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Tritium inventory in Li_2ZrO_3 blanket

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Abstract

Recently, we have presented the way to estimate the tritium inventory in a solid breeder blanket considering effects of diffusion of tritium in the grain, absorption of water in the bulk of grain, and adsorption of water on the surface of grain, together with two types of isotope exchange reactions. It is reported in our previous paper that the estimated tritium inventory for a $LiAlO_2$ blanket agrees well with data observed in various in situ experiments when the effective diffusivity of tritium from the EXOTIC-6 experiment is used and that the better agreement is obtained when existence of some water vapor is assumed in the purge gas. The same way as used for a $LiAlO_2$ blanket is applied to a Li_2ZrO_3 blanket in this study and the estimated tritium inventory shows a good agreement with data obtained in such in situ experiments as MOZART, EXOTIC-6 and TRINE experiments. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

In order to estimate the release behavior of the bred tritium in a blanket system, it is necessary to know the contribution of such tritium transfer steps as: (1) tritium formation reaction in crystal grain, (2) diffusion of tritium in crystal grain, (3) interaction of tritium with irradiation defects in crystal grain, (4) adsorption of tritium on grain surface, (5) absorption of tritium into crystal grain, (6) isotope exchange reaction between gaseous hydrogen, H_2, in the gas stream and tritium on grain surface (isotope exchange reaction 1), (7) isotope exchange reaction between water vapor, H_2O, in the gas stream and tritium on grain surface (isotope exchange reaction 2), (8) water formation reaction on addition of H_2 to the blanket purge gas, (9) transfer of hydrogen isotopes and water through pores of the sintered pellet and (10) transfer of hydrogen isotopes and water through boundary layer formed on the surface of a sintered pellet to the gas stream, together with the system effect of tritium, which consists of (11) adsorption of tritium on piping surface, (12) isotope exchange reaction between gaseous tritium, HT or T_2, in the gas stream and water or –OH bases on piping surface, (13) isotope exchange reaction between tritiated water in the gas stream and water or –OH bases on piping surface, (14) permeation of tritium through piping materials, (15) absorption of tritium in piping materials and (16) flow condition of purge gas in each sub-unit constituting the blanket piping system, and the tritium behaviors in the monitor system such as (17) memory effect and (18) Jesse effect.

We have quantified the amount of water captured in Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4 in the previous papers [1–4] and have compared the tritium inventory in the blanket due to adsorption with that due to diffusion in the crystal grain, and have pointed out that inventory due to adsorption is much larger than that due to diffusion unless a large amount of H_2 or water vapor is added to the purge gas in the high temperature blanket when the grain size is smaller than 10 μm.

Occurrence of water formation in beds of various ceramic breeder materials on introduction of hydrogen to the purge gas has been reported by us [5]. This implies that effect of water vapor cannot be disregarded in consideration of tritium behavior in the blanket and that

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two types of isotope exchange reactions stated above should compete with each other on the surface of blanket materials when H_2 is added to the blanket purge gas.

Recently, we have presented the way to estimate the tritium inventory in a uniform solid blanket under the steady-state condition considering diffusion, absorption, adsorption and isotope exchange reactions [6]. The estimated tritium inventory for a $LiAlO_2$ blanket using our model agrees well with data observed in various in situ experiments such as LILA-3 [7], TEQUILA-1 [8], CORELLI-2 [9], MOZART [10], and EXOTIC-6 [11] experiments. It is also reported in our previous reports that better agreements are observed when the effectiveness correction factor representing the relative values in reaction rate of two isotope exchange reactions is introduced, and when existence of some water vapor is assumed in the purge gas. The same method as that used in calculation of the tritium inventory in a $LiAlO_2$ blanket is applied to estimate the tritium inventory in a Li_2ZrO_3 blanket in this study, and comparisons of the estimated tritium inventory with data from several in situ experiments are performed.

2. Inventory estimation method

Contributions of diffusion inventory in crystal grains I_D, absorption inventory in bulk of lithium ceramic I_{ab}, adsorption inventory on the grain surface I_{ad} and inventory due to the isotope exchange capacity on the grain surface I_{ex}, are discussed in our previous papers [12], and the total tritium inventory in the blanket packed with solid breeder particles made of spherical grains I_{Total} is given as

$$\begin{aligned} I_{Total} &= I_D + I_{ab} + I_{ad} + I_{ex} \\ &= G_T d_p^2/60D_T + Q_{ab}MP_{T_2O}\Big/\left(P_{T_2O}+P_{H_2O}+P_{H_2O'}\right) \\ &\quad + Q_{ad}MP_{T_2O} \\ &\qquad \Big/\left\{(P_{H_2}/\alpha_{ex})+\left(P_{T_2O}+P_{H_2O}+P_{H_2O'}\right)\Big/\alpha'_{ex}\right\} \\ &\quad + Q_{ex}MP_{T_2O} \\ &\qquad \Big/\left\{(P_{H_2}/\alpha_{ex})+\left(P_{T_2O}+P_{H_2O}+P_{H_2O'}\right)\Big/\alpha'_{ex}\right\}, \end{aligned} \tag{1}$$

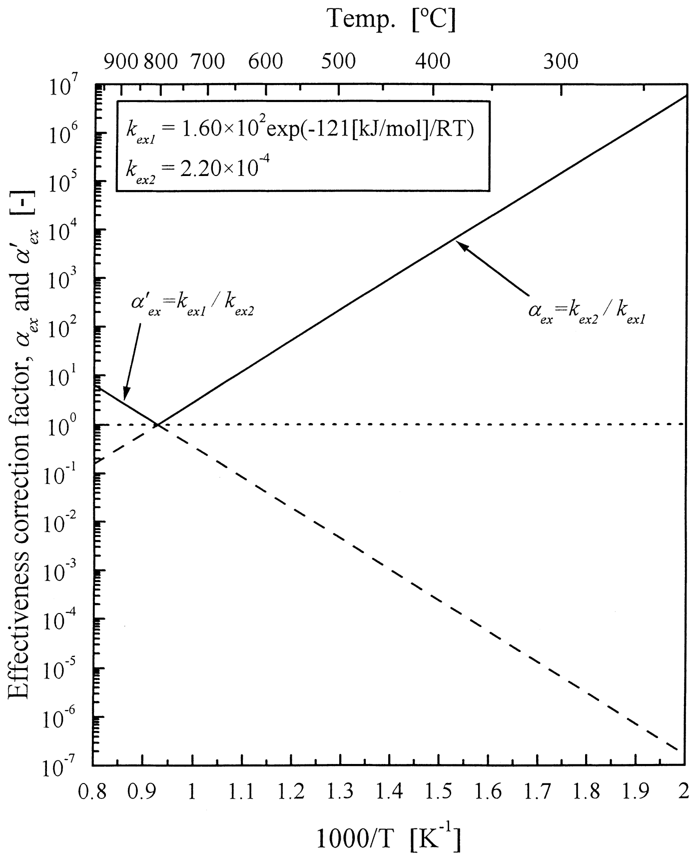

Fig. 1. Temperature dependency of effectiveness correction factor.

where

G_T	tritium generation rate in the whole blanket (mol/s)
d_p	grain diameter (m)
D_T	effective diffusivity of tritium in grain (m^2/s)
P_{H_2}	partial pressure of H_2 in the purge gas (Pa)
P_{H_2O}	partial pressure of H_2O swamped to the purge gas (Pa)
$P_{H_2O'}$	partial pressure of residual H_2O in the purge gas (Pa)
M	amount of Li ceramics in blanket (mol)
α_{ex}, α'_{ex}	effectiveness correction factor (–)
Q_{ab}	amount of water absorption (mol H_2O/mol Li compound)
Q_{ad}	amount of water adsorption (mol H_2O/mol Li compound)

The partial pressure of tritium in the purge gas, P_{T_2O}, is given as

$$P_{T_2O} = P_{He}G_T/G_{He} \text{ (Pa)}, \tag{2}$$

where all tritium bred in the grain is considered to be released in the chemical form of water, and P_{He} (Pa) and G_{He} (mol/s) are total pressure of helium purge gas and flow rate, respectively.

It is assumed in the uniform blanket model of this study that the isotope exchange reaction 1 and the isotope exchange reaction 2 compete each other in taking-up of tritium from the breeder surface if both H_2 and H_2O exist in the purge gas. In such a case, the effectiveness correction factor shown in Eq. (1) is given by

$$\left.\begin{aligned}\alpha_{ex} &= k_{ex2}/k_{exl}\\ \alpha'_{ex} &= 1\end{aligned}\right\}\text{when } k_{ex2} \geqslant k_{ex1},$$

or

$$\left.\begin{aligned}\alpha_{ex} &= 1\\ \alpha'_{ex} &= k_{ex1}/k_{ex2}\end{aligned}\right\}\text{when } k_{ex2} \geqslant k_{ex1}, \tag{3}$$

where k_{exl} and k_{ex2} mean the rate constant of the isotope exchange 1 and that of isotope exchange 2, respectively. Accordingly, the effectiveness correction factor means the relative intensity of two isotope exchange reactions.

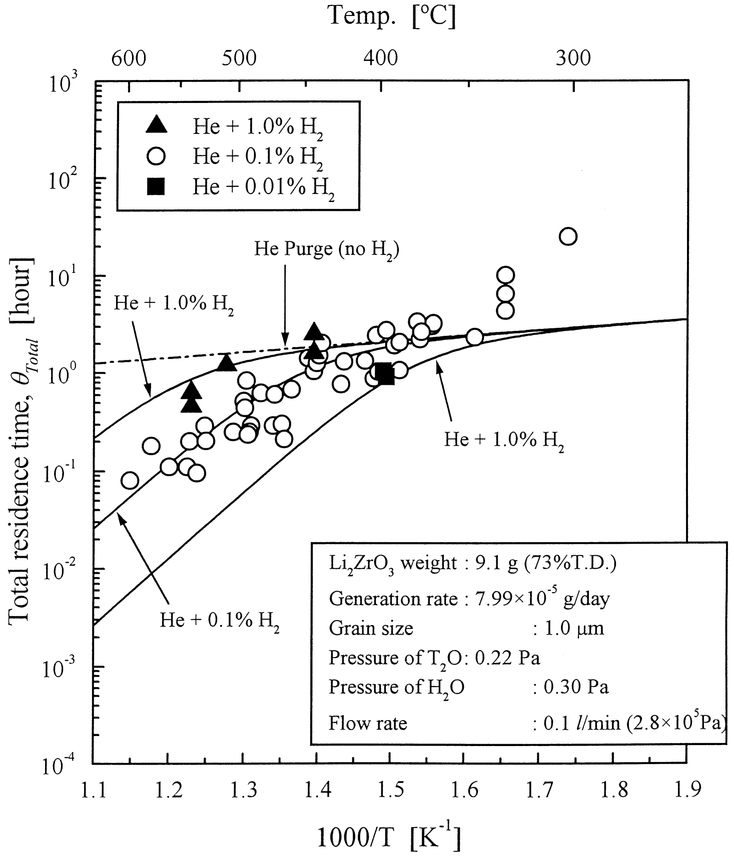

Fig. 2. Comparison of estimated residence time due to surface inventory with observed total residence time at EXOTIC-6 experiment.

The total partial pressure of water in various forms is given as

$$P = P_{T_2O} + P_{H_2O} + P_{H_2O'} \text{ (Pa)}, \tag{4}$$

where HTO is treated as a mixture of $1/2T_2O$ and $1/2H_2O$ in this study following the way taken in consideration of tritium behavior in a catalyst bed or a adsorption bed by the present authors [13].

The mass transfer resistance at transfer of tritium through pores of sintered pellets and that through boundary layer are considered to be negligibly small in this study.

The average residence time of tritium at each transfer step is given by division of inventory by the tritium generation rate. Then, the total average residence time in a solid breeder blanket is given as

$$\begin{aligned}\theta_{\text{Total}} &= (I_D + I_{ad} + I_{ab} + I_{ex})/G_T \\ &= \theta_D + \theta_{ad} + \theta_{ab} + \theta_{ex}(\text{s}).\end{aligned} \tag{5}$$

As can be seen from the above equations, the effects of tritium generation rate, temperature, grain size, partial pressure of H_2, partial pressure of water vapor or flow rate of purge gas on each tritium inventory are different. Accordingly, it is necessary to understand the all mass transfer steps dominating the tritium migration behavior before estimation of the tritium inventory in the blanket operated under a certain condition. Other than the tritium inventory in the blanket material, the tritium inventory in the piping system, I_{system}, arisen from the system effect of tritium should be also taken into account of when small amount of tritium with high T/H ratio is handled in a piping system with large surface area.

3. Results and discussions

3.1. Surface inventory

It has been observed by the present authors that the amount of water adsorbed onto the surface of Li_2ZrO_3 is given as

$$Q_{ad} = 6.3 \times 10^{-6} A_{BET} P^{1/2} \exp\,(107(\text{kJ/mol})/RT)$$
$$(\text{mol } H_2O/\text{mol Li compound}), \tag{6}$$

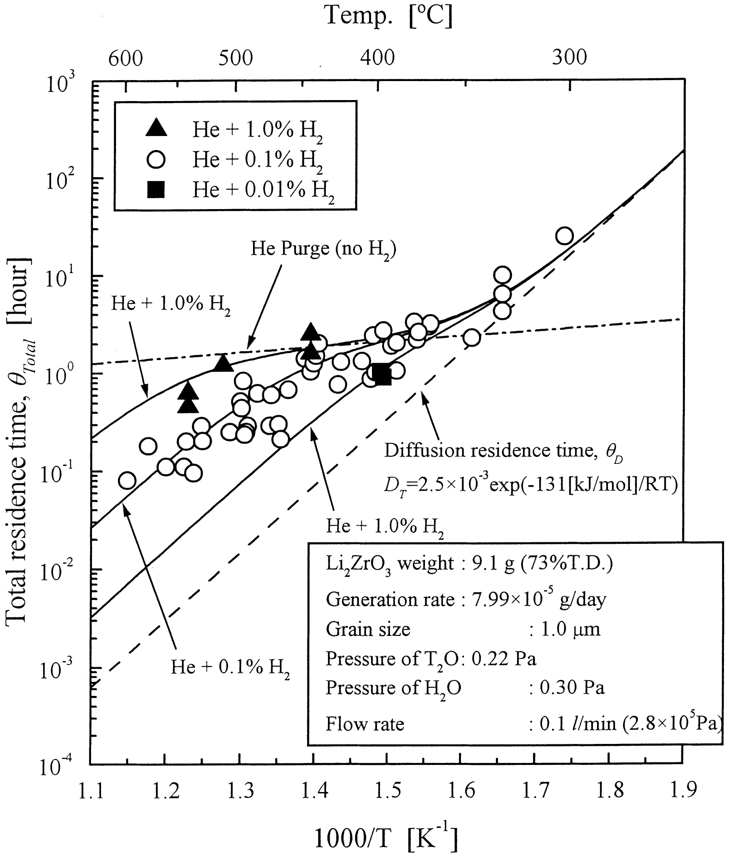

Fig. 3. Comparison of estimated total residence time with observed total residence time at EXOTIC-6 experiment.

where A_{BET} ($=6/\rho d_{\mathrm{p}}$, ρ: density (g/m^3)) is the BET surface area of the breeder particles.

It is also observed in the recent study that Li_2ZrO_3 has no isotope exchange capacity which is attributed to the –OH bases strongly bounded to the grain surface, though $LiAlO_2$, Li_4SiO_4 and Li_2O have a fair amount of the isotope exchange capacity in addition to the adsorption capacity. No absorption capacity of H_2 or H_2O into bulk of Li_2ZrO_3 particles has been observed in our study [12]. Accordingly, the surface inventory of tritium in a Li_2ZrO_3 blanket depends on the adsorption inventory.

Following the result of our recent study [14], the isotope exchange reaction rate between H_2 in the purge gas and tritium on the grain surface of Li_2ZrO_3, r_{exl}, is shown by

$$r_{\mathrm{exl}} = k_{\mathrm{exl}} a_v C_{\mathrm{H_2}} \left\{ 1 - \frac{q_{\mathrm{H_2O}}/(q_{\mathrm{H_2O}}+q_{\mathrm{T_2O}})}{C_{\mathrm{H_2}}/(C_{\mathrm{H_2}}+C_{\mathrm{T_2}})} \right\} \ (\mathrm{mol/m^3\ s}), \quad (7)$$

where k_{exl} (m/s) is the reaction rate constant and a_v ($=$A/V) the specific surface area of Li_2ZrO_3 grains in a packed bed.

In the recent study of the present authors [14] the following equation is obtained for k_{exl} in the Li_2ZrO_3 bed:

$$k_{\mathrm{exl}} = 1.6 \times 10^2 \exp(-121\ (\mathrm{kJ/mol})/RT)\ (\mathrm{m/s}). \quad (8)$$

The present authors also have presented the following equation for the rate constant of the isotope exchange reaction between H_2O in the purge gas and tritium on the surface of 304SS:

$$k_{\mathrm{ex2}} = 2.20 \times 10^{-4}\ (\mathrm{m/s}). \quad (9)$$

The effectiveness correction factors defined in Eq. (3), $\alpha_{\mathrm{ex}}(=k_{\mathrm{exl}}/k_{\mathrm{ex2}})$ and $\alpha'_{\mathrm{ex}}(=k_{\mathrm{ex2}}/k_{\mathrm{exl}})$, are evaluated using above equations in this study as shown in Fig. 1, assuming that k_{ex2} on Li_2ZrO_3 is similar to k_{ex2} on 304SS.

Then, the surface inventory of tritium in a Li_2ZrO_3 blanket can be evaluated for various conditions using Eqs. (2)–(4).

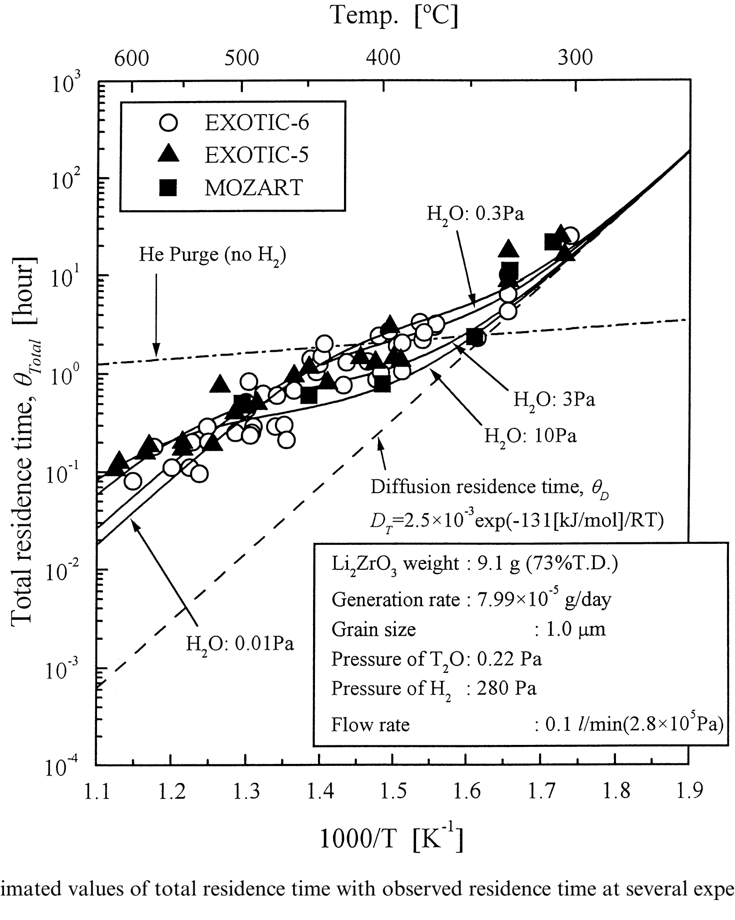

Fig. 4. Comparison of estimated values of total residence time with observed residence time at several experiments (EXOTIC-5, 6 and MOZART).

The total residence time of tritium in the Li_2ZrO_3 bed measured in the EXOTIC-6 experiment by Kwast et al. [11] is compared by the average residence times due to surface inventory in Fig. 2 which are estimated following the way presented in this study. It is known from this figure that the surface inventory controls the total tritium inventory in the Li_2ZrO_3 bed of the EXOTIC-6 experiment when the bed temperature is higher than 650 K, because the surface inventory estimated for various conditions agree with data observed by Kwast et al. It is also concluded from this comparison that some amount of water vapor exists in the blanket purge gas because assumption of existence of water vapor gives better agreement. In the latest paper, Kwast et al. reported that the bed temperature in their EXOTIC experiments could have been lower than the observed temperature by about thirty degrees [15]. In that case, good agreement of our estimation with their data is obtained when existence of water vapor of 10–20 Pa (35–70 ppm) is assumed in their purge gas. However, the higher observed temperature is used in the further discussion of their study because no observed evidence is presented in their discussion about the temperature gradient in Li_2ZrO_3 bed.

3.2. Diffusion inventory

The total residence time observed in the EXOTIC-6 experiment rapidly increases with decrease of temperature in the lower temperature range than 600 K as shown in Fig. 2. Two causes can be presented to explain this tendency. One is to explain by decrease of the effective diffusivity of tritium in grain and the other is to explain by sorption phenomena of tritium to the piping surface of the experimental apparatus. It is reasonably assumed that interaction of tritium with irradiation defects makes the tritium transfer rate in grain so slow. Accordingly, it is taken in this study for the time being that the diffusion process of tritium in Li_2ZrO_3 grains gives the main effect on the total residence time in the lower temperature range as shown in Fig. 3, though the residence time due to diffusion is only one-thousandth of the total residence time observed in the EXOTIC-6 experiment when the diffusivity of tritium by Kudo and Okuno [16] is used in estimation.

Then, the effective diffusivity of tritium in Li_2ZrO_3 under the irradiation condition is given by the curve fitting method as

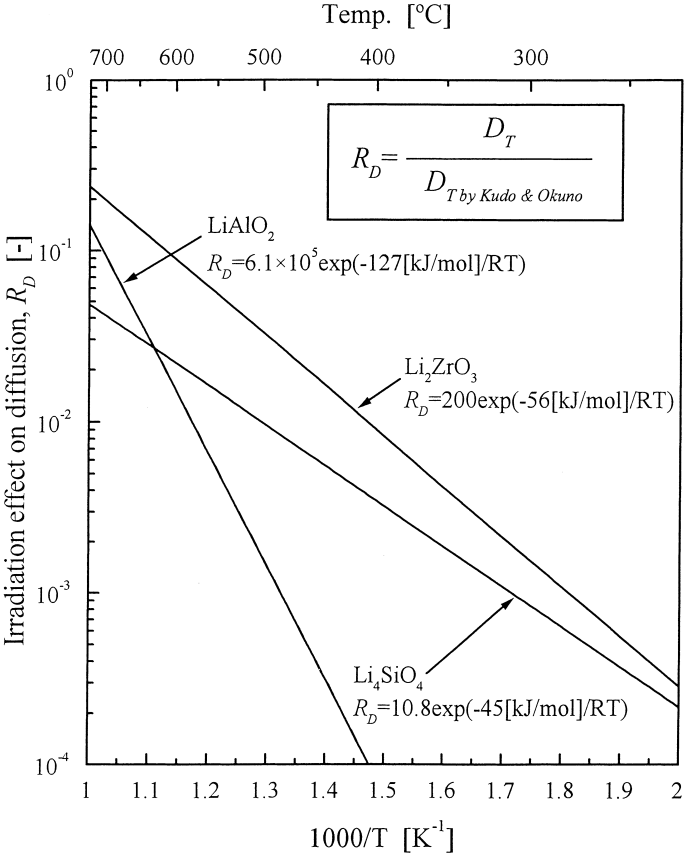

Fig. 5. Temperature dependency on irradiation effect on tritium diffusivity.

$$D_T = 2.5 \times 10^{-3} \exp(-131\ (\mathrm{kJ/mol})/RT)\ (\mathrm{m^2/s}). \quad (10)$$

The total residence times observed in the EXOTIC-5 and MOZART experiments are shown in Fig. 4 together with data obtained in the EXOTIC-6 experiments for the case where 0.1% H_2 in He is used as the purge gas, and the estimated value of this study shows good agreement with those data as can be also seen from this figure.

The effect of interaction of tritium with irradiation defects is obtained from comparison of the effective diffusivity shown by Eq. (10) with diffusivity of tritium obtained using Li_2ZrO_3 with no defects.

The irradiation effect on the tritium diffusivity, R_D, is compared for Li_2ZrO_3, $LiAlO_2$ and Li_4SiO_4 in Fig. 5 where the effective diffusivities are evaluated by the present authors using data obtained in the EXOTIC-6 experiment:

$$R_D = D_T/D_{T\ \mathrm{by\ Kudo\ and\ Okuno}}(-) \quad (11)$$

The diffusivities reported by Kudo and Okuno [16] are used as the standard in the above equation because they are the only researchers who have measured the diffusivity for Li_2O, $LiAlO_2$, Li_2ZrO_3 or Li_4SiO_4 in the same manner and because their diffusivity is larger than the most diffusivity by other works for each blanket material. This figure implies that the mobility of defects is very small in the temperature below 873 K, and that the mobility of defects in $LiAlO_2$ is much lower than that in Li_2ZrO_3 or Li_4SiO_4.

The effect of grain size on the total residence time of tritium obtained when the diffusivity from data by Kwast et al. [11] is compared in Fig. 6 for the Li_2ZrO_3 blanket purged by He with 100 Pa H_2, where operation of a 1 GWe D–T fusion reactor (thermal conversion efficiency: 30%) with Li_2ZrO_3 blanket having 70 tons of Li is supposed. Then, the total residence time of 1 hour corresponds to the tritium inventory of 16.7 g in the whole blanket since the tritium breeding ratio is assumed to be 1.0 in this estimate. It is known from this figure that the diffusion inventory is negligible in comparison with the surface inventory in a Li_2ZrO_3 blanket above 673 K when the grain size is 1 μm and the diffusion inventory becomes dominant if the blanket temperature is 573 K. However, the diffusion inventory is dominant even in such a high temperature blanket as

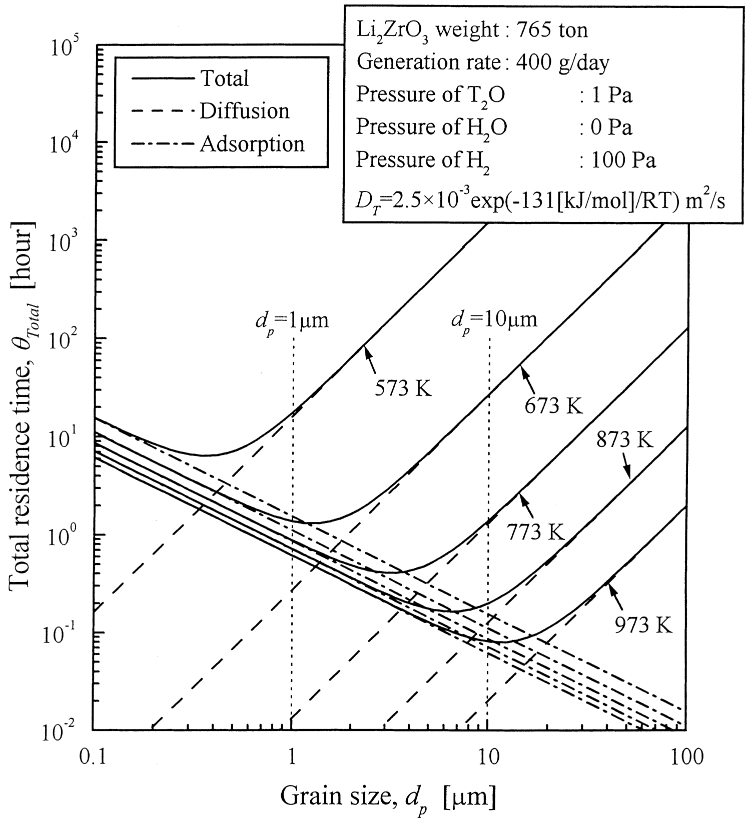

Fig. 6. Effect of grain size on residence time for Li_2ZrO_3 blanket (He +100 Pa H_2 purge, D_T: Kwast et al.).

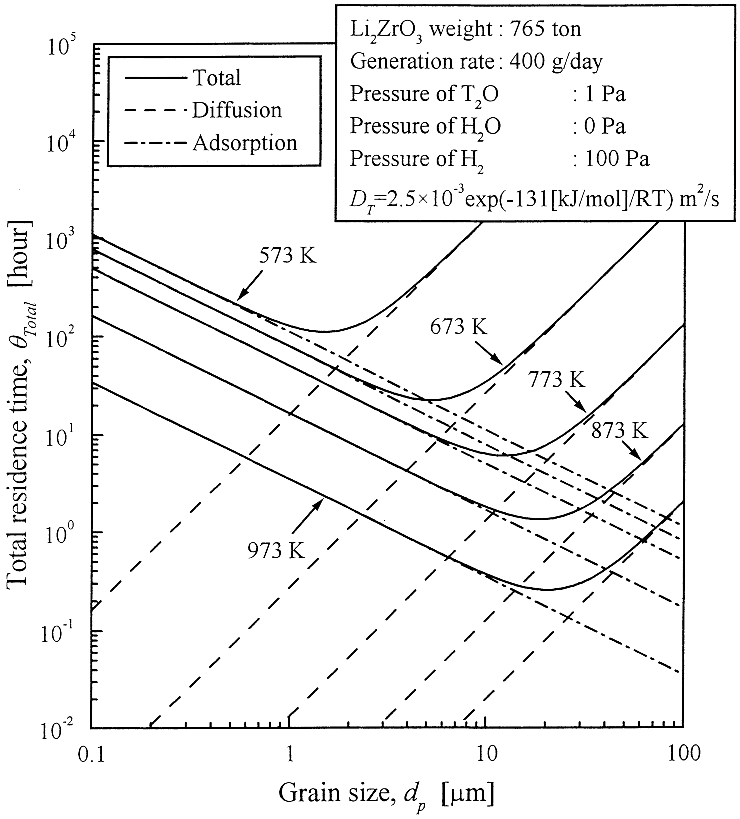

Fig. 7. Effect of grain size on residence time for Li_2ZrO_3 blanket (He +100 Pa H_2 +1 Pa H_2O purge, D_T: Kwast et al.).

773 K when the grain size is 10 μm. However, as shown in Fig. 7, the surface inventory becomes larger if the blanket purge gas contains 1 Pa of water vapor because of the contribution from two types of isotope exchange reactions.

The tritium inventory obtained from these figures implies that the tritium inventory in blanket will not become the main inventory in a D–T fusion reactor because the total inventory is estimated at several kilograms even for the ITER scale reactor.

3.3. Inventory in piping system

The total residence times measured in the TRINE experiment by Alvani et al. [17] are shown in Fig. 8 for both cases where He with 20 Pa H_2 and H_2 with 200 Pa H_2 are used as Li_2ZrO_3 bed purge gas, and the tendency of these data is not well explained by Eq. (1) of this study. It can be assumed that the system effect is remarkable in the TRINE experiment because the tritium generation rate is only one-seventeenth of the EXOTIC-6 experiment. The packed bed of Zn particles placed to convert HTO to HT in the TRINE experiment also contributes to increase the system effect, because it has been experienced by the present authors that the Zn bed traps some amount of tritium. If the overall residence time due to the system effect of the TRINE experiment is assumed to be 20 h for the case where 20 Pa H_2 is used and 2 h for the case where 200 Pa H_2 is used, the observed residence time in the TRINE experiment can be well represented by the estimated curves as shown in Fig. 9. Because the system effect arisen from the sorption behavior of tritium to the piping surfaces can change the shape of the response curve of tritium especially when a small amount of tritium is handled in a long piping, the quantitative clarification about the sorption behaviors of tritium on piping surfaces is also required for further discussions on release behaviors of tritium from lithium ceramic materials.

4. Conclusions

The tritium inventory in the Li_2ZrO_3 blanket under the uniform and steady state condition is estimated by considering the processes of diffusion in grain, adsorption on the grain surface and two isotope exchange

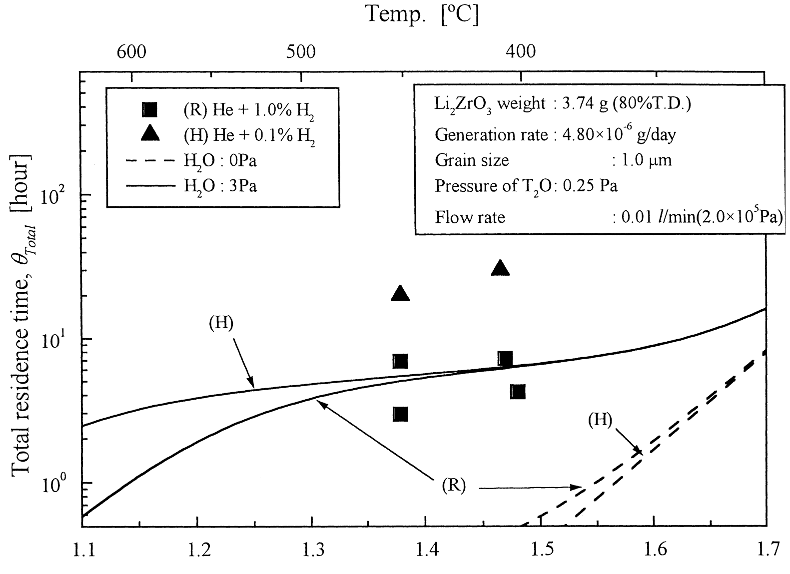

Fig. 8. Comparison of estimated values of total residence time with observed residence time at TRINE experiment.

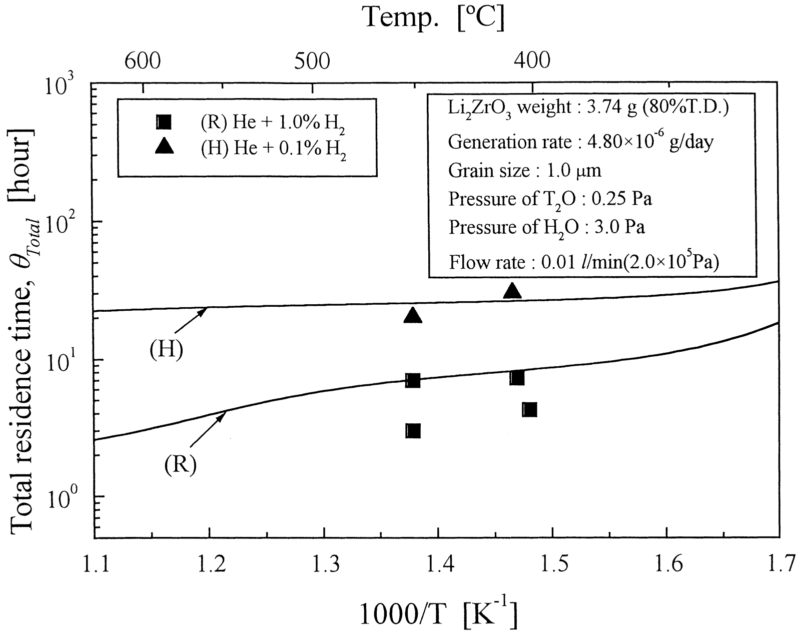

Fig. 9. Comparison of estimated values of total residence time with observed residence time at TRINE experiment where residence time due to the system effect is taken into account.

reactions between H_2 or H_2O and tritium on the grain surface.

Estimation using the model of this study gives a good agreement with total residence time reported in various in situ experiments for Li_2ZrO_3 when the effective diffusivity evaluated in this study using the residence time reported by Kwast et al. (EXOTIC-6) is applied.

It is also observed that system effect arisen from interaction of tritium with piping surfaces of the experimental apparatus can give profound effects on estimate of tritium inventory.

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