2O vapor obtained at the experiment using the
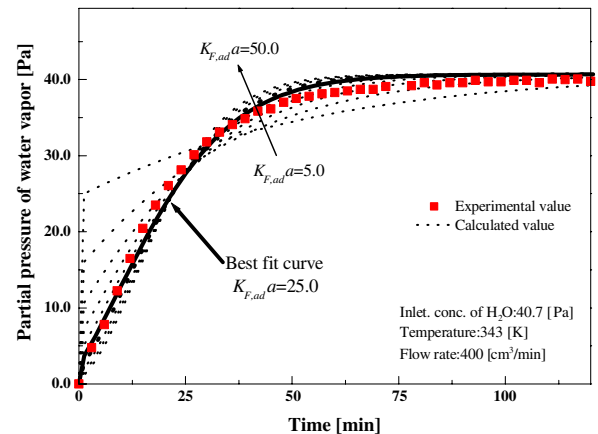

Fig. 5. Comparison of adsorption breakthrough curve using H_2O with calculated values.

packed bed of cement particles by way of example. Comparison of the numerically estimated curve applying Eqs. (1), (3), (4) and (11) shows that the value of $25.0\,(s^{-1})$ for the overall mass transfer capacity coefficient, $K_{F,ad}a$, gives the best fit curve to the experimental data.

$$K_{F,ad}a = 25.0\ (s^{-1}). \tag{13}$$

This value of the overall transfer capacity coefficient, $K_{Fad}a$, also applied to other water vapor conditions. The grain size of the cement paste was measured by using a scanning electron microscope (SEM) shown in Fig. 1, and the specific surface area, $a\,(m^{-1})$, was estimated as,

$$a = 1.91 \times 10^5\ (m^{-1}). \tag{14}$$

therefore, $K_{F,ad}$ was given by the following value,

$$K_{F,ad} = 1.31 \times 10^{-4} \ (m/s). \tag{15}$$

4.2. Overall mass transfer coefficient representing isotope exchange reaction

Fig. 6 shows the change of concentration of water vapor and heavy water vapor with time at the exit of the outer channel for the case when the D_2O vapor pressure in the He gas introduced to the inner channel is 1263.6 Pa. Even though D_2O vapor was introduced to the inner channel, only H_2O was observed in the outer channel at the initial stage of the experiment because of the isotope exchange reaction in the matrix of cement paste. The D_2O concentration increased as the isotope exchange reaction came to an equilibrium state. As discussed later the breakthrough curve (1) for H_2O coincides with the breakthrough curve obtained when only H_2O is introduced to the inner channel.

The calculated breakthrough curves shown in Fig. 6 were obtained by solving numerically the Eqs. (1)–(12) using $K_{F,ex}$ as the parameter. In this calculation the diffusion coefficient of H_2O obtained in the previous paper, $D_{H_2O} = 1.30 \times 10^{-10} \ (m^2/s)$, was used as the diffusion coefficient of D_2O assuming that the isotope effect is negligible. Comparison of the estimated curves with observed data gives the best fit curve of 3.0 (s^{-1}) for $K_{F,ex}a$.

$$K_{F,ex}a = 3.0 \ (s^{-1}). \tag{16}$$

Then, $K_{F,ex}$ was given as,

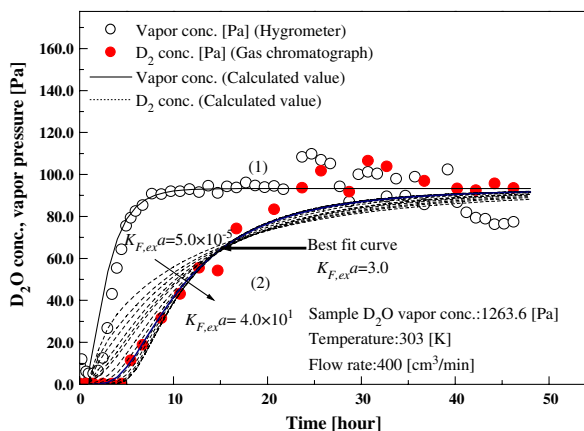$$K_{F,ex} = 1.57 \times 10^{-5} \ (m/s). \tag{17}$$

Fig. 6. Permeation experiment using heavy water vapor in cement paste.

Comparison of Eqs. (13) and (16) shown that the isotope exchange reaction is about one order slower than the adsorption reaction.

The isotope exchange capacity, S, in the cement paste was calculated by integrating the difference between the breakthrough curve (1) for total water vapor and curve (2) for D_2O. The isotope exchange capacity means total amount of water used as isotope exchange reaction in chemically adsorption water and structural water.

$$S = 1.24 \times 10^{-3} \ (mol/g\text{-}cement). \tag{18}$$

The isotope exchange capacity observed in this study is about 15% of the amount of chemically adsorbed water and structural water reported in the previous paper of the present authors, and is about 20% of the reported value by Numata et al. [9]. The adsorption amount of physically adsorbed water estimated from the curve (1) in Fig. 6 is also only 24% of the estimated amount from the adsorption isotherm reported in the previous paper [5]. It is considered for small isotope exchange capacity and small amount of adsorbed water that the there may exist short cut paths in the wall of cement paste tube.

4.3. Estimation of permeation behavior of tritiated water through cement wall

4.3.1. Comparison of tritiated water permeation and water vapor permeation

To compare the difference of water vapor and tritiated water vapor behavior in permeation through the cement paste, simulations were carried out by using experimental results in this study assuming that the overall mass transfer coefficient representing the exchange reaction for heavy water could be used for tritiated water considering that there is only a little isotope effect between the behavior of heavy water vapor and tritiated water vapor in cement paste. Isotope exchange capacity in cement paste was applied to total amount of chemically adsorbed water and structural water at simulations. Change of H_2O concentration in cement paste is shown in Fig. 7 for the case when a wall of dried cement paste with thickness of 0.05 m is placed between the air with vapor pressure of 3167 Pa and the air with no water vapor. This figure shows that more than one month is required to make an equilibrium condition for water permeation through the cement paste wall with thickness of 0.05 m. Other estimations show that it takes more
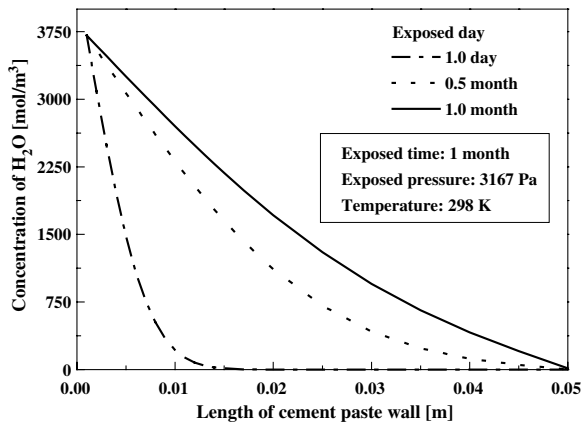
Fig. 7. Distribution of H_2O concentration in cement paste wall.

than several years to have equilibrium condition when thickness is 1.0 m.

Change of tritiated water concentration in cement paste is shown in Fig. 8 for the case when the cement paste wall is placed between the air with tritiated water vapor of 3167 Pa and the dry air for one month. It is known from comparison of Figs. 7 and 8 that existence of the chemically adsorbed water and structural water, in other wards isotope exchange capacity, makes the tritium uptake larger. It is also known from Fig. 8 that the permeation behavior of H_2O released from the chemically adsorbed water and structural water through the isotope exchange reaction becomes similar to the behavior of H_2O introduced to the wall surface. These observations imply that reported in the previous paper [5]. The decontamination of tritium with drying procedure does not give the effective result
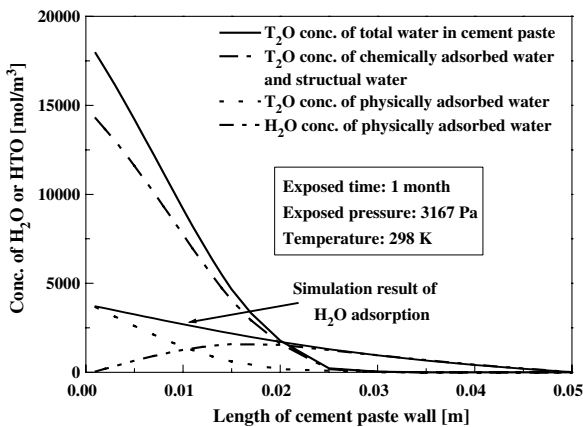
because only physically adsorbed waters can be taken out with dry gas purge.

4.3.2. Permeation behavior of tritiated water released to a room surrounded with cement wall

In this reaction permeation behavior of tritiated water released to a room surrounded with cement walls is discussed. The tritium handling room used in this simulation is a cube with 10 m in length and has the 0.1 m thickness wall made of cement paste. It is also assumed that five wall faces are effective for water permeation to the outer space. Other conditions at this estimation are listed in Fig. 9 and Table 3. The simulation stops when the breakthrough time t_B is obtained where t_B means the time when 1% of the initially released tritium is transferred to the outer atmosphere. Figs. 10 and 11 show the change of the tritium concentration profile in the wall of cement paste for the case when tritiated water is released to a small room having volume of $1000 \, m^3$ kept in an outer room of which space is $10^{10} \, m^3$. It is known from comparison of Figs. 10 and 11 that tritium profiles in the cement paste wall have almost no effect from the initial vapor pressure in a small room notwithstanding the direction of flow of H_2O which is decided from the vapor pressure in a small room and that in a outer room. This is also known from comparison in Fig. 12, which shows the change of tritium concentration in a small room with time. The breakthrough time t_B of tritium obtained for various conditions is compared in Table 3 and this Table shows that t_B for tritiated water is 5 times longer than t_B for H_2O. This table also shows that higher vapor pressure in the outer longer room promote the transfer of tritium from the small room because

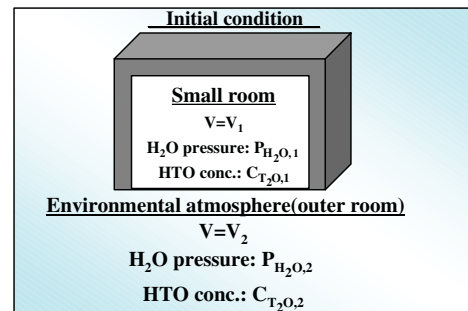Fig. 8. Distribution of HTO concentration in cement paste wall.

Fig. 9. The boundary conditions of the permeating simulation of HTO.

Table 3
Comparison of the permeation rate of water vapor with tritiated water

	$P_{H_2O,1}$ (Pa)	$C_{HTO,1}$ (Bq/m^3)	$P_{H_2O,2}$ (Pa)	$C_{HTO,2}$ (Bq/m^3)	Breakthrough time t_B (1% of initial amount) [in days]
1	3167	0.0	950.1	0.0	73.6
2	3167	4.07×10^8	950.1	0.0	315.5
3	950.1	4.07×10^8	950.1	0.0	317.5
4	100	4.07×10^8	950.1	0.0	318.3
5	3167	4.07×10^8	2533	0.0	287.7
6	950.1	4.07×10^8	2533	0.0	288.1
7	100	4.07×10^8	2533	0.0	289.7

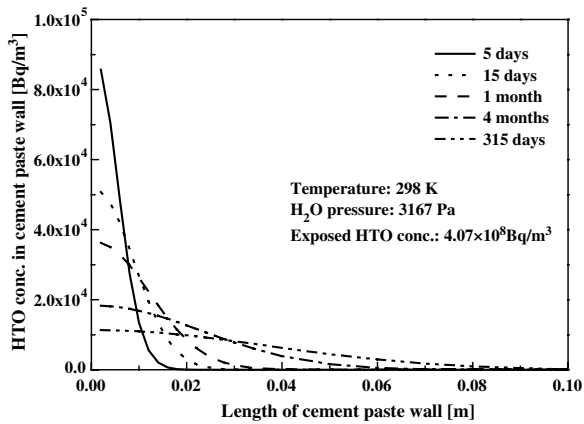*Temperature: 298 K, length of cement paste wall: 0.1 m, $V_1 = 1000 \text{ m}^3$, $V_2 = 10^{10} \text{ m}^3$.

Fig. 10. Distribution of HTO concentration in cement paste wall at H_2O pressure of 3167 Pa.

Fig. 11. Distribution of HTO concentration in cement paste wall at H_2O pressure of 100.0 Pa.
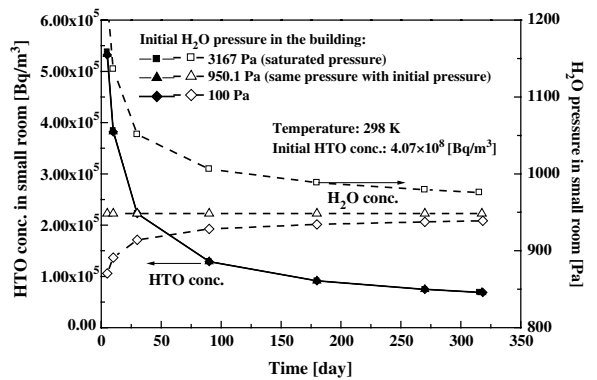
Fig. 12. HTO and H_2O concentration in small room with time.

increase of physically adsorbed water makes the driving force of tritium diffusion larger. This implies that tritiated water permeation to the environmental atmosphere becomes larger when the humidity of the air is higher.

5. Conclusion

The overall mass transfer coefficients representing the adsorption of water vapor and that representing the isotope exchange reaction in the cement paste were experimentally determined in this study. Calculation using the experimental results in this study shows that the existence of the isotope exchange capacity in the cement paste makes the behavior of tritium more complex and tritium inventory larger.

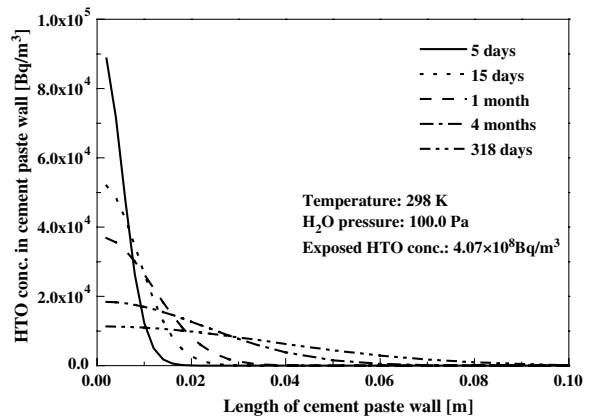Simulation in this study indicates that the humidity in a room gives little effect on permeation of tritium released into a room though the humidity in the environmental air gives effect to some extent.

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