

#### 4.4

### Chemical Form of Tritium Released from Solid Breeder Materials and the Influences of it on a Bred Tritium Recovery Systems

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#### Abstract

The ratio of HTO in total tritium was measured at release of the bred tritium to the purge gas with hydrogen using the thermal release after irradiation method, where neutron irradiation was performed at JRR-3 reactor in JAERI or KUR reactor in Kyoto University. It is experimentally confirmed in this study that not a small portion of bred tritium is released to the purge gas in the form of HTO form ceramic breeder materials even when hydrogen is added to the purge gas. The chemical composition is to be decided by the competitive reaction at the grain surface of a ceramic breeder material where desorption reaction, isotope exchange reaction 1, isotope exchange reaction 2 and water formation reaction are considered to take part.

Observation in this study implies that it is necessary to have a bred tritium recovery system applicable for both HT and HTO form to recover whole bred tritium. The chemical composition also decides the amount of tritium transferable to the cooling water of the electricity generation system through the structural material in the blanket

system. Permeation behavior of tritium through some structural materials at various conditions are also discussed.

## 1. introduction

It is required to develop an efficient tritium fueling cycle keeping the overall tritium breeding ratio larger than 1.0 and a reliable tritium confinement system assuring the radio-active safety of tritium in construction of the D-T fusion reactor. The blanket is the place where the tritium recovery system has contact with the cooling system for electricity generation at the elevated temperature. Therefore, design of efficient means to recover bred tritium with minimum permeation loss is to be made. Tritium behavior in the breeding blanket is discussed in this study targeting the chemical form of tritium at release to blanket purge gas from solid breeder materials because the chemical form of tritium in the blanket purge gas gives profound effect on design of tritium recovery means and at estimation of permeation loss.

It seems to be taken as the common recognition to add about 1,000ppm of hydrogen to the blanket purge gas probably for recovery of tritium as HT form, and the recovery method of the bred tritium is discussed so far mostly based on this recognition, though the reason has not been clearly explained.

It has been reported by the present authors that water vapor is generated from various solid breeder materials at introduction of hydrogen to the purge gas at the elevated temperature [1-3]. It has been also reported by the present authors that the isotopes exchange reaction between tritium on the grain surface of breeder material and water vapor in the purge gas, named as the isotope exchange reaction 2 by the present authors, is the fastest surface reaction among reactions considered to take place at release of bred tritium from solid breeder blanket such as absorption, adsorption and desorption, isotope exchange reaction between tritium on grain surface and hydrogen in gas phase (named as the isotope exchange reaction 1)[4-6]

In this study, the ratio of HTO in total tritium was measured at release of the bred tritium to the purge gas with hydrogen using the thermal release after irradiation method, where neutron irradiation was performed at JRR-3 reactor in JAERI or KUR reactor in

Kyoto University. Additionally, Permeation rate of hydrogen through palladium-silver alloy at introduction of water vapor to hydrogen gas was measured to consider a bred tritium recovery system useful for both HT and HTO form tritium.

## 2. Preparatory consideration

### 2.1 Tritium release mechanism

In order to understand the tritium behavior in a blanket system packed with sintered pebbles of micro crystal grains of ceramic breeder material, 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 to the grain surface,
- (3) interaction of migrating tritium with irradiation defects formed in crystal grain,
- (4) adsorption or desorption of tritium on grain,
- (5) absorption of tritium into bulk of crystal grain,
- (6) isotope exchange reaction between molecular form 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 grain surface at addition of  $H_2$  to the blanket purge gas especially at high temperature,
- (9) transfer of hydrogen isotopes and water through pores of the sintered pebbles,
- (10) transfer of hydrogen isotopes and water through boundary layer formed on the surface of a sintered pebbles to the gas stream.

Steps (1), (2) and (3) decide the diffusion inventory of tritium which corresponds to the amount of tritium in the bulk of crystal grains when no absorption occurs. Tritium release behavior at low temperature is considered to be strongly affected by these tritium transfer steps. Step (5) decides the absorption inventory due to absorption of water vapor or molecular form hydrogen into the bulk of grain. The present authors have observed that water vapor is absorbed into  $Li_2O$  at the higher blanket temperature though  $Li_2TiO_3$ ,  $LiAlO_2$ ,  $Li_2ZrO_3$  and  $Li_4SiO_4$  have no detectable absorption capacity of water or molecular form hydrogen, steps (4), (6), (7) and (8) decide the surface

inventory of tritium which corresponds to the amount of tritium on the surface of crystal grains. These reactions compete at the grain surface also to decide the chemical form of tritium released into the purge gas. Then, it can be said that the amount of tritium permeable from blanket system to coolant of electricity generation system is controlled by steps (4), (6), (7) and (8). Step (9) decides the tritium inventory in micro pores of the sintered pebbles. Steps (10) decides the tritium inventory under diffusion through the boundary layer formed around the sintered pebbles. The experimental results on tritium inventory so far indicates that effect of steps (9) and (10) are negligible [4,5].

It must be kept in mind that the same amount of oxygen as bred tritium is also liberated from the breeder materials to make water with hydrogen added to the purge gas.

Above consideration indicate that a certain part of the bred tritium must be released into the blanket purge gas as the form of HTO. Accordingly, it is necessary to check if the ratio of HTO in bred tritium is negligible or not in design of the bred tritium recovery system.

## 2. 2 Hydrogen Transfer in metals

The permeation of hydrogen through a metallic membrane essentially involves the following consecutive steps.

- (1) Transfer of the molecule from the gas phase to the membrane surface.
- (2) Dissociation of the molecules to single atoms on the surface
- (3) Transfer of an atom from the surface to the bulk of the metal
- (4) Diffusion of gas atoms through the membrane under the concentration gradient established
- (5) Transfer of atoms from the solution to the surface at the permeation secondary side
- (6) Recombination of atoms to form molecules on the permeation secondary side
- (7) Desorption of gas from the membrane surface.

It is considered that introduction of water vapor to hydrogen gas has an effect on steps (2) and (6). This consideration indicates that permeation rate of tritium through the structural material in the blanket system decreases when the bred tritium is released into the blanket purge gas as the form of both HT and HTO.

### 3. Experimental

#### 3. 1 Experiment to release tritium from ceramic breeder blanket

Release curves of bred tritium from various ceramic breeder materials such as  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{TiO}_3$ , or  $\text{LiAlO}_2$  were obtained applying the out-pile temperature programmed desorption method using the experimental apparatus of which schematic diagram is shown in Fig. 1. A 0.4-1g sample of breeder particles contained in a quartz tube filled with helium gas was irradiated with the thermal neutron at JRR-4 reactor in JAERI or at the Kyoto University Research Reactor. The flux of thermal neutron was  $4.0 \times 10^{13}$  n/cm<sup>2</sup>s and  $1.6 \sim 2.8 \times 10^{13}$  n/cm<sup>2</sup>s in JAERI and KUR, respectively. The irradiated sample was purged by  $\text{N}_2$  gas with hydrogen of various partial pressures and the temperature of the sample bed was changed linearly from room temperature to 1073K with the rising rate of 5K/min. The flow rate of the purge gas was 100STPcm<sup>3</sup>/min. The release behavior of total tritium, HT and HTO, was measured using the first 50cc ionization chamber connected to the experimental apparatus shown in Fig. 1 where humidified  $\text{N}_2$  gas was introduced to the purge gas at the inlet of the ionization chamber to diminish the memory effect following the result reported elsewhere [7-9]. The release behavior of tritium as the HT form was followed by the second ionization chamber placed after the water bubbler.

After the purging procedure of each sample was finished, purge of the apparatus using humidified  $\text{N}_2$  gas was performed to estimate the amount of tritium trapped to the surface of piping between outlet of sample bed and inlet of first ionization chamber. This amount is considered to be negligible when the bred tritium is released to the purge gas in the HT form because the trapping rate of tritium to the piping surface through the isotope exchange reaction 1 is very slow as reported by the present authors [10,11].

#### 3. 2 Experiment concerning permeation of hydrogen through palladium alloy at introduction of water vapor to hydrogen gas

Schematic diagram of the experimental apparatus of this study is shown in Fig. 2. A tube of palladium with 25% silver (Pd75%-Ag25%, 125mm long, 4.8mm inner diameter and 5.0mm outer diameter, purchased from Nilaco Co.) was concentrically placed in quartz tube, and copper tube and brass joints were used as the piping materials.

Argon gas with hydrogen was used as the sample gas to the inner and outer flow channels. The flow rate of the process gas to each channel was 0.4l/min at the standard condition. The sample gas was initially passed through the packed bed of Pd-NT catalyst to change residual oxygen to water. Then, the sample gas was passed through the water bubbler at 277K to add about 8000ppm of the water vapor before introduction to the permeation test section. Temperature of the permeation membrane was changed from 373 to 573K using an electric furnace.

The permeation rates were measured by the steady-state method and the experiments were carried out as follows. First, Ar gas with about 1% H<sub>2</sub> was passed through both channels of the permeation test section and the test section heated up step-wisely to 573K to active the permeation membrane. Secondly, the temperature of the test section was set to the experimental temperature and the experimental sample gas was passed through the test section until the permeation of hydrogen reached the steady state. Then, the concentration of hydrogen at inlet and outlet of both channels was measured by gas-chromatography.

#### 4. Results and Discussion

The release curves of total tritium and tritium of HT form observed for Li<sub>4</sub>SiO<sub>4</sub> (grain size 1.2 micro meter, pebble size 1mm, made by FzK), Li<sub>2</sub>TiO<sub>3</sub> (grain size 1 micro meter, pebble size 1mm, made by CEA), Li<sub>2</sub>ZrO<sub>3</sub> (grain size 13 micro meter, pebble size 1mm, made by MAPI) and LiAlO<sub>2</sub> (grain size 1 micro meter, pebble size 4mm, made by JAERI) are compared in Figs. 3-7, respectively, where the N<sub>2</sub> gas with 1000 or 10000 ppm hydrogen is used as the purge gas. It can be seen from these figures that most bred tritium from Li<sub>4</sub>SiO<sub>4</sub>, Li<sub>2</sub>TiO<sub>3</sub> and Li<sub>2</sub>ZrO<sub>3</sub> is released as HTO though most tritium is released as HT form LiAlO<sub>2</sub> in the condition of this experiment and that the ratio of HT in the released tritium increases with rise of the temperature that gives vigorous release of bred tritium from breeder materials. It is known from comparison of Fig. 3 with Fig. 4 that the higher hydrogen concentration in the purge gas gives the higher HT ratio. It is considered by the present authors that competition of water desorption reaction of tritium as HTO, isotope exchange reaction 1 to produce HT and isotope exchange reaction 2 to produce HTO decide the ratio of HTO to HT [4,5].

The reactions considered to occur on the grain surface of solid breeder materials at tritium release are listed in **Table 1** for various temperature regions under various purge gas conditions.

The isotope exchange reaction 1 gives almost no contribution at low temperature even when 1,000-10,000ppm of hydrogen is added to the purge gas because its reaction rate observed for  $\text{Li}_2\text{TiO}_3$ ,  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{ZrO}_3$ ,  $\text{LiAlO}_2$  or  $\text{Li}_2\text{O}$  is so slow at the temperature lower than 600K [10,11]. On the contrary, the exchange reaction 2 works effectively to remove from the grain surface as HTO even when only a small amount of water vapor is included in the purge gas because its reaction rate is large even at temperature. At the same time, tritium trapped on the grain surface is released as the form of HTO through desorption reaction according to the adsorption isotherm of physically adsorbed water. Accordingly, at the lower temperature than 600K the main chemical form of released tritium to the purge gas is considered to be HTO form. At the higher temperature of breeder bed, the composition of HT is supposed to increase because the reaction heat of the isotope exchange reaction 1 is much larger than that of the isotope exchange reaction 2 [10,11]. The water formation reaction, however, becomes vigorous on the grain surface at the higher temperature than 750K to supply water to the purge gas. This phenomenon makes the HTO composition large through increase of water vapor to accelerate the isotope exchange reaction 2 and decrease of hydrogen in the purge gas to decelerate the isotope exchange reaction 1.

The observed results compared in **Fig. 3-7** and in **Table 2** well correspond to the prediction stated above.

It is necessary to keep the overall tritium breeder ratio large than 1.0 to develop a D-T fusion reactor having the self sustained fuel cycle. From this viewpoint, the bred tritium in the blanket must be recovered with high efficiency. Then, understanding about the chemical composition of the bred tritium released to the blanket purge gas is important for design of the recovery system and for estimation of tritium permeation to the outer region of the fuel system. Experimental results of this study indicated that further quantitative discussion about the chemical composition of the bred tritium is required because it is revealed in this study that not a small amount of tritium can be released

from solid breeder materials as the HTO form even when the purge gas with hydrogen is applied.

One solution is to have a precious metal catalyst bed at the outlet of the blanket purge gas to convert HTO to HT with help of the isotope exchange reaction 1 as proposed by the present authors elsewhere [6].

It is considered that the Palladium alloy system with the precious metal catalyst for isotope exchange is effective to recover bred tritium in HT and HTO form.

The temperature dependence of H<sub>2</sub> permeabilities through palladium alloy are shown in Fig. 8 when the water vapor was introduced to sample gas of the permeation primary side(case1), the permeation secondary side(case2), both side(case3) and neither side(case4). The permeability of this work are given by the following equation :

$$K_H = 1.70 \times 10^{-9} \exp(-9.82[\text{kJ/mol}]/RT) \text{ [mol m/m}^2 \text{ s Pa]} \text{ -----(case4)}$$

It can be seen from Fig. 8 addition of water vapor gives no effect on hydrogen permeation that at 573K, but water vapor gives hindering effect on permeation at the lower temperature.

This result indicates that the existence of HTO or H<sub>2</sub>O in the blanket gas prevents recovering tritium with high efficiency when the Palladium alloy system is used in recovery of bred tritium.

## 5. Conclusion

It is experimentally confirmed in this study that not a small portion of bred tritium is released to the purge gas in the form of HTO from ceramic breeder materials even when hydrogen is added to the purge gas. The chemical composition is decided by the competitive reaction at the surface of solid breeder materials where desorption reaction, isotope exchange reaction 1, and isotope exchange reaction 2 take part. The water formation reaction at addition of hydrogen also plays a role to increase the ratio of HTO.

Observation in this study implies that it is necessary to have a bred tritium recovery system useful for both HT and HTO form tritium.

It is observed that the water vapor prevents hydrogen permeation through Palladium alloy at lower temperature.

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Table 1 Comparison of tritium release characteristic from solid breeder materials

	Room temp ~ 573K	573K ~ 773K	773K ~ 973K	973K ~
Dry purge gas	Adsorption /desorption	Adsorption /desorption	Adsorption /desorption Li liberation	Adsorption /desorption Li liberation
Purge gas with hydrogen	Adsorption /desorption	Adsorption/ desorption Water formation Isotope exchange 2 Isotope exchange 1	Adsorption /desorption Water formation Li liberation Isotope exchange 2 Isotope exchange 1 Surface condition change	Adsorption /desorption Water formation Li liberation Isotope exchange 1 Isotope exchange 2 Surface condition change
Purge gas with water vapor	Isotope exchange 2 Adsorption/ desorption Li liberation (Li <sub>2</sub> O)	Isotope exchange 2 Adsorption/ desorption Li liberation (Li <sub>2</sub> O)	Isotope exchange 2 Adsorption/ desorption Absorption (Li <sub>2</sub> O) Li liberation	Isotope exchange 2 Adsorption/ desorption Absorption (Li <sub>2</sub> O) Li liberation

Table 2 Comparison of tritium release characteristic from solid breeder materials

Breeder material	Li <sub>2</sub> TiO <sub>3</sub> (CEA)	Li <sub>2</sub> TiO <sub>3</sub> (CEA)	Li <sub>4</sub> SiO <sub>4</sub> (FzK)	Li <sub>2</sub> ZrO <sub>3</sub> (MAPI)	LiAlO <sub>2</sub> (JAERI)
Purge gaz	10000ppmH <sub>2</sub> /N <sub>2</sub>	1000ppmH <sub>2</sub> /N <sub>2</sub>	10000ppmH <sub>2</sub> /N <sub>2</sub>	10000ppmH <sub>2</sub> /N <sub>2</sub>	10000ppmH <sub>2</sub> /N <sub>2</sub>
Irradiated place	JAERI	JAERI	KUR	JAERI	JAERI
Neutron flux [cm <sup>-2</sup> ·s <sup>-1</sup> ]	4 × 10 <sup>13</sup>	4 × 10 <sup>13</sup>	1.65 × 10 <sup>13</sup>	4 × 10 <sup>13</sup>	4 × 10 <sup>13</sup>
Irradiation time	100min	100min	3min	100min	30min
Theoretical tritium breeding amount [μ Ci]	875.8	875.8	39.74	629.66	281.09
Beginning of tritium release [min]	80~90	70~80	100	100~110	1st: 60~70 2nd: 110~120
Temp. giving peak in release curve [°C]	360	280	430	520	1st: 300 2nd: 590
Tritium amount counted by I.C.1 [μ Ci]	717.84	1114.56	20.4	625.92	113.4
Tritium amount counted by I.C.2 [μ Ci]	64.32	24.12	1.91	64.32	79.2
Tritium(I.C.2) /Tritium(I.C.1)	0.0896	0.0216	0.0938	0.1028	0.6984

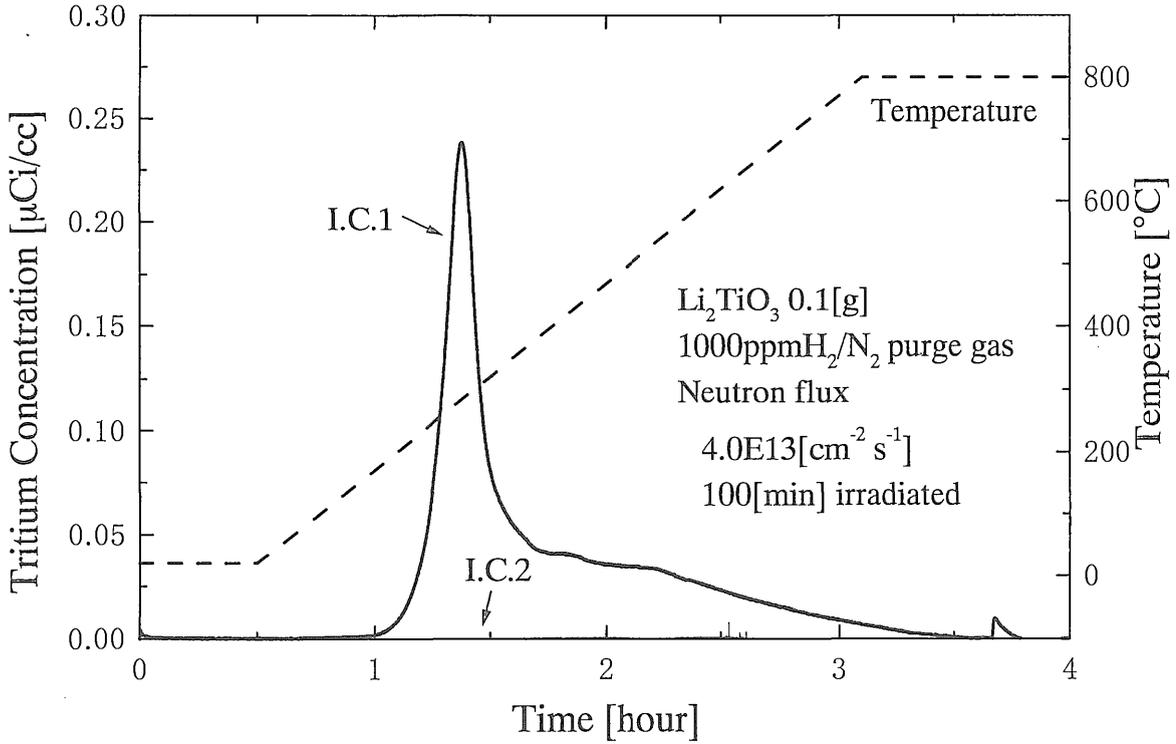


Fig. 3 Tritium release from  $\text{Li}_2\text{TiO}_3$  bed purged by 1,000ppm hydrogen.

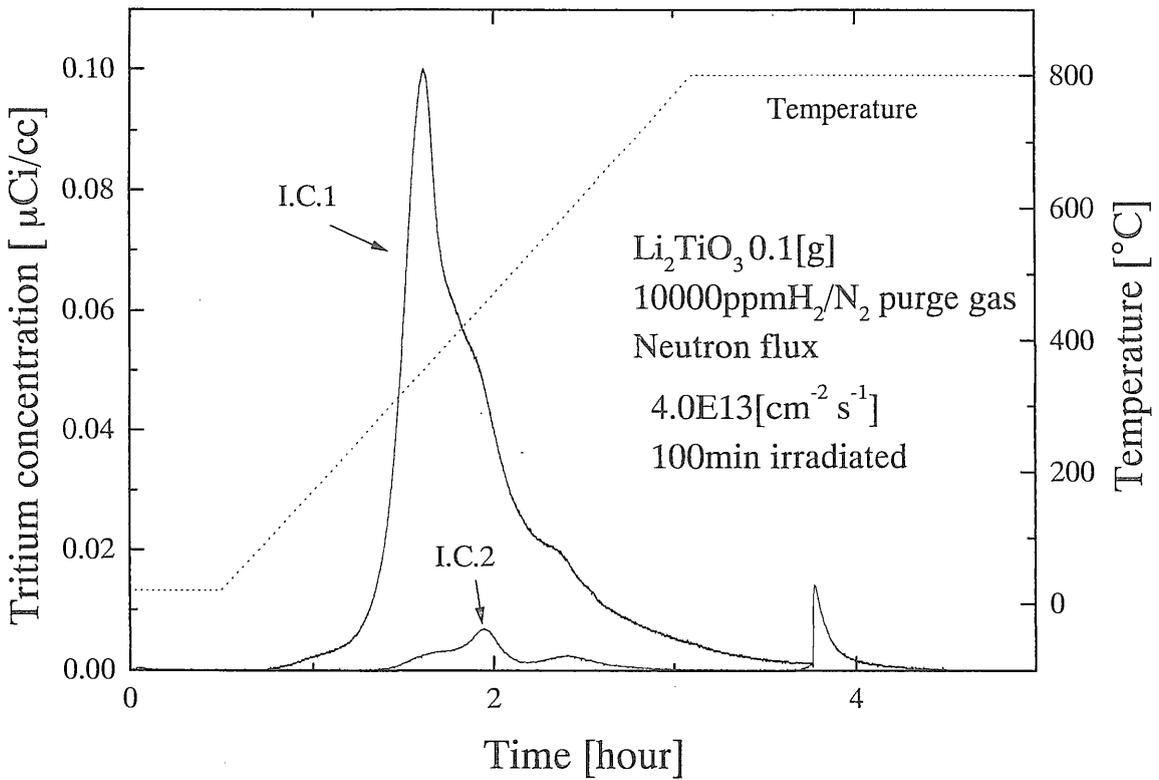


Fig. 4 Tritium release from  $\text{Li}_2\text{TiO}_3$  bed purged by 10,000ppm hydrogen.

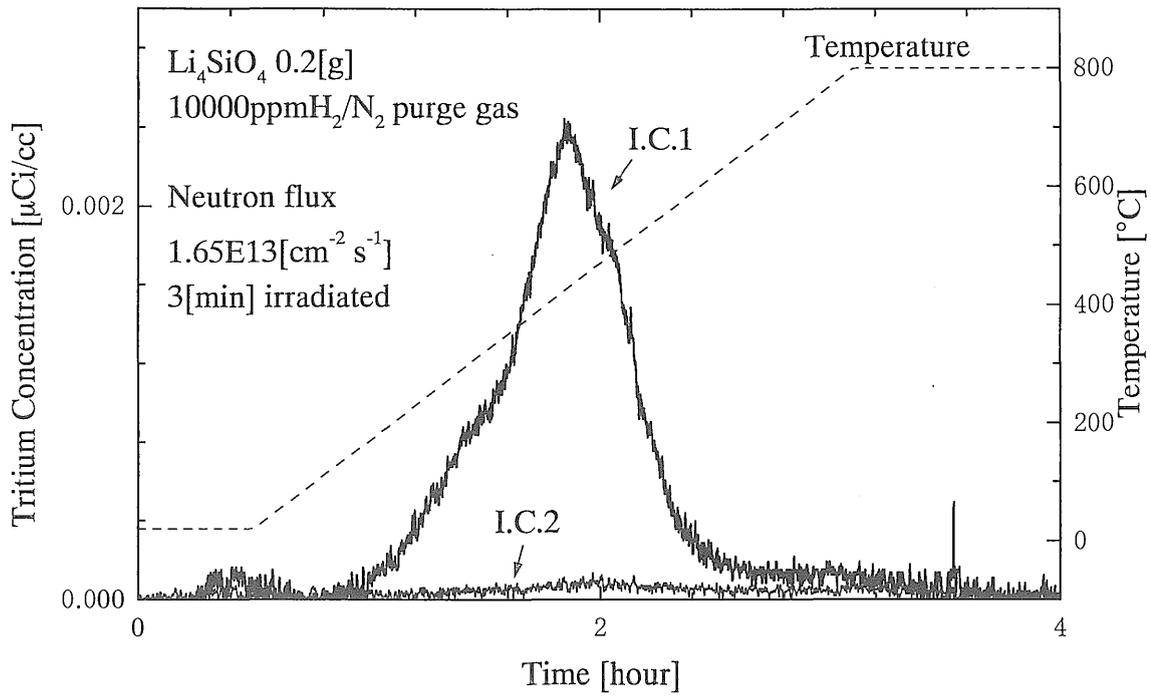


Fig. 5 Tritium release from Li<sub>4</sub>SiO<sub>4</sub> bed purged by 10,000ppm hydrogen.

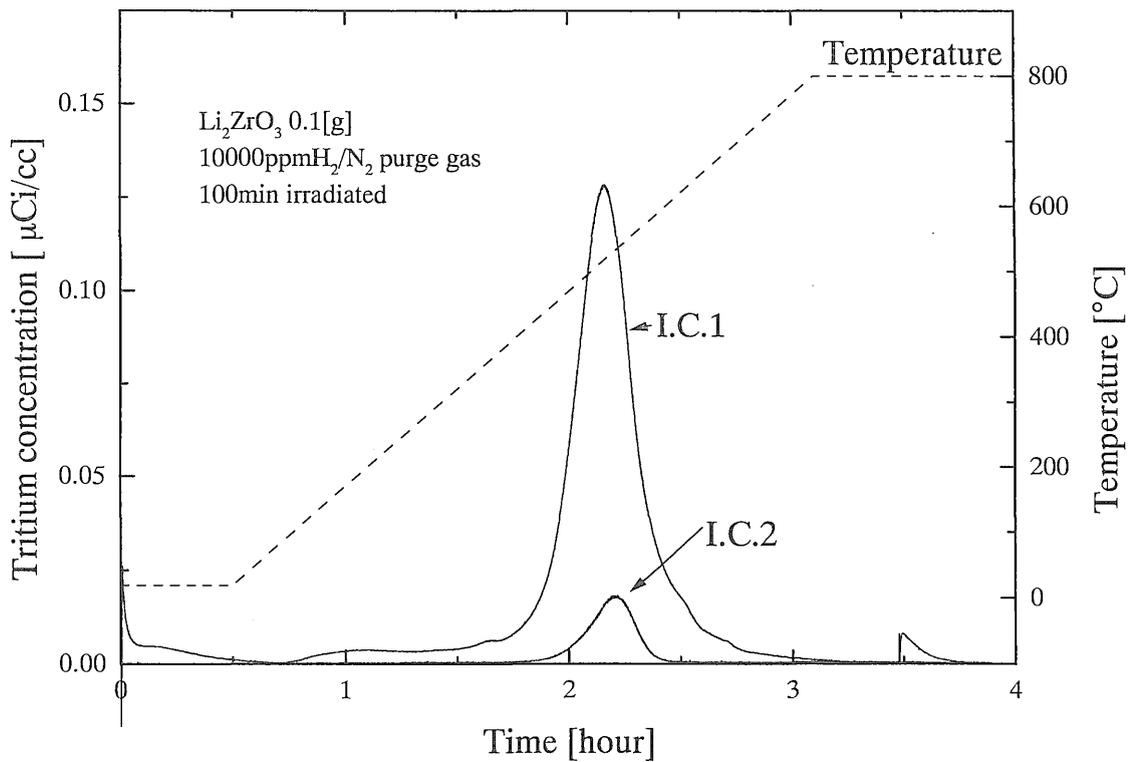


Fig. 6 Tritium release from Li<sub>2</sub>ZrO<sub>3</sub> bed purged by 10,000ppm hydrogen.

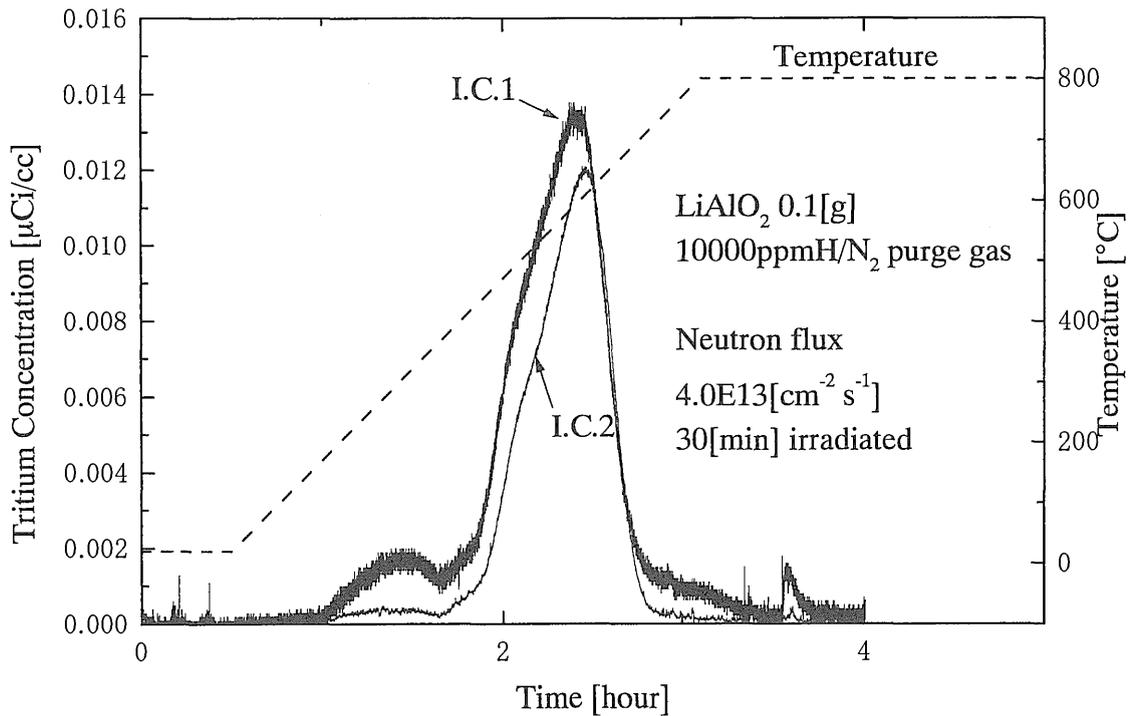


Fig. 7 Tritium release from LiAlO<sub>2</sub> bed purged by 10,000ppm hydrogen.

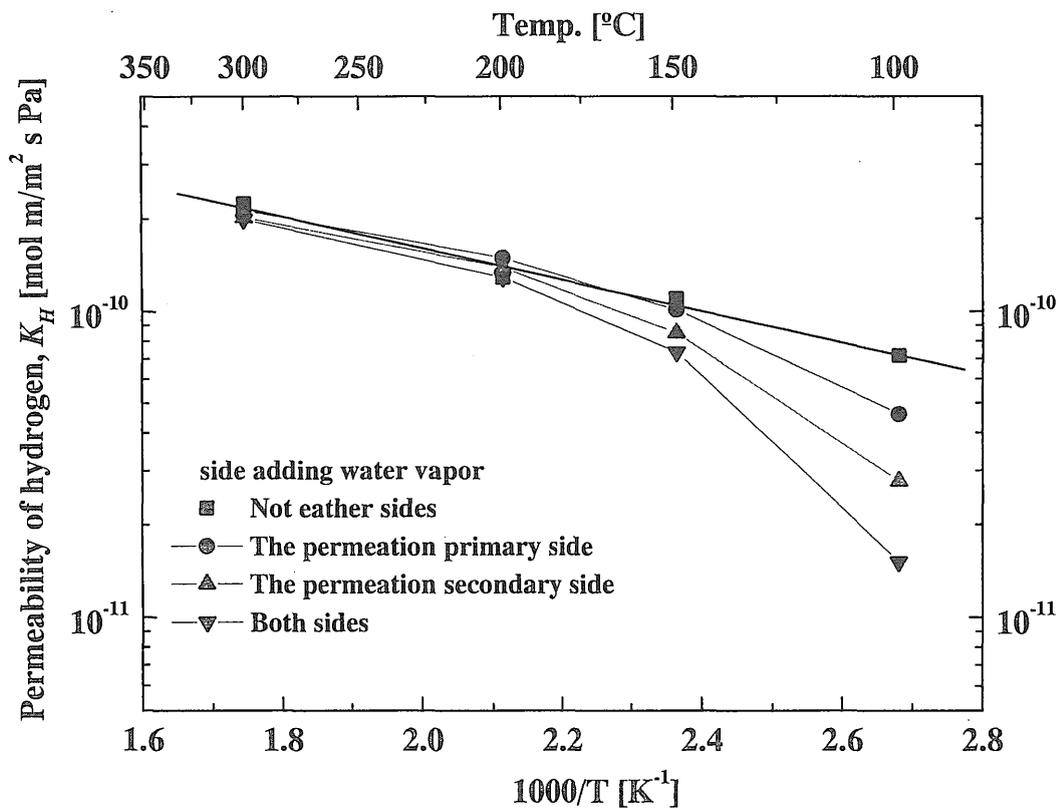


Fig. 8 H<sub>2</sub> permeabilities through palladium alloy at the introduction of water vapor to the sample gas

## 5. Session 4 - Material Development and Properties

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