Tritium Release from Ceramic Breeders with Catalytic Function

Kenzo Munakata[1], Toshihiko Kawano[1], Atsushi Baba[1], Takahiro Kawagoe[1], Yoshihiro Yokoyama[1], Toshiharu Takeishi[1], Masabumi Nishikawa[1], Hideki Nakashima[1], Hirotake Moriyma[2], Keizo Kawamoto[2], Kenji Okuno[3]
[1]Kyushu University, Department of Advanced Energy Engineering Science, Interdisciplinary Graduate School of Engineering Science, Kasuga 816-8580, Japan
[2]Kyoto University, Research Reactor Institute, Osaka 590-0494, Japan
[3]Shizuoka University, Radiochemistry Research Laboratory, Faculty of Science, 422-8529, Japan
Phone: +81-92-642-3784 Fax: +81-92-642-3784
E-mail: kenzo@nucl.kyushu-u.ac.jp

1. Introduction

Most current designs of D-T fusion reactor blankets employ ceramic breeders such as Li_2O, $LiAlO_2$, Li_2ZrO_3 and Li_4SiO_4. With regard to these ceramic breeders, a helium gas containing approximately 0.1 % of hydrogen would be used to extract tritium via isotopic exchange reactions that take place at the surface. In previous studies, the isotope exchange reactions and water adsorption at the surface of several ceramic blanket materials were investigated[1-3]. The results revealed that these isotope exchange reactions proceed fast only at higher temperatures. Because of the strong temperature dependency of the exchange reactions, a considerable decrease in the reaction rate takes place as the temperature is lowered. Taking into consideration that there is a broad temperature distribution within a blanket module[2], it is anticipated that the tritium bred in regions of lower temperature will presumably be poorly recovered, which would lead to increased overall steady state tritium inventories in the blanket module.

In order to obtain an improved recovery of tritium from a blanket over a broad range of temperatures, the effect of catalytic active metal additives, such as platinum and palladium, on the heterogeneous isotope exchange reactions at the breeder - sweep gas interface was examined in our previous work[4]. The results of the study revealed that isotope exchange reactions proceed fast if catalytic additive metals are deposited on the surface of a Li_4SiO_4 ceramic breeder; we designated this type of breeders as “Catalytic Breeders”. This time, the authors conducted out of pile annealing tests using the catalytic breeder materials irradiated in a research reactor and investigated the effect of catalytic additives on the tritium release from the ceramic breeder material.

2. Preparation of catalytic breeder

Platinum was deposited on ceramic breeder pebbles (Li_4SiO_4, 0.51-0.94 mm (av. 0.68 mm) in diameter, >98 %TD) by the incipient wet impregnation method generally used for the fabrication of catalysts. The Li_4SiO_4 pebbles were donated by FzK (Research Center Karlsruhe) in Germany. In the fabrication procedure, a solution of platinum tetra ammonium nitrate $Pt(NH_3)_4(NO_3)_2$ was pored dropwise onto the previously dried Li_4SiO_4 pebbles. After this treatment, the wet Li_4SiO_4 pellets were dried in an oven. The obtained precursors were

calcined and reduced in a quartz tube reactor at 400°C. The details of the fabrication procedure are cited in our previous report[4]. The sample ceramic breeder (Pt/ Li_4SiO_4) used in this work is the exactly same one as that used in our previous study[4]. The exact content of the deposited Pt has not yet been determined, but according to the mass balance in the fabrication process the concentrations can be estimated being within a range of 0.7 to 2 wt %.

3. Irradiation of ceramic breeders and experiments

Li_4SiO_4 and Pt/ Li_4SiO_4 breeder materials were irradiated in Kyoto University Research Reactor with the neutrons flux of 2.75×10^{13} $cm^{-3}s^{-1}$ for 1 min. The research reactor has several ports for irradiation tests, and the port Pn-2 was used to irradiate the breeder materials. The neutron energy spectrum at Pn-2 is shown in Fig. 1[6]. The breeder pebbles were encapsulated in quartz tubes (6 mm$\phi\times$60 mm) with low-pressure He gases, and which were placed in sample holders made of polyethylene. Before encapsulation, breeder pebbles were dried under dry He gas streams for 12 h by raising their temperature stepwise up to 400°C. The sample holders were transported to the core of the thermal reactor with the help of pressurized air. After irradiation, the quartz tubes were mechanically broken and the breeders were placed in reaction tubes for annealing experiments. All procedures are carried out in a glove box of which moisture level is less than 1 ppm. Accordingly, the breeder materials were never exposed to the atmosphere before and during experiments.

Figure 2 shows the neutron spectrum at Pn-2 calculated from the data shown in Fig. 1. Figure 2 also shows the cross section of the reactions related to tritium production from ^{6}Li and ^{7}Li, which were taken from JENDL-Dosimetory file[7]. As shown in this figure, there are higher neutron fluxes in the lower energy region. The cross section of the ^{6}Li(n,t) reaction is high at the lower energy region, whereas the cross section of the ^{7}Li(n,n't) is very low in the region of thermal neutron. Therefore, the ^{6}Li and neutron reaction is the dominating path for the production of tritium. Figure 3 shows the response (production of neutron flux $\phi(E)$ and cross section $\sigma(E)$) for ^{6}Li as a function of neutron energy. This figure verifies that almost all

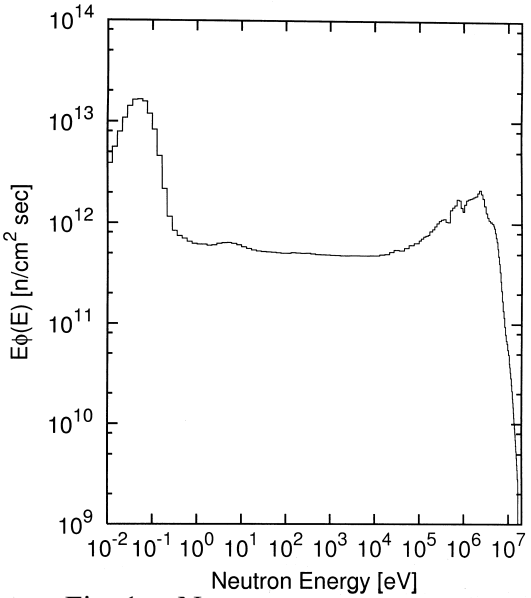

Fig. 1 Neutron energy spectrum at Pn-2 in KUR

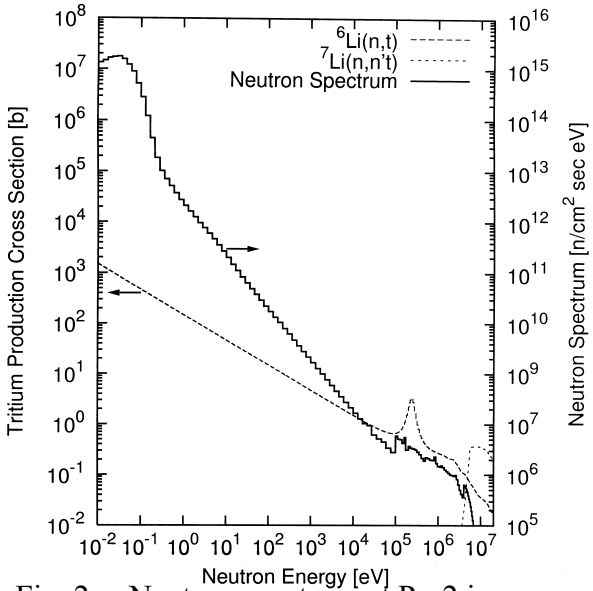

Fig. 2 Neutron spectrum at Pn-2 in KUR and cross section of nuclear reaction for tritium production

tritium is produced by low energy neutrons.

A schematic diagram of the annealing experiment is shown in Fig. 4. The experimental conditions are summarized in Table 1. 0.2 g of Pt/Li_4SiO_4 or Li_4SiO_4 pebbles were placed in the quartz tube reactor. The reactor tube was heated with an infrared image furnace, and thus the bed temperature can be raised to set temperatures within 1 - 2 min. A 1000 ppm H_2/Nitrogen gas was used as the purge gas, and the gas flow rate was controlled with conventional mass flow controllers. The gases employed were purified with a trap containing 5A molecular sieve (MS5A) to remove residual water vapor. The concentrations of tritium in inlet and outlet streams of the reactor were traced with an ionization chamber (made of stainless steel) of which effective volume was 90 cm^3. The applied voltage between the electrodes of the ion chamber was 90 V. Just before the process gas was introduced into the ionization chamber, the gas was mixed with a nitrogen gas containing 10000 ppm of H_2O to avoid system effects in the ionization chamber. The system effects are caused by tritium sorbed on the surface of the electrodes, which induces incorrect electric outputs from the ionization chambers. Tritium are sorbed via adsorption or isotope exchange reactions, and thus the addition of high concentration water vapors to the process gases enables to prevent the sorption of tritium on the surface of the electrodes[5]. The exit gas was treated with MS5A adsorbent beds and water bubblers.

Table 1 Experimental conditions

Breeder	(1) Li_4SiO_4 (pebble size 0.68 mm, >98 %TD) (2) Pt/Li_4SiO_4
Irradiation condition	Neutron flux: 2.75×10^{13} $cm^{-3}s^{-1}$ Irradiation time: 1 min
Amount of breeders	0.2 g
Sweep gas	1000 ppm H_2/N_2 (1000ppm H_2O/N_2 only at 900 °C)
Gas velocity	100 cm^3/min
Bed diameter	~4 mm
Temperature	20 – 900 °C

4. Results of out of pile annealing experiments

Figure 5 shows a result of out of pile annealing tests for the Li_4SiO_4 pebbles irradiated in the thermal reactor; the figure shows the change in tritium level in the outlet

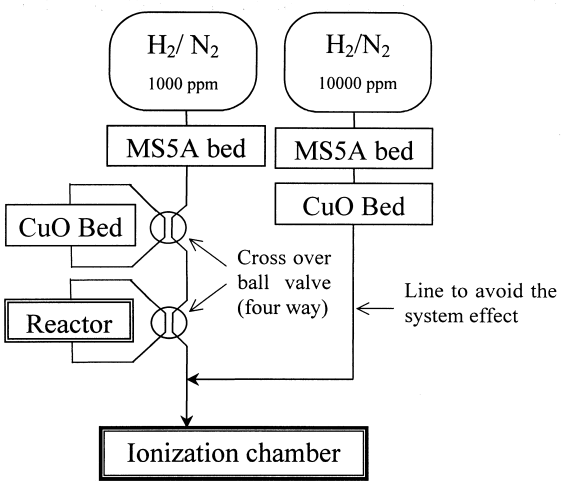

Fig. 3 Response of nuclear reaction for tritium production

Fig. 4 Schematic diagram of apparatus for the annealing experiment

stream of the reactor. The flow rate of the sweep gas (1000 ppm H_2/N_2) was 100 ml/min. The reactor temperature was raised stepwise from ambient temperature to 300, 500, 700 and finally 900 °C. At each temperature (300, 500 and 700 °C), the reactor temperature was held constant for 15 min. The sweep gas was replaced with a 1000 ppm H_2O/N_2 gas at 15 min after the reactor temperature was raised to 900 °C to ensure the release of total amounts of tritium bred in the breeder materials via exchange reactions. As seen in this figure, the amount of tritium released from the Li_4SiO_4 pebbles increased with increasing temperature when the reactor temperature was lower than 900 °C. In total, 14.5 μCi (5.4×10^5 Bq) of tritium was released. The amounts of tritium released at each temperature are presented in Table 2. The largest amount of tritium (46 % of the total amount of tritium) was released at 700 °C, but only 15 % of the total amount of tritium was released at 300 °C.

Table 2 Fractional amount of tritium released at each temperature

Temp. [°C]	Fractional release [%]	
	Li_4SiO_4	Pt/Li_4SiO_4
20	0.1	0.7
300	15.3	27.5
500	32.8	54.3
700	46.4	15.6
900	3.7	1.8
900 (water purge)	1.5	0.1
Total amount Released	14.5 μCi (5.4×10^5 Bq)	13.3 μCi (4.9×10^5 Bq)
Total amount of tritium estimated	19.5 mCi (7.20×10^5 Bq)	19.2 mCi (7.10×10^5 Bq)

The result of out of pile annealing tests for the Pt/Li_4SiO_4 breeder is shown in Fig. 6. The reactor temperature was raised stepwise as described above. The flow rate of the sweep gas was also 100 ml/min; the experimental condition for this experiment was same as that for the experiment shown above. In this case, 13.3 μCi (4.9×10^5 Bq) of tritium was totally released. The amounts of tritium released at each temperature are presented in Table 2. The largest amount of tritium (54 % of the total amount of tritium) was released at 500 °C. 28 % of the total amount of tritium was released even at 300 °C. By comparing this result with that for the Li_4SiO_4 pebbles, it is seen that the amount of tritium released was increased at lower temperatures

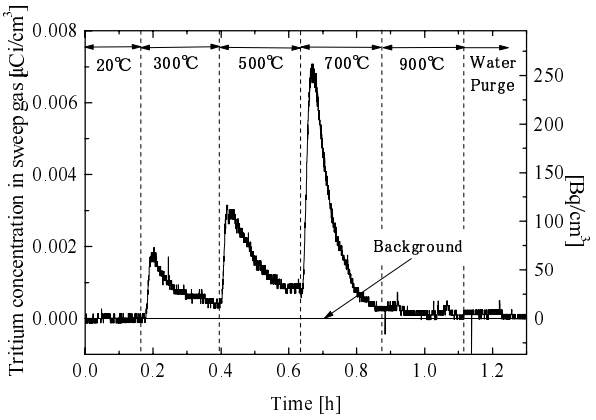

Fig. 5 Change in tritium concentration in outlet stream of Li_4SiO_4 bed

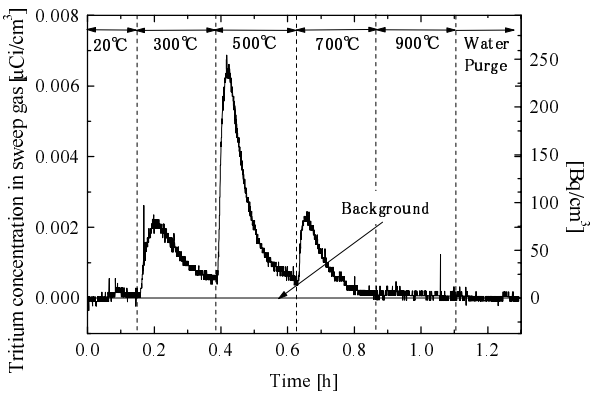

Fig. 6 Change in tritium concentration in outlet stream of Pt/Li_4SiO_4 bed

when the catalytic additive was impregnated into the Li_4SiO_4 pebbles. These results suggest that addition of catalytic additive metals to the ceramic breeder is an effective way to enhance the tritium release rate at lower temperatures.

As shown in Table 2, the total amounts of tritium produced in the breeder materials were 14.5 mCi for Li_4SiO_4 and 13.3 mCi for 1.5% Pt/ Li_4SiO_4, which were calculated from the results of the out of pile annealing experiments. The amounts of tritium produced in the breeder materials were also estimated from the neutron spectrum and the nuclear cross section shown in Figs. 2 and 3. In the estimation, the self-shielding effect was ignored. The amounts of tritium calculated in this way were 19.5 mCi for Li_4SiO_4 and 19.2 mCi for 1.5% Pt/ Li_4SiO_4 (see Table 2). The difference between the experimental and estimated values is approximately 25 %. This difference is probably because of change in neutron spectrum at Pn-2 in KUR; the neutron spectrum shown above was measured more than ten years ago and the present neutron spectrum is though to be somewhat different from the result of the previous measurement. The other probable reason is the negligence of the self-shielding effect in neutronic calculations, since ^6Li has a high cross section for the consumption of neutrons.

5. Conclusions

Catalytic breeders were fabricated by impregnating lithium silicate with platinum. Out of pile annealing experiments were conducted using irradiated ceramic breeders. The results of the experiments indicate that tritium bred in the catalytic breeder material is released at lower temperatures compared with the breeder material with no catalyst.

The amounts of tritium produced in the breeder materials were estimated by using the neutron spectrum and the nuclear cross section without consideration of self-shielding effects. In the estimation, the self-shielding effect was ignored. Comparison of experimental and calculated amounts of tritium produced indicates that the difference between the values is approximately 25 %.

Acknowledgment

The authors wish to thank to Prof. K. Kobayashi for giving data for the neutron spectrums in KUR.

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