Control of Chemical Forms of Tritium in FLiNaK under Low Flux Neutron Irradiation*)

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The use of the isotopic exchange between tritium produced in molten salts and hydrogen molecules in a sweep gas has been proposed as a way of recovering tritium in a self-cooled molten salt liquid blanket system [1–3]. In the present study, rate coefficients of the isotopic exchange for molten FLiNaK (LiF-NaF-KF) have been evaluated in a series of low flux neutron irradiation experiments with an AmBe neutron source at the OKTAVIAN facility of Osaka University in Japan. Approximately 300 cm^3 of FLiNaK were irradiated at 773 K in an Inconel 600 crucible, and tritium released from the free surface of FLiNaK has been swept by a pure He gas or He+H_2 (0.1%) gas. The change in the amounts of soluble tritium (TF, HTO) and insoluble tritium (HT) recovered by water bubblers has been evaluated in each sweep gas to evaluate the effectiveness of the tritium recovery with the isotopic exchange.

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1. Introduction

Molten fluoride salts, such as FLiBe (LiF-BeF_2) and FLiNaBe (LiF-NaF-BeF_2), are candidates for the tritium breeder/coolant in a self-cooled liquid blanket system of the helical fusion reactor FFHR [4]. FLiNaK is used as a simulant of FLiBe and FLiNaBe because it has similar physical properties and is less harmful to health [5]. FLiNaK itself could be a candidate for the tritium breeder/coolant with Pb as a neutron multiplier in a Be free liquid blanket concept [6]. It is considered important for the tritium recovery in the liquid blankets to understand tritium behaviors systematically for FLiBe, FLiNaBe, and FLiNaK. While FLiBe and FLiNaBe can form polyatomic ions, such as BeF_4^{2-} [7], it is considered that each ion in FLiNaK exists individually due to absence of Be. In the cases of FLiBe and FLiNaBe, free F^- ions are produced when Be in the polyatomic ions disappear in Be(n,2n) nuclear reactions. Corrosive TF can be produced by combining tritium with the free F^- ions. Although tritium in FLiNaK can possibly produce TF, there are few studies on tritium behaviors in FLiNaK. Effects of the isotopic exchange between tritium produced in FLiNaK and hydrogen molecules on tritium behaviors have not been examined either.

Tritium behaviors in FLiBe under neutron environment were studied in the fast neutron source reactor YAYOI of the University of Tokyo [1–3]. The previous research has shown the change in chemical forms of tritium released from FLiBe under various H_2 concentrations in sweep gases. These studies indicate that HT is produced with the isotopic reaction, T^+ (in FLiBe) + H_2 (in gas) $\rightarrow$ H^+ (in FLiBe) + HT (in gas). The results showed that larger amounts of tritium were released as HT in a sweep gas with higher H_2 concentrations. In the Kyoto University Research Reactor, the rate coefficient of the isotopic exchange reaction was also evaluated for solid FLiBe at 573 K [8].

In the present study, the low flux neutron irradiation experiments with an AmBe neutron source are performed on FLiNaK to evaluate tritium behaviors. The effects of the isotopic exchange under the neutron environment on tritium behaviors are evaluated by pure He and He+H_2 (0.1%) gases. Change in chemical forms of tritium in each sweep gas and the rate coefficient of the isotopic exchange for FLiNaK are described in this paper.

2. Experimental

Figure 1 shows a schematic diagram of the neutron irradiation experimental system with an AmBe neutron source for molten FLiNaK. Neutrons emitted from the neutron source have energies up to 10.7 MeV and the intensity is $\sim 2 \times 10^6$ n/s. Approximately 300 cm^3 of FLiNaK is kept at 773 K in an Inconel 600 crucible, the thickness of which is 3 mm for the cylindrical shell and 8 mm for the

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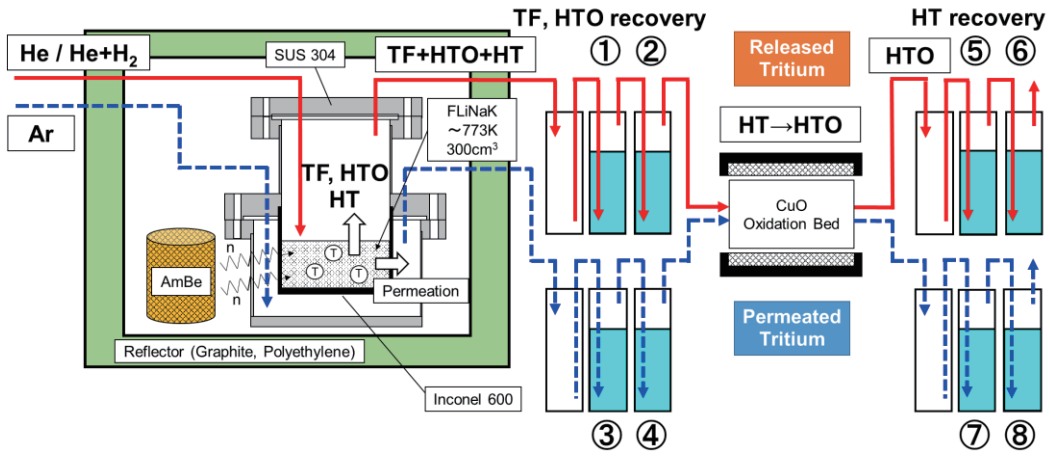

Fig. 1 Schematic diagram of irradiation experiments with an AmBe neutron source for molten FLiNaK.

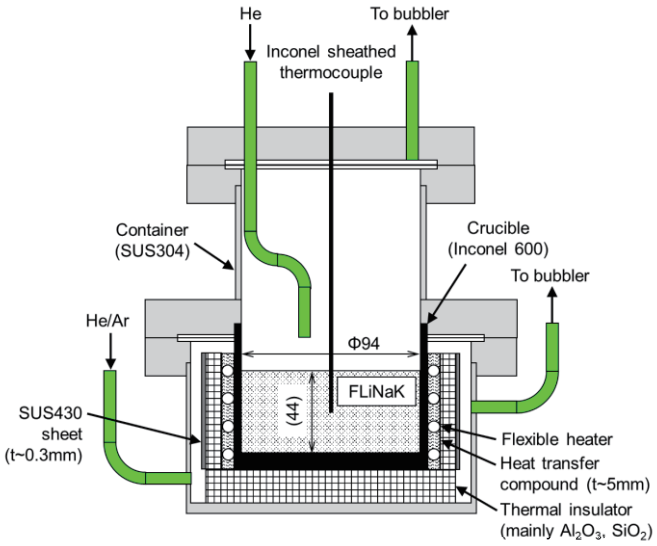

Fig. 2 Cross-section of FLiNaK container (unit: mm).

bottom. The nickel based alloy of Inconel 600 has been selected considering its corrosion resistance in FLiNaK and strength at high temperature [9]. Figure 2 shows a cross section of the FLiNaK container. Tritium released directly from the free surface of FLiNaK is denoted as "Released Tritium", and tritium that permeates through the crucible is denoted as "Permeated Tritium" as shown in Fig. 1. Soluble tritium (TF, HTO) and insoluble tritium (HT) in a sweep gas are recovered separately by water bubblers. Insoluble tritium, HT, is converted into soluble HTO by CuO oxidation beds before the tritium recovery. The amounts of recovered tritium are measured by a liquid scintillation counter. The flow rate of sweep gases is typically set to 25 sccm throughout the experiments. The effects of the isotopic exchange between tritium produced in FLiNaK and hydrogen molecules in a sweep gas are evaluated by a He gas containing 1020 ppm H_2 (hereinafter referred to as He+H_2 (0.1%) gas).

Before starting a series of irradiation experiments using the He+H_2 (0.1%) gas, the total amount of tritium recovered by a pure He gas (purity of 6N) in a steady state was compared with the calculated tritium production rate to confirm the validity of the experimental system. The tritium production rate in FLiNaK was calculated as 10.6 Bq/week using the Monte Carlo simulation code MCNP6 with the nuclear data libraries ENDF/B-VII.1 [10]. Table 1 shows the amounts of tritium recovered for one week in our previous experiments using a pure He sweep gas [11]. The results were obtained by the tritium recovery for 165 hours, which is approximately one week, from the accumulated neutron irradiation time (i.e., the time from the start of neutron irradiation) of 828 hours. The total amount of recovered tritium was 12.0 Bq/week in a steady state, and the value was close to the calculated value, 10.6 Bq/week. While a certain amount of tritium might be trapped on the crucible and pipes, tritium released from FLiNaK reached the steady state after one week of irradiation. The following analyses of tritium behaviors could be successfully performed in the present study.

Table 1 Amounts of recovered tritium (pure He gas) [11].

	TF, HTO [Bq/week]	HT [Bq/week]
Released tritium	11.6±0.29	0.0±0.04
Permeated tritium	0.2±0.04	0.2±0.04
Total	11.8±0.29	0.2±0.06

Since the amounts of permeated tritium were significantly small in comparison with released tritium, only released tritium is considered in the following discussion for simplification. The amount of permeated tritium could be estimated to be much smaller than that of released tritium assuming that the driving tritium gas pressure is low [11] and tritium permeation flux is limited by metal surface reactions [12].

Table 2 Amounts of recovered tritium (He+H_2 (0.1%) gas).

	TF, HTO [Bq/week]	HT [Bq/week]
Released tritium	5.5±0.15	6.6±0.45
Permeated tritium	0.2±0.04	0.2±0.04
Total	5.7±0.16	6.8±0.45

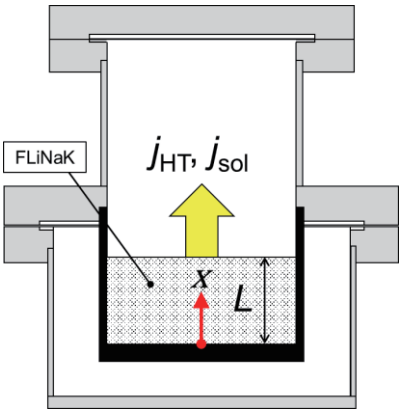

Fig. 3 Calculation model of tritium release from FLiNaK in a one-dimensional diffusion equation.

3. Results and Discussion

Table 2 shows the amounts of the recovered tritium by the He+H_2 (0.1%) gas for one week. The results were obtained from the tritium recovery for 168 hours from the accumulated neutron irradiation time of 472 hours. The total amount of the recovered tritium is 12.5 Bq/week, and that is comparable with the value in the case of the pure He gas. Although 100% of released tritium is soluble in the case of the pure He gas, only 45% is soluble in the He+H_2 (0.1%) gas. The isotopic exchange between tritium produced in FLiNaK with hydrogen molecules in the He+H_2 (0.1%) gas resulted in the production of 55% HT.

A one-dimensional diffusion equation is applied to an approximate modeling of tritium behaviors in molten FLiNaK and tritium release from the FLiNaK free surface, as shown in Fig. 3. Tritium is assumed to be released by direct desorption of soluble tritium (i.e., TF, HTO), and/or released as HT with the isotopic exchange between tritium produced in FLiNaK and hydrogen molecules in a sweep gas. The one-dimensional diffusion equation with tritium generation is below:

$$\frac{\partial C_F}{\partial t} = D\frac{\partial^2 C_F}{\partial x^2} + S, \tag{1}$$

where C_F (x, t) is the tritium concentrations in FLiNaK, D is the diffusion coefficients of tritium for FLiNaK (= 7.32 $\times 10^{-9}$ m^2/s at 773 K [13]) and S is the tritium production rate per volume of FLiNaK (= 11.6 Bq/{(300 $\times 10^{-6}$ m^3) $\times$ (7 $\times$ 24 $\times$ 3600 s)} = 6.4 $\times 10^{-2}$ Bq/m^3/s). The measurement value of 11.6 Bq/week in Table 1 is used as the tritium production rate assuming that the tritium recovery rate and the tritium production rate are the same in a steady state.

The initial tritium concentration in FLiNaK, C_{F0}, is assumed to be zero because pure He, He+H_2 (0.1%), and pure He gases were flowed through the crucible for 329.5 hours, 254 hours, and 188 hours, respectively, before neutron irradiation to remove residual tritium. A reflecting boundary condition at $x = 0$ is selected since tritium is hardly permeated, as shown in Table 1 and Table 2. Assuming that the direct desorption of soluble tritium and the isotopic exchange reaction on the free surface of FLiNaK ($x = L$) is of the first order dependence on C_F and H_2 concentration in a sweep gas [8], the initial and boundary conditions are expressed as follows:

$$C_F(x, 0) = 0, \tag{2}$$

$$\frac{\partial C_F}{\partial x} = 0 \qquad \text{at } x = 0, \tag{3}$$

$$j_{Sol} = -D\frac{\partial C_F}{\partial x} = k_{Sol}C_F \qquad \text{at } x = L, \tag{4a}$$

$$j_{HT} = -D\frac{\partial C_F}{\partial x} = k_{H_2}p_{H_2}C_F \qquad \text{at } x = L, \tag{4b}$$

where j_{Sol} and j_{HT} are the fluxes of released soluble tritium (TF, HTO) and HT, respectively. k_{Sol} is the rate coefficient for the desorption of the soluble tritium, k_{H_2} is the rate coefficient for the isotopic exchange reaction, and p_{H_2} is the H_2 concentration in the sweep gas (= 0.1 vol. H_2%). Eq. (4a) is used as a boundary condition at $x = L$ to obtain k_{Sol} from curve fitting of the amount of tritium recovered in the pure He gas. The value of k_{H_2} can be derived from the ratio of Eq. (4a) to Eq. (4b) by the amount of the recovered HT and soluble tritium in Table 2 as follows:

$$k_{H_2} = \frac{j_{HT}}{j_{Sol}} \times \frac{k_{Sol}}{p_{H_2}} = \frac{6.6}{5.5} \times \frac{k_{Sol}}{0.1}. \tag{5}$$

Here, the unit of k_{H_2} is m/s/vol. H_2%.

Since tritium recovered by the water bubblers is integrated amounts, the following equation is used in the cases of the pure He gas to evaluate the change in the integrated amounts of tritium recovered after the AmBe source was placed and removed:

$$Q = \int_0^t j_{Sol}Adt, \tag{6}$$

Q is the integrated amount of recovered tritium, and A is the area of the FLiNaK free surface. The plots in Fig. 4 show the integrated amounts of tritium recovered after the AmBe neutron source was placed in our previous experiments using a pure He sweep gas [11]. The plots are the integrated amounts of tritium recovered at 24, 48, and 284 hours from the initiation of neutron irradiation. The value of k_{Sol} has been obtained as 3.6 $\times 10^{-7}$ m/s with curve

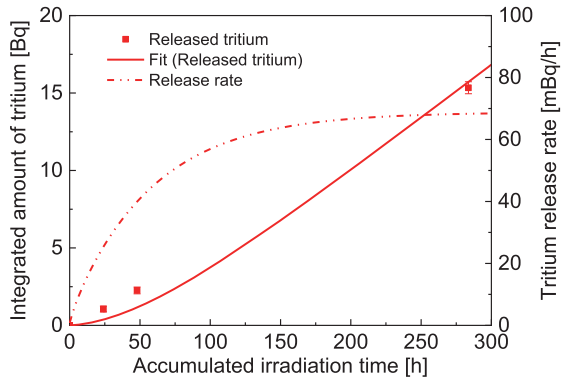

Fig. 4 Integrated amounts of tritium recovered after the AmBe neutron source was placed [11].

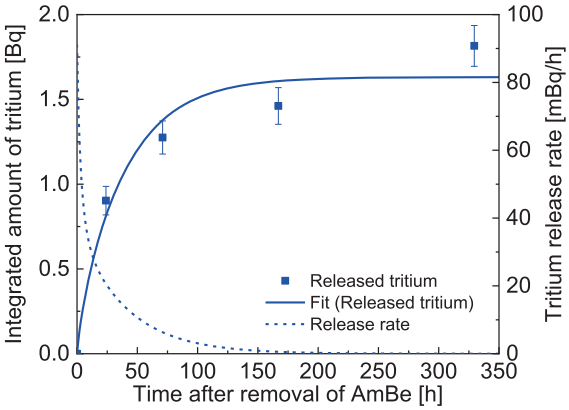

Fig. 5 Integrated amounts of tritium recovered after the AmBe neutron source was removed [11].

fitting. This figure also shows the tritium release rate calculated by Eq. (4a) by the obtained rate coefficient. The change in the integrated amounts of tritium recovered is evaluated after the AmBe source was removed (i.e., $S = 0$ in Eq. (1)). The experiments are started after the tritium release rate reached a steady state with the accumulated neutron irradiation time of 7 weeks (1176 hours). The plots in Fig. 5 show the integrated amounts of recovered tritium in the experiments after the AmBe neutron source was removed [11]. The initial condition in this experiment is $C_F(x,0) = C_{F0}$. The value of k_{Sol} has been obtained as 9.4×10^{-7} m/s with curve fitting.

From Eq. (5), the value of k_{H_2} is estimated as 4.3×10^{-6} - 1.1×10^{-5} m/s/vol. H_2%. The values of k_{H_2} are more than 10 times larger than the value of 1×10^{-7} m/s/vol. H_2% which was obtained for solid FLiBe at 573 K [8]. The ratio of HT to soluble tritium obtained in this study is more than 3 times larger than the result for FLiBe at 873 K using a He+H_2 (0.1%) gas [2]. The difference in the rate coefficient and the ratio of HT to soluble tritium may be because of the difference in temperature of the salts or chemical structure in the salts (e.g., the presence of polyatomic ions in FLiBe). Although further study is required, the present results indicate that tritium recovery utilizing the isotopic exchange between tritium produced in molten FLiNaK and hydrogen molecules in a sweep gas is considered possible.

4. Summary

In the present study, to explore the possibility of the tritium recovery with the isotopic exchange between tritium produced in molten FLiNaK and hydrogen molecules in a sweep gas, a series of low flux neutron irradiation experiments with an AmBe neutron source have been performed for molten FLiNaK at 773 K. Tritium produced in FLiNaK is swept out by pure He and He+H_2 (0.1%) gases, and recovered by water bubblers separating soluble tritium (TF, HTO) and insoluble HT. The changes in the integrated amounts of recovered tritium have well fitted to the curves provided by a one-dimensional diffusion equation considering tritium production. By introducing the He+H_2 (0.1%) gas, approximately one-half of the amount of released tritium has been recovered as HT, which is produced with the isotopic reaction between tritium produced in FLiNaK and hydrogen molecules in the sweep gas. The rate coefficient of the isotopic exchange reaction for molten FLiNaK at 773 K has been 4.3×10^{-6} - 1.1×10^{-5} m/s/vol H_2%. The value has been an order of magnitude larger than that for solid FLiBe at 573 K.

The obtained results indicate the possibility of tritium recovery from FLiNaK with the isotopic exchange. Tritium recovery experiments are planned using sweep gases with different H_2 concentrations to examine the relation between the H_2 concentration and the ratio of HT to soluble tritium. Similar neutron irradiation experiments for molten FLiNaBe are also planned for systematic understanding of tritium behaviors in molten salts.

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