



Modeling of tritium release from ceramic breeder materials by focusing on transport process in breeder grain

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Abstract

The effect of water vapor on the releases of tritium from a lithium silicate was investigated. Out of pile tritium release experiments were conducted using the ceramic breeder irradiated in a research reactor. Tritium was released from the lithium silicate breeder material using a nitrogen sweep gas with 0.1% water vapor. It was found that the addition of water vapor to the sweep gas greatly enhances the release rate of tritium from the ceramic breeder. The results of the tritium release experiment were analyzed using a numerical model of diffusion control. However, the analysis indicates that the assumption of only diffusion control cannot reproduce the experimental results. Thus, the effect of trapping sites was also considered in the model. It was found that the model with the trapping site effect reproduce the experimental tritium release curve.

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1. Introduction

Tritium produced in ceramic breeder materials such as Li_2O , Li_4SiO_4 , LiAlO_2 , Li_2ZrO_3 and Li_2TiO_3 is extracted using helium sweep gases containing 0.1% of hydrogen, in most current designs of D–T fusion reactor blankets with ceramic breeder materials. Hydrogen is added to the sweep gases to improve the extraction of tritium via isotopic exchange reactions. In our previous studies, the isotope exchange reactions and water adsorption at the surface of several ceramic blanket materials were investigated [1–4]. The results indicate that the isotope exchange reaction at the breeder gas/solid interface proceeds fast only at relatively elevated temperatures. The effect of catalytically active metal additives, such as platinum and palladium, on the het-

erogeneous isotope exchange reactions at the solid breeder/sweep gas interface was examined in previous work [3,4]. The results indicate that the isotope exchange reactions on the surface of Li_4SiO_4 are greatly enhanced with such catalytic additives. Evidently, out of pile annealing tests with irradiated Pt/ Li_4SiO_4 and Pd/ Li_4SiO_4 breeders, which contain noble metals, revealed that the release of tritium from the breeder is accelerated, particularly at lower temperatures [5–7]. The authors also investigated the effect of water vapor in the sweep gas on the release of tritium from the Li_4SiO_4 breeder [8], and found that the addition of water vapor to the sweep gas enhances the release rate of tritium. Comparison of the results for experiments with the humid sweep gas and that with the catalytic breeder materials suggests that the addition of water vapor to the sweep gas gives almost the same effect on the enhancement of tritium release rate as the catalyst metals. These are probably caused by the acceleration of the exchange reaction that takes place on the surface of the breeder material. The release of tritium from ceramic

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breeder materials includes various transport steps such as diffusion in the grain, surface reactions on the grain surface, diffusion in the pores of breeder pebbles, etc. Therefore, the rate of these transport processes should be quantified step by step. In this sense, the result of tritium release experiment with the wet sweep gas can be used to further investigate the transport process in the breeder grain, since the surface reactions are thought to be significantly enhanced by the wet gas purge. In this work, the result of the tritium release experiment with the wet sweep gas was analyzed using a numerical model, in which the surface effect was eliminated. The diffusivity of tritium in a lithium silicate breeder material was quantified using the numerical model.

2. Overview of experimental results

Out of pile annealing experiments were conducted using Li_4SiO_4 pebbles (0.51–0.94 mm (av. 0.68 mm) in diameter, >98%TD) irradiated in the Kyoto University Research Reactor. Among the candidate breeder materials mentioned above, Li_4SiO_4 is known to have attractive natures for lithium density, compatibility with the structure materials, release performance of bred tritium, etc. The breeder pebbles (0.3 g) encapsulated in quartz tubes were irradiated for 2 min in the thermal reactor with a neutron flux of $2.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. After irradiation, the breeder materials were placed in a reactor tube made of quartz for experiments. The concentrations of tritium in the inlet and outlet streams of the reactor were traced with an ionization chamber. Details of the experiments were given in our previous literature [5–8]. The reactor temperature was raised at the rate $5 \text{ }^\circ\text{C}/\text{min}$ up to $900 \text{ }^\circ\text{C}$ after the sweep gas (100 ml/min) was introduced to the reactor. After the bed temperature reached $900 \text{ }^\circ\text{C}$, the reactor temperature was held at $900 \text{ }^\circ\text{C}$.

The solid line in Fig. 1(a) gives the result of an out of pile test with the Li_4SiO_4 pebbles irradiated in the thermal reactor and a sweep gas of the 0.1% H_2/N_2 . The release curve has two peaks; one peak is observed at near $400 \text{ }^\circ\text{C}$ and the other at near $600 \text{ }^\circ\text{C}$. Although the tritium level dropped almost to the background level at $900 \text{ }^\circ\text{C}$, tritium was again released when the sweep gas was replaced with gas containing 0.1% of water vapor. The result of another out of pile annealing tests for the Li_4SiO_4 pebbles with 0.1% $\text{H}_2\text{O}/\text{N}_2$ sweep gas is shown in Fig. 1(b). Only one major peak was observed in the tritium release curve, which is a great difference compared with the release curve in the case of the 0.1% H_2/N_2 sweep gas. No tritium release was observed when the sweep gas was changed to the N_2 gas containing 0.5% of H_2O at $900 \text{ }^\circ\text{C}$. More details of the experimental results shown above are reported in the previous literature [8]. In the previous work, the authors investigated the effect

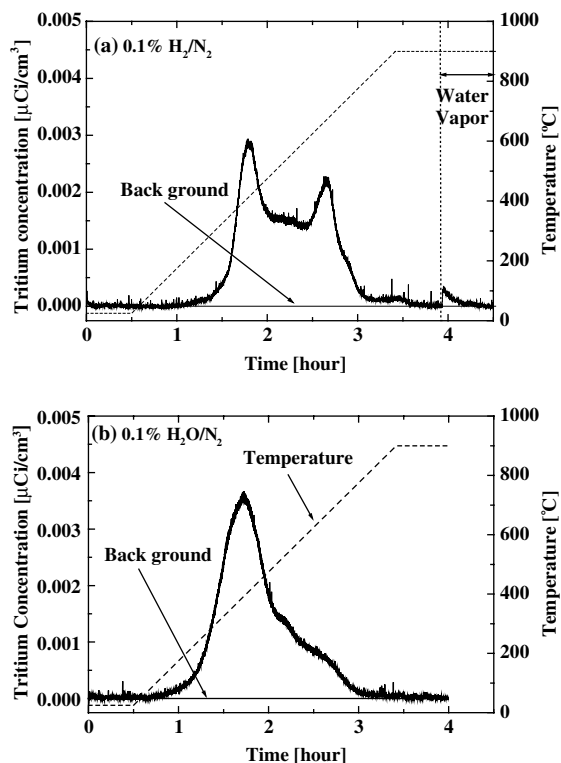


Fig. 1. Out of pile annealing tests for Li_4SiO_4 with (a) 0.1% H_2/N_2 sweep gas and (b) 0.1% $\text{H}_2\text{O}/\text{N}_2$ sweep gas. (Amount of breeder: 0.3 g; Flow rate: 100 ml/min; Irradiation time: 2 min and Neutron flux: $2.75 \times 10^{13} \text{ cm}^{-2}/\text{s}$.)

of the deposition of catalyst metals such as Pt and Pd in Li_4SiO_4 breeder [5–7]. The results reveal that the deposition of these noble metals greatly enhances the release rate of tritium since isotope exchange reactions taking place on the surface of the grain are promoted with the help of such catalysts. Moreover, release curve obtained for breeders with catalysts are quite similar to the release curve shown in Fig. 1(b). Thus, it is concluded that water vapor contained in the sweep gas also promotes the isotope exchange reaction on the grain surface. Therefore, the release behavior shown in Fig. 1(b) could be based on diffusion in the grains. With this assumption, the authors analyzed the release curve obtained with the 0.1% $\text{H}_2\text{O}/\text{N}_2$ sweep gas.

3. Numerical modeling and results of analysis

The release curve of tritium shown in Fig. 1(b) was first analyzed with the diffusion model. The diffusion model is expressed as

$$r^2 \frac{\partial q}{\partial t} = \frac{\partial}{\partial r} \left(r^2 D \frac{\partial q}{\partial r} \right), \quad (1)$$

where q , r and t are tritium concentration in breeder material [Ci/m³], length in spherical coordinate in the crystal grain [m] and time [s], respectively. The diffusivity D could be written as

$$D = D_0 \exp(-E_a/RT), \quad (2)$$

where D_0 is the frequency factor of diffusivity [m²/s]. This differential equation was numerically solved using the finite volume discretization method and Crank–Nicholson differential scheme. If the surface reaction is assumed to proceed quite fast, the boundary conditions become

$$q|_{r=R} = 0, \quad (3)$$

$$D \frac{\partial q}{\partial r} \Big|_{r=0} = 0, \quad (4)$$

where R is the radius of crystal grains in the breeder pebbles. The grain diameter was determined to be 5 μm using an electron microscope. The absolute temperature T in Eq. (2) was increased at the rate of 5 K/min in computation. The numerical program was coupled with an algorithm of a least squares analysis, and the values of D_0 and E_a were simultaneously determined by fitting the calculated release curve to the experimental release curve.

Fig. 2(a) shows the best-fit release curve obtained in this way. The experimental data (collected every 1 min) are plotted as open symbols and the calculated release curve is shown as a solid line. The trend in the release curve was fairly reproduced, but the calculated release curve is not in good agreement with the experimental data, particularly in the higher temperature region. The optimized values of D_0 and E_a were 1.4×10^{-12} m²/s⁻¹ and 4.8×10^4 J/mol, respectively. The value of the activation energy obtained is almost identical to the value reported by Okuno et al. [9] for lithium silicate.

Because of the unsatisfactory results shown above, the authors tested another model. In this model, the effect of trapping sites in the crystal grain was incorporated in the diffusion model. The model is expressed as

$$r^2 \frac{\partial q}{\partial t} = \frac{\partial}{\partial r} \left(r^2 D \frac{\partial q}{\partial r} \right) - r^2 k_T q (q_{T,0} - q_T) + r^2 k_D q_T, \quad (5)$$

$$r^2 \frac{\partial q_T}{\partial t} = r^2 k_T q (q_{T,0} - q_T) - r^2 k_D q_T, \quad (6)$$

where k_T , k_D , $q_{T,0}$ and q_T are rate constant of the trapping reaction [m³/Ci s], rate constant of the detrapping reaction [s⁻¹], concentration of trapping site [Ci/m³] and concentration of tritium in trapping sites [mol/m³], respectively. With regard to the trapping and detrapping reactions, other researchers also used a similar model for the case of the thermal reemission of hydrogen isotopes from graphite [10,11]. The trapping and detrapping

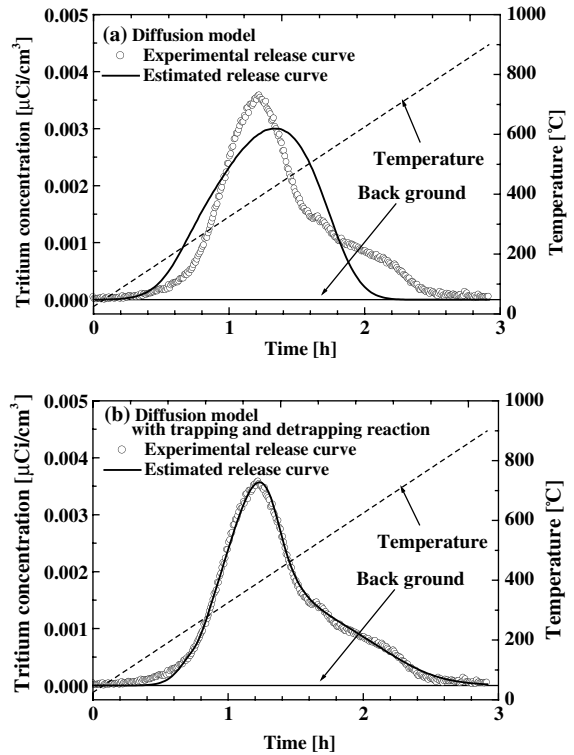


Fig. 2. Comparison of experimental release curve and numerical computations with: (a) diffusion model and (b) diffusion model with trapping and detrapping reactions.

reactions are thought to be an activation process, and thus they could be in the form of

$$k_T = k_{T,0} \exp(-E_T/RT), \quad (7)$$

$$k_D = k_{D,0} \exp(-E_D/RT), \quad (8)$$

where $k_{T,0}$, $k_{D,0}$, E_T and E_D are frequency factor for the trapping reaction [m³/Ci s], frequency factor for the detrapping reaction [s⁻¹], activation energy of the trapping reaction [J/mol] and activation energy of the detrapping reaction [J/mol], respectively. The differential equations were also numerically solved. The absolute temperature T was increased at the rate of 5 K/min. The numerical program was also coupled with an algorithm of the least squares analysis, and the values of D_0 , E_a , $q_{T,0}$, $k_{T,0}$, $k_{D,0}$, E_T and E_D were simultaneously determined by fitting the calculated release curve to the experimental release curve. Fig. 2(b) shows the best-fit release curve, indicating that the experimental release curve is quite well reproduced. From the optimized values, the following equations are obtained:

$$D = 5.8 \times 10^9 \exp(-86100/RT), \quad (9)$$

$$k_T = 3.25 \times 10^3 \exp(-137000/RT), \quad (10)$$

$$k_D = 1.68 \times 10^8 \exp(-118000/RT), \quad (11)$$

$$q_{T,0} = 1.03 \times 10^2 \text{ [Ci/m}^3\text{]}, \quad (12)$$

In the least squares analysis, a lot of initial values were tested, however the convergence was attained only when the values mentioned above were obtained. The values of the optimized activation energies of trapping and detrapping reactions are almost identical. The value of activation energy of the diffusivity is 1.8 times as large as that obtained for the simple diffusion model. The result shown above suggests that the incorporation of trapping and detrapping of tritium by trapping sites is effective for modeling the release behavior of tritium.

Comparison of the result of this work and the values reported by Okuno et al. [9] shows that the value of the activation energy for diffusivity obtained in this work is about twice as large as that obtained by Okuno et al. It is also suggested that the absolute values of diffusivity at around 600 °C are almost coincident with their values, whereas at lower temperatures our values of diffusivity are smaller than their values by approximately one order of magnitude. The concentration of trapping sites expressed in the unit of Ci/m³ was found to be almost the half of the concentration of tritium bred in the breeder. Abramkovs et al. [12] have reported that the concentration of defects formed in Li₄SiO₄ during irradiation is 100–1000 times larger than the concentration of bred tritium. Thus, it is believed that only a small fraction of the defects or defect clusters act as trapping sites, if such trapping sites arise from irradiation defects.

4. Conclusions

Out of pile annealing experiments were conducted using irradiated Li₄SiO₄. In the experiments, two types of sweep gas were used. One is nitrogen gas containing hydrogen and the other is nitrogen gas with water vapor. The results of the experiments indicate that tritium bred in the breeder material is released at lower temperatures when the sweep gas with water vapor is used. The experimental result was analyzed using numerical models. It was found that a simple diffusion model cannot reproduce the experimental release curve, but that the incorporation of trapping and detrapping reactions in the diffusion model successfully reproduces the experimental release curve.

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