4.3 Tritium Release Behavior from Irradiated Li$_4$SiO$_4$

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INTRODUCTION

Ability to predict behavior of tritium in different breeding blanket materials under various operating reactor conditions is required for design of fusion reactor blanket system because recovery of bred tritium with high efficiency and reduction of tritium transfer to the cooling system are demanded in design of the blanket system. Tritium transport and release behavior from breeding materials consist of complex processes in bulk and surface of grain of the breeding materials. In order to quantify the tritium release behavior, it is important to distinguish the rate controlling steps that contribute to tritium release, and it is considered that the rate controlling step can change in the presence of water vapor or hydrogen in the purge gas.

It is considered that following mass transfer processes contribute to the release of tritium bred in blanket materials: $^1,2$ (Figure 1)

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) absorption of tritium into the bulk of grain;
5) adsorption and desorption of tritium on grain surface;
6) isotope exchange reactions between gaseous hydrogen, H$_2$, in the gas stream and tritium on grain surfaces (isotope exchange reaction 1);
7) isotope exchange reactions between water vapor, H$_2$O, in the gas stream and tritium on grain surfaces (isotope exchange reaction 2);
8) water formation reactions in addition of H$_2$ to the blanket purge gas;
9) transfer of hydrogen isotopes and water through pores of sintered pellets;
10) transfer of hydrogen isotopes and water through boundary layer formed on the surface of a sintered pellets to the gas stream.

In this paper we propose a model to explain tritium release behavior from irradiated Li$_4$SiO$_4$ made by Forschungszetrum Karlsruhe (FzK) recently as the standard Li$_4$SiO$_4$ sample for
tritium breeding. The release curves were obtained by the out-pile temperature programmed desorption (TPD) techniques in a series of experiments in Japan Atomic Energy Research Institute (JAERI). In the model formation, a number of mass transfer steps in the bulk of breeder grain and those on the surface of grain were taken into account. There were diffusion of tritium in the grain, adsorption and desorption of water on the surface of grain, two types of isotope exchange reactions, water formation reaction at addition of hydrogen to the purge gas.

EXPERIMENTAL

Li$_4$SiO$_4$ pebbles from Forschungszentrum Karlsruhe (FzK) were irradiated in Japan Atomic Energy Research Institute (JAERI) for 50 minutes by thermal neutron of which flux was $4.0 \times 10^{13} \text{ m}^{-2} \text{s}^{-1}$. Various properties are compared in Table I about experimental conditions.

Tritium release curves of bred tritium were obtained applying the out-pile temperature programmed desorption (TPD) techniques using the experimental apparatus of which diagram is schematically shown by Figure 2. The first ionization chamber was used to measure the change of total tritium and the second ionization chamber placed after a water bubbler was used to measure the concentration of molecular form tritium, respectively.

Dry nitrogen gas, nitrogen with hydrogen gas or nitrogen with water vapor gas was used as the tritium purge gas to compare the effect of reactions on the grain surface. Water vapor was introduced to the system gas at the inlet to the ionization chamber when dry nitrogen gas or nitrogen with hydrogen gas was used as the purge gas to diminish the tritium memory effect consulting the result by the present authors reported elsewhere. $^3$)

RESULTS AND DISCUSSION

Figure 3 shows the tritium release curves obtained when irradiated Li$_4$SiO$_4$ sample beds were purged by dry nitrogen gas, nitrogen with 10,000 ppm hydrogen gas and nitrogen with 10,000 ppm water vapor gas where temperature of the bed was raised from temperature to 800 ˚C with the up-rate of 5 ˚C/min. This figure shows that tritium is released much faster than cases of any other purge gas when nitrogen with water vapor gas is used as the purge gas. Identical phenomena are observed for other solid breeder materials, and this tendency can be explained by the faster reaction rate of isotope exchange reaction$^2$ compared to the rate of desorption at dry gas condition or the rate of isotope exchange reaction 1 at addition of hydrogen. It is also known from Figure 3 that the tritium release curve obtained at dry N$_2$ purge is similar to the release curve when N$_2$ with 10,000 ppm hydrogen is used. This is explained as follows that the rate of isotope exchange reaction 1 does not become large enough to give effect on the shape of tritium release from the Li$_4$SiO$_4$ experimented in this study. It is confirmed in this study that only a negligible amount of tritium is released as the chemical form of HT from Li$_4$SiO$_4$ when dry N$_2$ gas or N$_2$ with water vapor is used as the purge gas. As can be seen from the output curve of the second ionization chamber shown in Figure 4, only a little tritium is released from Li$_4$SiO$_4$ as
the chemical form of HT even when 10,000 ppm hydrogen is added to the purge gas. This confirms the preceding assumption that the isotope exchange reaction 1 does not become big enough to make HT on the grain surface of Li$_4$SiO$_4$. Then, it can be said that use of the release curve with purge gas added by H$_2$ for estimation of diffusivity in grain may lead to the erroneous results. Accordingly, the apparent tritium diffusivity in Li$_4$SiO$_4$ was estimated by fitting of the tritium release curve purged by N$_2$ with water vapor taking the diffusivity, rate of isotope exchange reaction 2, rate of desorption as adjustable parameter following the way reported previously by the present authors.

Figure shows comparison of the estimated release curve with the experimental tritium release curve and the estimated release curve if only the diffusivity estimated in this study is considered to be effective in the tritium transfer process. The apparent diffusivity of tritium in bulk of Li$_4$SiO$_4$, the overall mass transfer coefficients representing the isotope exchange reaction 2 and desorption are obtained as follows from the curve fitting in this study.

\[
D_T = 3.0 \times 10^{-7} \exp(-79.5 \frac{[kJ/mol \cdot K]}{RT}) \ [m^2/s] \quad (1)
\]

\[
K_{ex2} = 2.0 \times 10^{-7} \ [m/s] \quad (2)
\]

\[
K_{ad} = 1.07 \times 10^{-5} \exp(-41.3 \frac{[kJ/mol \cdot K]}{RT}) \ [m/s] \quad (3)
\]

Figure 6 compares the diffusivities of tritium in Li$_4$SiO$_4$ estimated so far various ways by different authors.\textsuperscript{5-7} It is supposed that diffusivities reported previously may include the surface effect though the value obtained in this study exclude it.

Figure 7 shows comparison of the overall mass transfer coefficient representing the isotope exchange reaction 2 and water desorption obtained in this study with reported values for the mass transfer coefficients representing water desorption on Li$_4$SiO$_4$\textsuperscript{6}, isotope exchange reaction 1 on Li$_4$SiO$_4$\textsuperscript{9}, isotope exchange reaction 2 on metal surface\textsuperscript{10} and water formation reaction on Li$_4$SiO$_4$ where the concentrations in the purge gas are taken as the variables. This figure shows the mass transfer coefficient for the isotope exchange reaction 2 is almost similar to the mass transfer coefficient for water desorption. It is also known from this figure that the mass transfer coefficients for isotope exchange reaction and water desorption are much larger than the mass transfer coefficients for isotope exchange reaction 1 and water formation reaction. It can be also seen from this figure that the water formation reaction proceeds a little faster than the isotope exchange reaction 1 in the whole range of temperature.

CONCLUSION

The apparent tritium diffusivity in crystal grain of Li$_4$SiO$_4$ was quantified in this study which was estimated by fitting of tritium release curve obtained when N$_2$ with 10,000 ppm water vapor was used as the purge gas. This is done because much faster release of bred tritium is observed when irradiated Li$_4$SiO$_4$ is purged by N$_2$ with water vapor than any other purge gas.
Most tritium was released in the chemical form of HTO even when 10,000 ppm hydrogen was added to the purge gas. This reason is explained by the slow reaction rate of isotope exchange between hydrogen in purge gas and tritium on the grain surface in comparison with the reaction rate of desorption of water vapor or water formation reaction on the grain surface.

REFERENCES
6) UCLA-Eng. 86 44 (1987)
Table I Experimental conditions

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<th>Li$_2$SiO$_4$(FzK)</th>
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<tr>
<td>Grain size, $d_g$</td>
<td>1.2 $\mu$m</td>
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<td>Pebble size, $d_p$</td>
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<td>Theoretical density</td>
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<td>Irradiation time</td>
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Fig. 1 Tritium release model from the tritium breeder materials
Fig. 2 Schematic diagram of experimental apparatus

Fig. 3 Tritium release curves for Li$_2$SiO$_4$
Fig. 4 Tritium release curve purged by N₂ with hydrogen gas

Fig. 5 Simulation for tritium release curve purged by water addition gas
Fig. 6 Comparison of diffusivities estimated from different authors

\[ (1) D_i = 3.0 \times 10^{-7} \times \text{Exp}(-79.5\text{kJ}/RT) \]

\[ (2) \text{ This work} \]
\[ (3) \text{ Okuno and Kudo} \]
\[ (4) \text{ FINESSE (UCLA)} \]
\[ (5) \text{ Nishikawa (Exp. Values of Kwast et al.)} \]

Fig. 7 Comparison of overall mass transfer coefficients