

Modeling of HT and HTO release from irradiated lithium metazirconate

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Abstract

Modeling studies of tritium release from irradiated Li_2ZrO_3 (MAPI) pebbles have been carried out in order to evaluate the effect of purge gas composition on tritium release behavior. The release characteristics were obtained by temperature programmed desorption (TPD) technique in the series of post-irradiation experiments in JRR-4 research reactor of JAERI. Nitrogen with hydrogen at various partial pressures (100 and 1000 Pa) was used as a purge gas. Two sets of ionization chambers and its dedicated electrometers allowed the tritium concentration to be monitored in the chemical form of HT and overall tritium concentration in the mixture HT and HTO simultaneously during desorption runs. The tritium release curves were numerically fitted in order to evaluate the mass transfer coefficients.

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1. Introduction

Tritium transport and release behavior from a solid breeding blanket is a major concern in design and further operation of D–T fusion reactors. In the present design helium cooled breeding blanket ceramic pebble beds are purged with a helium stream containing 0.1% of hydrogen. The addition of hydrogen improves the tritium extraction due to isotopic exchange reactions that occur on the surface of the ceramic grains.

Tritium release from irradiated Li_2ZrO_3 , Li_2TiO_3 , Li_4SiO_4 have been investigated by out of pile temperature programmed desorption method (TPD) in Kyoto University Research Reactor [1] and in JRR-4 reactor in JAERI. In the previous study [2] numerical modeling of

tritium release spectra from irradiated Li_2ZrO_3 was performed considering the diffusion of tritium in the bulk of grains, adsorption/desorption of water on the surface of grains and isotope exchange reaction between water vapor in the gas stream and tritium on grain surfaces. The tritium release kinetics were interpreted by assuming that bulk diffusion and isotope exchange reaction were the rate-determining steps in the presence of water in the purge gas. In the case of pure nitrogen purge gas the diffusion and desorption/adsorption were assumed to be the rate-determining process.

When hydrogen is added to the purge gas the isotope exchange reaction (1) between hydrogen in the purge gas and tritium released from the bulk as HTO takes place on the surface of the grains. The isotope exchange reaction (1) on non-irradiated breeding ceramics has been extensively studied by several authors [3–5].

In the present paper the tritium release spectrum obtained for irradiated Li_2ZrO_3 purged with nitrogen containing the 0.1% or 1% of hydrogen were fitted numerically in order to characterize the isotope exchange reaction (1).

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2. Experimental

The Li_2ZrO_3 pebbles used in TPD experiments were made by Mitsubishi Atomic Power Industries, Inc. (MAPI). After pre-treatment 0.1 g of sample contained in a quartz ampule have been irradiated for 100 or 200 min in the JRR-4 research reactor in JAERI at a neutron flux of 4.0×10^{13} n/cm²s. After irradiation the quartz capsules were opened in a glove box and the irradiated pebbles placed into the removable reaction bed of the TPD apparatus.

The schematic diagram of the apparatus is shown in Fig. 1. The basic design is similar to the design of the apparatus used at the Kyoto University Reactor (KUR) [1]. Tritium analysis in the outlet gas is carried out by a set of two ionization chambers, with a measuring volume 66 cm³, and an intermediate water bubbler to allow for a discrimination between HT and HTO. The first chamber (IC1) measures the overall tritium content in the gas stream, while the second chamber (IC2) measures only the HT form of released tritium.

During the tritium release runs the samples were purged by dry N_2 , N_2 with H_2 of various partial pressures, or humidified N_2 . The sample temperature was raised linearly from room temperature to 1073 K at a rate of 5 K/min. Humidified N_2 was added into the inlet stream of reactor bed before terminating an experiment in order to assure the release of residual tritium from the sample.

3. Theoretical consideration

The model described in this paper considers diffusion, adsorption and desorption and exchange reactions on

the surface of the grain as rate-controlling mechanisms in tritium release. For simplification only H_2 , T_2 , H_2O and T_2O were taken into account.

3.1. Diffusion of tritium in the crystal grain

The model assumes that all tritium atoms are equivalently mobile in a grain, that grains can be treated as spherical with equal diameters and that the tritium obeys the following diffusion equation written in spherical coordinates

$$\frac{\partial C_{\text{T.g}}(r, t)}{\partial t} - D_{\text{T.g}}(T) \frac{\partial^2 C_{\text{T.g}}(r, t)}{\partial r^2} - \frac{2D_{\text{T.g}}(T)}{r} \frac{\partial C_{\text{T.g}}(r, t)}{\partial r} = S_{\text{T}}, \quad (1)$$

where $C_{\text{T.g}}$ is the concentration of tritium ions in the bulk of grain [mol/m³], $D_{\text{T.g}}$ is the effective diffusivity of tritium in a grain [m²/s], r is the radial coordinate [m], S_{T} is the tritium generation rate [mol/m³s] and t is the time coordinate [s].

Under post-irradiation conditions we assume that the tritium distribution in the crystal grain is uniform and that the tritium generation rate is zero. Therefore, the initial and boundary conditions for Eq. (1) can be expressed as follows:

$$C_{\text{T.g}}(r, 0) = C_0, \quad (2)$$

$$C_{\text{T.g}}(a, t) = 0, \quad (3)$$

$$\left(\frac{\partial C_{\text{T.g}}(r, t)}{\partial r} \right)_{r=0} = 0, \quad (4)$$

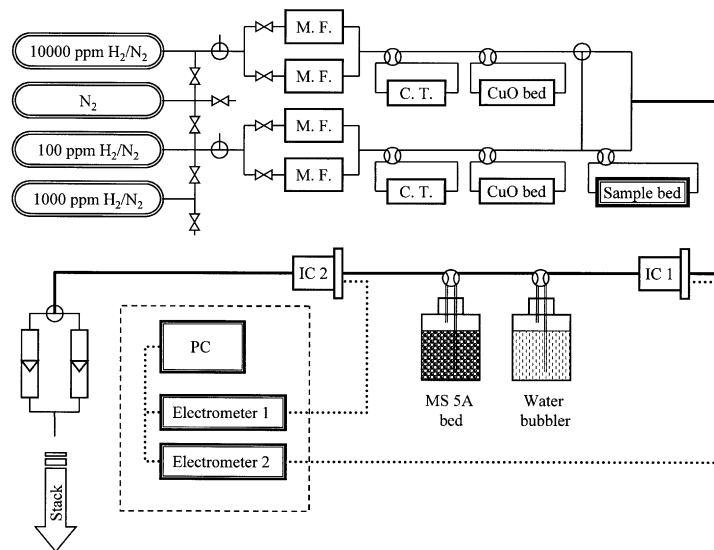


Fig. 1. Schematic diagram of the experimental apparatus.

where a is the grain radius [m] and C_0 is the initial tritium concentration in the bulk of the grain [mol/m³].

The diffusion coefficient $D_{T,g}$ can be assumed to be space-independent and expressed in terms of its pre-exponential factor D_0 [m²/s] and an activation energy E_D [J/mol] by

$$D_{T,g} = D_0 \exp(-E_D/RT). \quad (5)$$

3.2. Mass balance in the packed bed

The mass balance in the packed bed is expressed assuming perfect mixed flow reactor conditions by following equations obtained by Nishikawa et al. [6,7] referring Perry's 'Chemical Engineering's Handbook' [8]:

- mass balance of hydrogen, H₂, in gas stream

$$\varepsilon \frac{dC_{H_2}}{dt} - \frac{1}{V} (v_{in} C_{H_2}^{in} - v_{out} C_{H_2}^{out}) - K_{F,ex1} a_v X_1 = 0, \quad (6)$$

- mass balance of hydrogen, T₂, in gas stream

$$\varepsilon \frac{dC_{T_2}}{dt} - \frac{1}{V} (v_{in} C_{T_2}^{in} - v_{out} C_{T_2}^{out}) + K_{F,ex1} a_v X_1 = 0, \quad (7)$$

- mass balance of water, H₂O, in gas stream

$$\varepsilon \frac{dC_{H_2O}}{dt} - \frac{1}{V} (v_{in} C_{H_2O}^{in} - v_{out} C_{H_2O}^{out}) - K_{S,ad} a_v X_3 - K_{F,ex2} a_v X_2 = 0, \quad (8)$$

- mass balance of tritiated water, T₂O, in gas stream

$$\varepsilon \frac{dC_{T_2O}}{dt} - \frac{1}{V} (v_{in} C_{T_2O}^{in} - v_{out} C_{T_2O}^{out}) - K_{S,ad} a_v X_4 + K_{F,ex2} a_v X_2 = 0, \quad (9)$$

- mass balance of water, H₂O, on the surface of grain

$$\gamma \frac{dq_{H_2O}}{dt} + K_{S,ad} a_v X_3 + K_{F,ex1} a_v X_1 + K_{F,ex2} a_v X_2 = 0, \quad (10)$$

- mass balance of tritiated water, T₂O, on the surface of grain

$$\gamma \frac{dq_{T_2O}}{dt} + K_{S,ad} a_v X_4 - K_{F,ex1} a_v X_1 - K_{F,ex2} a_v X_2 = S_{T_2O}, \quad (11)$$

where

$$S_{T_2O} = -\frac{a_v}{\gamma} D_{T,g} \left(\frac{\partial C_{T,g}(r,t)}{\partial r} \right)_{r=a}, \quad (12)$$

$$X_1 = C_{T_2}^{out} - \frac{(C_{H_2}^{out}/K + C_{T_2}^{out}) q_{T_2O}}{q_{H_2O} + q_{T_2O}}, \quad (13)$$

$$X_2 = C_{T_2O}^{out} - \frac{(C_{H_2O}^{out} + C_{T_2O}^{out}) q_{T_2O}}{q_{H_2O} + q_{T_2O}} \quad (14)$$

for $(q_{H_2O} + q_{T_2O} - q^*) \geq 0$,

$$X_3 = \frac{q_{H_2O}}{q_{H_2O} + q_{T_2O}} (q_{H_2O} + q_{T_2O} - q^*), \quad (15)$$

$$X_4 = \frac{q_{T_2O}}{q_{H_2O} + q_{T_2O}} (q_{H_2O} + q_{T_2O} - q^*) \quad (16)$$

for $(q_{H_2O} + q_{T_2O} - q^*) \leq 0$,

$$X_3 = \frac{C_{H_2O}^{out}}{C_{H_2O}^{out} + C_{T_2O}^{out}} (q_{H_2O} + q_{T_2O} - q^*), \quad (17)$$

$$X_4 = \frac{C_{T_2O}^{out}}{C_{H_2O}^{out} + C_{T_2O}^{out}} (q_{H_2O} + q_{T_2O} - q^*) \quad (18)$$

and where a_v is the specific surface area of the packed bed [m²/m³], C is the concentration in the gas stream [mol/m³], K is the equilibrium constant of isotope exchange reaction (1), $K_{F,ex1}$ is the overall mass transfer coefficient of isotope exchange reaction (1) [m/s], $K_{F,ex2}$ is the overall mass transfer coefficient of isotope exchange reaction (2) [m/s], $K_{S,ad}$ is the overall mass transfer coefficient of adsorption [g/m²s], q is the amount of adsorbed water [mol/g], q^* is the amount of water adsorption equilibrated with the concentration of water vapor in the gas phase for adsorption [mol/g], S_{T_2O} is the tritiated water generation rate on grain surface [mol/g], t is the time coordinate, V is the volume of the packed bed [m³], v is the flow rate of process gas [m³/s], γ is the bed density [g/m³], and ε is the void fraction of the packed bed.

4. Results and discussion

Figs. 2–5 show the change in the tritium concentration in the outlet gas of the reaction bed as a result of temperature programmed desorption runs for Li₂ZrO₃ pebbles irradiated in JRR-4 with neutron fluences 2.4×10^{17} and 4.8×10^{17} cm⁻². As seen by comparing Figs. 2 and 3 the release of tritium in the presence of H₂O enhanced substantially over the release in pure N₂. We consider that the tritium transfer resistance on the surface of the lithium ceramics is diminished by the isotope exchange reaction (2) between water vapor in the gas stream and tritiated water adsorbed on the surface. The same effect was obtained in the case of tritium decontamination from the surface of various piping materials [9].

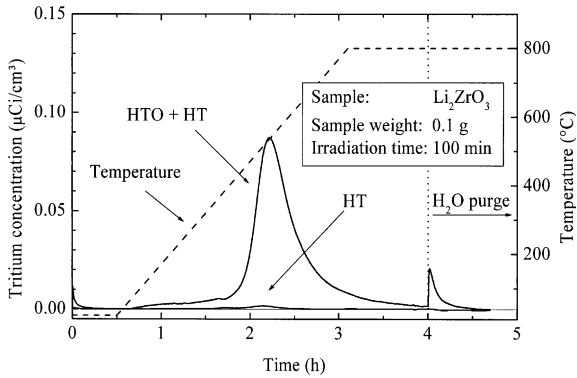


Fig. 2. Tritium release curve for Li_2ZrO_3 purge by N_2 .

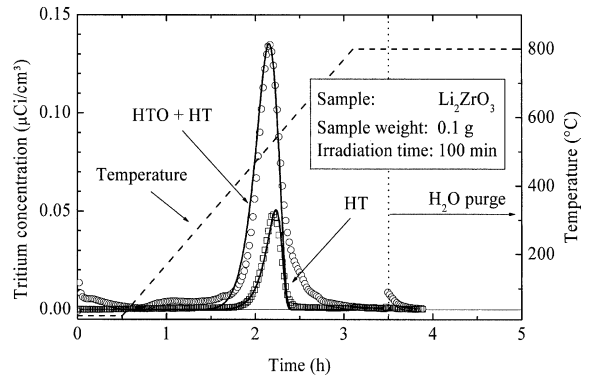


Fig. 5. Tritium release curve for Li_2ZrO_3 purge by N_2 with 10000 ppm H_2 (symbols and lines are the experimental and calculated curves, respectively).

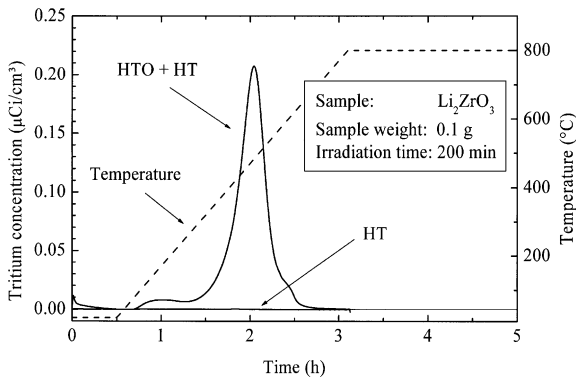


Fig. 3. Tritium release curve for Li_2ZrO_3 purged by N_2 with 10000 ppm water vapor.

Figs. 4 and 5 show that the shape of overall (HT + HTO) release curves at temperatures below 673 K are similar in spite of the change of H_2 concentration from 0 to 1000 ppm. The percentage of tritium released in the form of HT was found to be only about 6% and

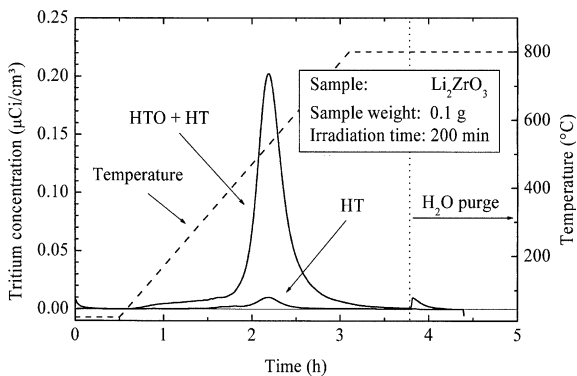


Fig. 4. Tritium release curve for Li_2ZrO_3 purge by N_2 with 1000 ppm H_2 .

24% when 1000 ppm and 10 000 ppm of H_2 , respectively, was added to the purge gas. This observation coincides with the fact that the rate of the isotope exchange reaction (1) is small and not effective in tritium recovery as HT at temperatures lower than 700 K.

The tritium release in the presence of water in the purge gas was studied in a previous paper [2], by assuming that bulk diffusion and isotope exchange reaction (2) were the rate-determining steps. The diffusivity was assumed to be a simple Arrhenius type temperature dependence while the mass transfer coefficient of the isotope exchange reaction (2), $K_{F,ex2}$ was assumed to be constant [10]. In the case of pure N_2 purge the diffusion and desorption/adsorption were assumed to be the rate-determining steps. The contribution of isotope exchange reaction (2) to the tritium release was assumed to be negligible since dry N_2 was employed for release.

Bulk diffusivity and overall mass transfer coefficients of surface phenomena evaluated in a previous study were utilized in order to solve numerically the system of differential equations described in the previous section. The overall mass transfer coefficient of isotope exchange reaction (1) was assumed to have an Arrhenius type of temperature dependence [3]

$$K_{F,ex1} = K_{ex1}^0 \exp(-E_{ex1}/RT), \quad (19)$$

where K_{ex1}^0 is the temperature independent pre-exponential factor [m/s], E_{ex1} is the activation energy [J/mol] and T is the absolute temperature [K]. Temperature was increased linearly at a rate 5 K/min. The values of hydrogen concentration in the purge gas were set to 1000 and 10 000 ppm in compliance with experimental spectra. The evaluation of tritium release spectra were performed by curve fitting procedures which allowed us to determine the values of the pre-exponential factor and the activation energy of the isotope exchange reaction (1).

The best fit obtained for the Li_2ZrO_3 sample purged with 10 000 ppm H_2/N_2 is shown in Fig. 5. The experimental data are shown as open circles and squares for HTO + HT and HT release, respectively, and the calculated curves are shown as solid lines. The values determined for activation energy and pre-exponential factor were 142 kJ/mol and 1.7 m/s, respectively. The experimental curves are reasonably reproduced, however the tritium release at higher temperature was not described well. The discrepancy compared to observed spectra suggests that another mass transfer process is involved in the tritium transport. This process is attributed to desorption of tritium trapped on an adsorption sites with higher activation energies on the surface of crystal grains and released as HTO at higher temperatures. Assuming that desorption from the sites with different activation energy runs independently the present model can be applied for fitting a main release peak of HTO together with the HT release.

The overall mass transfer coefficient of the isotope exchange reaction (1) estimated in the present work and values obtained by Baba et al. [3] in the experiments with unirradiated Li_2ZrO_3 can be compared as follows:

$$K_{F,\text{exl}} = 1.7 \exp(-148000/RT), \quad (20)$$

$$K_{F,\text{exl}} = 1.6 * 10^2 \exp(-121000/RT). \quad (21)$$

As can be seen by comparing Eq. (19) and Eq. (20) the pre-exponential factor estimated in the present paper (first equation) is two orders of magnitude smaller than value given by Baba et al. Either the differences in experimental methods or another aspect of tritium transport could be the reason of this discrepancy.

5. Conclusions

Out of pile TPD experiments with Li_2ZrO_3 were performed in the JRR-4 research reactor in JAERI using N_2 containing H_2 at various partial pressure as purge gas. When H_2 is added to the purge gas, tritium was released as HT form due to isotope exchange reaction (1). However, the rate of isotope exchange reaction (1) was found to be small and only 6% of tritium was released as HT when 0.1% H_2 was in the N_2 purge gas. The tritium release curves were analyzed numerically by applying the presented model. The overall mass transfer coefficient of isotope exchange reaction (1) was evaluated by curve fitting, taking into account the diffusion of tritium in the bulk as well as adsorption/desorption of tritium on the surface of the grains.

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