Study on Tritium Recovery from Breeder Materials

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For the development of fusion reactor blanket systems, some of the key issues on the tritium recovery performance of solid and liquid breeder materials were studied. In the case of solid breeder materials, a special attention was focussed on the effects of irradiation on the tritium recovery performance, and tritium release experiments, luminescence measurements of irradiation defects and modeling studies were systematically performed. For liquid breeder materials, tritium recovery experiments from molten salt and liquid lithium were performed, and the technical feasibility of tritium recovery methods was discussed.

1. Introduction

The blanket system is a key component of fusion reactors since it involves tritium breeding and energy extraction, both of which are critically important for the practical use of fusion energy. Blanket concepts can be devided into solid and liquid ones, and a number of distinct materials and design options have been proposed[1]. For the selection and further development of the blanket systems, the performance assessment of each system is required, and extensive studies are thus being performed. Although much information has been obtained, a number of key issues still remain to be solved.

In our research program, some of the key issues on the tritium recovery performance have been studied for the development of the blanket systems. For solid blanket systems, we have devoted our efforts to the effects of irradation on the tritium recovery performance of solid breeder materials, which remain unclear in spite of their importance at actual blanket conditions. Tritium release experiments, luminescence measurements of irradiation defects and modelling studies have been performed with various lithium containing ceramics. For liquid blankets, on the other hand, we have performed some preliminary experiments in order to provide a thermodynamic and kinetic basis for tritium recovery methods. Both of molten salt and liquid lithium systems have been studied, and the technical feasibility of tritium recovery from each system has been discussed.

2. Solid breeder materials

In a solid blanket system, tritium breeding lithium ceramics are attacked by high energy neutrons and energetic particles from nuclear reactions, and severe irradiation damage may be expected. The irradiation behavior of lithium ceramics is thus important for the performance assessment of solid blanket systems. The effects of irradiation on the tritium release behaviors and microstructural changes of lithium ceramics may be considered. For a clearer understanding of such effects, we have examined the candidate solid breeder materials of Li_2O, $LiAlO_2$, Li_2SiO_3, Li_4SiO_4, Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3.

2.1 Chemical consequences of irradiation

Tritium recovery from solid breeder materials has been investigated extensively, and a number of factors, namely solubility, diffusivity, surface reaction and desorption are recongized to participate in the tritium recovery process[2,3]. In addition to these, several investigations have suggested a definite role of irradiation defects. For example, the presence of the F^+ centers (an oxygen vacancy trapping an electron) in Li_2O have been observed in electron spin resonance studies[4,5]. Following these studies, an apparent effect of irradiation has been observed on the tritium behavior in Li_2O[6,7].

Fig. 1 shows the results of radiochemical measurement of tritium species produced in Li_2O by neutron irradiation. The chemical state distribution is found to be dependent on the neutron fluence; the T^- fraction increases and the T^+ fraction decreases with the increasing neutron fluence. This indicates the presence of the interactions of tritium with irradiation defects. The neutron fluence dependence is also observed in the tritium release behavior. As shown in Table 1, a fraction of tritium is recovered as non-condensable form (HT or T_2) with a hydrogen containing sweep gas and the HT fraction increases with the increasing neutron fluence.

It is interesting to note that similar effects of irradiation have been observed not only for lithium salts[8] but also for lithium alloys[9].

2.2 Production of irradiation defects

For a clearer understanding of the effects of irradiation, we have applied an in-situ luminescence measurement technique to some candidate solid breeder materials, and found that this technique is very useful to study the production behavior of irradiation defects at actual blanket condition[10-15]. Knowledge of the irradiation defect production is much improved and is extended to understand the tritium behavior under irradiation. Some progress is given here.

An important result has been obtained in the in-situ luminescence measurement of Li_2O[10]. As shown in Fig. 2, the luminescence band of the F^+ centers is predominantly observed at lower temperatures, while the band of the F^0 centers is observed at higher temperatures. This indicates the possible participation of the F^0 centers in the reactions of tritium at the temperatures of actual blanket conditions. Similar situations may be postulated for $LiAlO_2$[11] and other ternary lithium ceramics[12-14].

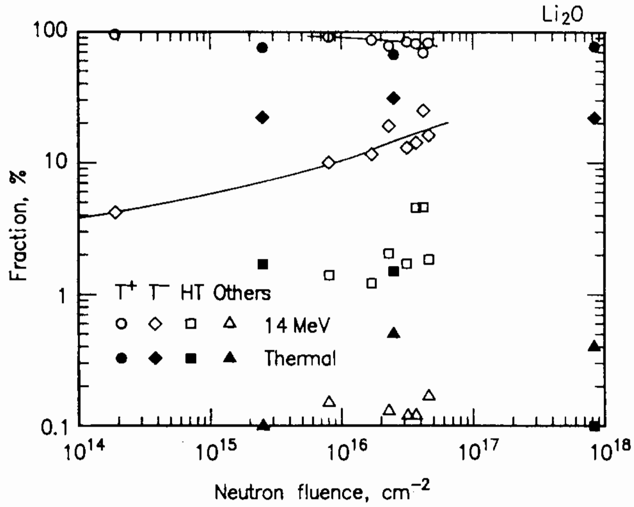

Fig. 1. Chemical state distribution of tritium formed in Li_2O as a function of neutron fluence. Open marks are for 14MeV neutrons[7] and full marks for thermal neutrons[6].

Table 1. The effect of neutron fluence on tritium recovery in the presence of hydrogen [7].

Neutron fluence (cm^{-2})	Fractional yield(%)[a]: HT recovered	HTO recovered	T^+ remaining[b]
$3.8x10^{16}$	92.4	6.7	0.9
$2.2x10^{16}$	81.6	10.9	7.5
$7.9x10^{15}$	34.0	44.4	21.6

[a] After the isothermal heating at 673K for 3h with a He-1%H_2 sweep gas.
[b] The fractions of tritium in the T^0 and T^- states are negligible.

In order to discuss some details of the reaction kinetics, the temperature transient behavior of irradiation defect production has been measured in Li_2O[15]. For a temperature increase, the luminescence intensity of the F^+ centers rapidly decreases. The response of the F^+ centers is so rapid and well consistent with the temperature dependence in Fig. 2. On the other hand, an abnormal temperature transient behavior has been observed for the F^0 centers;

an excess luminescence is observed at the temperature increase, as shown in Fig. 3. By considering the observations, the following reaction scheme has been given for the production mechanism of the F^+ and F^0 centers:

$$Li_2O \rightarrow Li_2O^* \quad (1)$$

$$Li_2O^* \rightarrow (F^+ \bullet O^-) + h\nu \quad (2)$$

$$2\,Li_2O^* \rightarrow 2\,F^0 + O_2 + 2\,h\nu' \quad (3)$$

$$(F^+ \bullet O^-) + Li_2O^* \rightarrow 2F^0 + O_2 + 2\,h\nu' \quad (4)$$

Reaction (1) represents the production of an excited Li_2O, Li_2O^*, by ion beam irradiation. The F^+ center is considered to be associated with an O^- interstitial under Coulomb interactions as $(F^+ \bullet O^-)$, and is produced by reaction (2), which dominates at lower temperatures. At higher temperatures, however, reactions (3) and (4) will take place and the F^0 centers and their partners, O_2 molecules, are produced.

Based on this reaction scheme, some calculations have been performed for the luminescence behavior. Agreements between the calculations and observations are satisfactorily good as seen in Figs. 2 and 3.

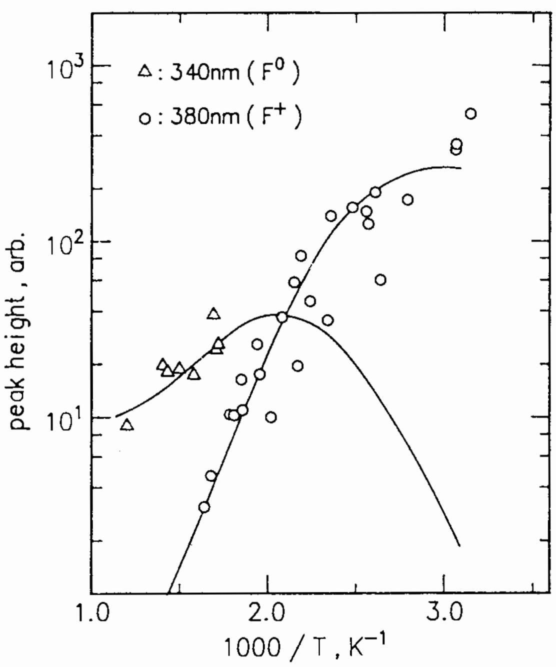

Fig. 2. Arrhenius plots of luminescence intensities of the F^+ and F^0 centers. Circles are experimental[10] and curves are calculated[15].

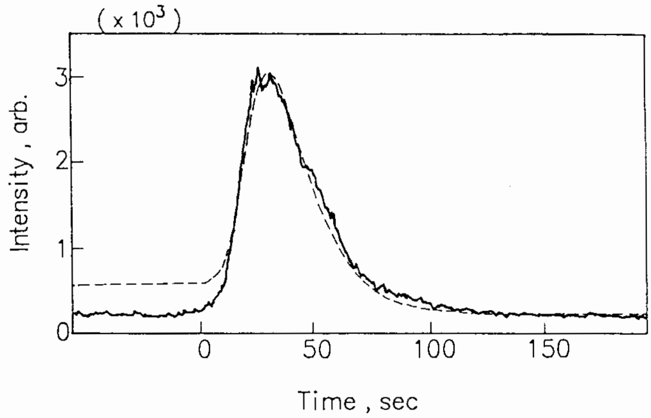

Fig. 3. Temperature-transient behavior of the 340nm luminescence for a change from 528K to 723K[15]. Irradiation time before a temperature increase was 10 min and irradiation current was 40nA. Solid curve is experimental and dashed is calculated.

2.3 Interactions of tritium with irradiation defects

It is very important to determine the interactions of tritium with irradiation defects for predicting the effects of irradiation under a high neutron flux at actual blanket conditions. An isothermal annealing experiment of neutron-irradiated Li_2O has thus been performed in order to know some details of the mechanisms and kinetics[16]. The tritium species of T^+, T^- and T^0(HT, T_2) remaining in the annealed sample have been analyzed by a radiometric method, and the chemical state distribution of tritium has been observed to change with the annealing temperature and time duration. As well as the F^+ centers, the F^0 centers (an oxygen vacancy trapping two electrons) are considered to act as the reducing agents and to interact with tritium species.

For the assessment of tritium release behavior of Li_2O under irradiation, a model reaction scheme has been presented by taking into account the interactions of irradiation defects with tritium, as shown in Fig.4[17]. Tritium is produced in Li_2O grains by nuclear reactions and stabilized in the chemical states of T^+(LiOT) or T^-(LiT). The tritium species interact with the F^0 centers and O_2 molecules which are predominantly produced at higher temperatures, and diffuses to the grain surface where the following surface reactions take place.

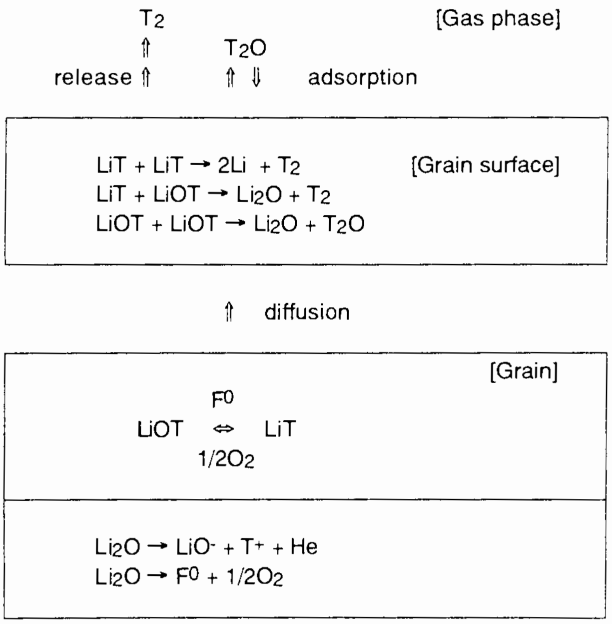

Fig. 4. Proposed reaction scheme for tritium release under irradiation[17]. Sweep gas contains no H_2. A similar reaction scheme is given in the presence of H_2.

$$LiT + LiT \rightarrow 2\,Li + T_2\uparrow \tag{5}$$

$$LiT + LiOT \rightarrow Li_2O + T_2\uparrow \tag{6}$$

$$LiOT + LiOT \rightarrow Li_2O + T_2O\uparrow \tag{7}$$

Tritium is thus released in the form of T_2 or T_2O to the sweep gas. By taking this reaction scheme, some predictions have been made and compared with the observations in the BEATRIX-II experiment. The observed tritium release behavior has successfully been interpreted.

It is important that irradiation defects participate in the reaction mechanisms even at such high temperatures, because material stability will be affected as well as tritium release kinetics. In the case of H_2-containing sweep gas, F^0 and O_2 are considered to react with H_2 at the grain surface as

$$F^0 + H_2 \rightarrow LiH \tag{8}$$

$$O_2 + 2\,H_2 \rightarrow 2\,H_2O\uparrow \tag{9}$$

Due to reaction (9), the moisture concentration of H_2O will increase with the increasing H_2 concentration in the sweep gas, as observed in the BEATRIX-II, and then the material degradation will be accelerated in the presence of H_2. Further studies are required for its importance.

For the further development of the model, the equilibrium constant and rate constant of each reaction are to be determined. Such data are still lacking at the present time, and are to be determined by further studies. As well as the steady state chemistry, the dynamic behavior of tritium release may be studied for the determination of these constants.

3. Liquid breeder materials

Liquid breeder materials are rather free from irradiation damage and have many inherent advantages over solid breeder materials. However, there are a number of difficult design issues for liquid blanket systems. We have studied the tritium recovery performance of both molten salt and liquid lithium systems, and the following results have been obtained.

3.1 Molten salt

Molten salt, especially LiF-BeF_2 mixture, called Flibe, is considered to be one of the candidate materials for the liquid blanket of fusion reactors. Many physical and chemical properties of Flibe have already been made clear in the studies on molten salt breeder reactors at Oak Ridge National Laboratory[18], but little is still known of tritium recovery in spite of its importance. In our study the tritium release behavior from molten Flibe was studied in order to know the technical feasibility of a tritium recovery process[19,20].

In the experiment, the condensable (TF) and non-condensable (HT) tritium species were separately recovered, and the mass transfer coefficients of both species at the interface beween the molten Flibe and sweep gas were determined[20]. The mass transfer coefficient of TF was obtained to be 3-5x10^{-4} cm s^{-1} at 823-973K and that of HT was about one order larger, as shown in Fig. 5. The diffusion coefficient of tritium in the molten Flibe was also measured. Such data may be useful for the performance assessment of a tritium recovery process from a kinetic point of view.

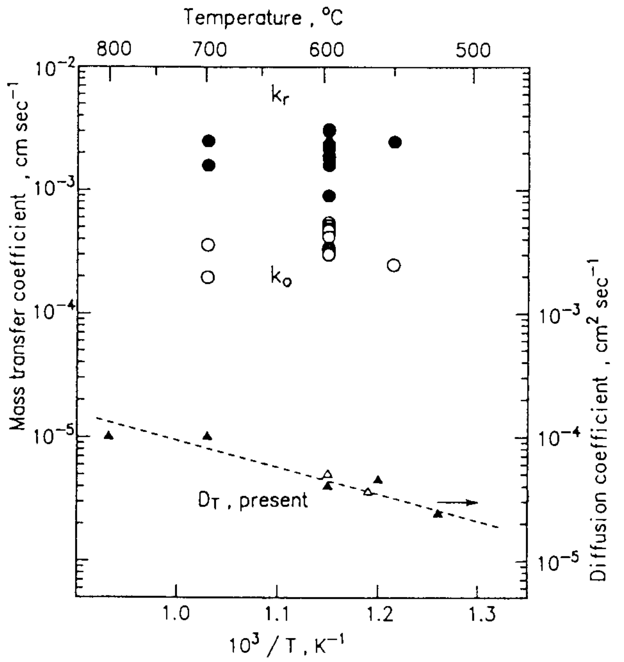

Fig. 5. Mass transfer coefficient and diffusion coeffecient of tritium in molten Flibe[20]. Open and full circles are the mass transfer coefficient of TF and HT, respcetively, and triangles the diffusion coefficient of T^+.

As observed in our experiment, tritium is released as TF and HT. The tritium recovery issues associated with the two species of TF and HT are rather different. The solubility of TF in molten Flibe is considerably high, hence the partial pressure is usually not a concern, but the inventry. On the other hand, the solubility of HT is very low and the difficult issue is to reduce the partial pressure to an acceptable value to reduce the permeation.

3.2 Liquid lithium

The self-cooled liquid lithium blanket system is one of the most promising[1]. Because of the higher tritium solubility, however, tritium recovery is recognized to be critically important for the use of this system. In order to meet a design goal of 1 wppm for the tritium inventry, a number of recovery methods has been proposed[21]. Among these, molten salt extraction proposed by Maroni et al.[22] is one of the most promising because it is essentially free from any solid state diffusion processes.

In support of the development of this method, our effort has been devoted to the thermodynamic and kinetic aspects of tritium extraction. We studied the equilibrium distribution of tritium in some typical molten salt extraction systems and discussed the thermodynamic basis of extraction[23]. The distribution coefficient of tritium was confirmed to be high enough that tritium could be easily extracted. We also studied the kinetic aspects of the extraction. The rate of tritium extraction from liquid lithium into molten salt was measured to evaluate the overall mass transfer coefficient[24], and the diffusion coefficient of tritium in lithium was measured[25]. All of these data suggested no major problem for the kinetics of molten salt extraction. The reference scheme was then evaluated with the obtained data as shown in Fig. 6 and the design goal of 1 wppm was shown to be attained by combining a reasonable number of extractor units. The results are thus encouraging the further development of this process.

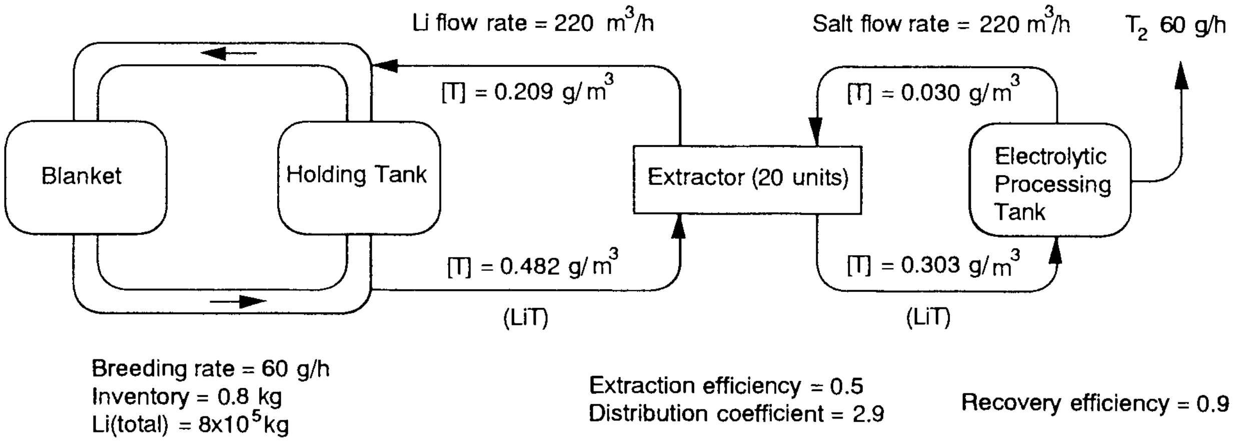

Fig. 6. Conceptual flow sheet of tritium recovery from liquid lithium[21].

There are a number of anticipated problems of molten salt extraction. The mutual solubility of the two liquids is one of the problems and may be important for the operation of extractor units. The presence of dissolved lithium metal in the salt phase is of some concern in connection with efficient electrolysis of LiT, but Calaway has indicated a favorable processing capability in his study [26]. On the other hand, the consequences of having salt dissolved in the lithium phase will be of greater significance for blanket neutronics, corrosion, hazardous transmutation products, etc. For its importance, the solubility of lithium salt into liquid lithium has recently been measured in typical systems, and some impacts on hazardous transmutation products have been evaluated[27]. However, the evaluation is only preliminary and more detailed evaluation is suggested.

4. Conclusions

For solid breeder materials, a series of experiments have been performed on the effects of irradiation on the tritium recovery performance, and the following results were obtained:

(1) The chemical consequences of irradiation on the tritium behavior in the solid breeder materials were studied, and irradiation defects were observed to play an important role in the reaction mechanisms.

(2) By applying an in-situ luminescence measurement technique, the production behavior of irradiation defects under ion beam irradiation was studied, and the mechanisms and kinetics were clarified in some details.

(3) By considering the participation of irradiation defects, a model reaction scheme was developed and successfully applied to the interpretation of the data of an in-situ tritium recovery experiment, called the BEATRIX-II.

(4) The effects of irradiation are thus important in the solid breeder materials, and further studies are suggested for the tritium release behaviors and microstructural changes of lithium ceramics.

For liquid breeder materials, some experiments have also been performed on the tritium extraction process, and the following results have been obtained:

(1) In the case of molten salt of $LiF-BeF_2$, the tritium release behavior was studied for some details of the kinetics, and the difficult issue was confirmed to reduce the tritium partial pressure to an acceptable value and to reduce the tritium permeation.

(2) For liquid lithium systems, our studies have supported that molten salt extraction is one of the most promising methods to meet the design goal of 1 wppm. The results are thus encouraging for the further development of this method.

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