核融合炉固体増殖ブランケットからのトリチウム回収に関する研究

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4. Study on Mass Transfer Rate of Water on Lithium Ceramics

4.1 Introduction

The diffusivity of tritium in the crystal grain of lithium ceramic breeder materials has been investigated by measurement of tritiated water release rate from the crystal grain[1~5]. Understanding of the process of diffusion of tritium in the crystal grain is important to understand the release behavior of tritium bred in the blanket. However, the release process of tritium bred in the blanket is complex and difficult to understand, because it is not only constituted with the process of diffusion in the grain but also that of diffusion in pore and that of surface reaction. At present, it is impossible to estimate the release behavior of tritium bred in the blanket because of shortage of data about tritium diffusion in pore and surface reaction and others. Therefore, the release behavior of tritium bred in the blanket are studied with the in-situ experiments based on the idea that the investigation of release behavior of tritium from the pellet under the condition of blanket for use is more realistic. Almost results of the in-situ experiments are analyzed assuming that the release process of tritium bred in the blanket is controlled with the process of tritium diffusion in the crystal grain. However, it is also pointed out from some results that the effect of surface reaction can not be ignored[6~18].

Present author has quantified the amount of water captured in lithium ceramic breeder material and compared the tritium inventory by sorption with that by diffusion at the chapter 3 of this study. Tritium inventory by sorption is much larger than that by diffusion in the crystal grain. Accordingly, it can not be considered that the process of tritium diffusion in crystal grain controls the release process of tritium bred in the blanket. And then, it have been confirmed that the tritium release rate was enhanced when hydrogen was added to the purge gas at the in-situ experiments[6,13,15,18]. These results suggest that tritium release process is possibly controlled by the process of surface reaction and that of pore diffusion.
As mentioned in the opening of this section, the diffusivity of tritium in the crystal grain have been obtained by measurement of release rate of tritium in the form of tritiated water. Therefore, it can be considered that values of diffusivity obtained from the release experiments also include the resistance due to surface reaction. Accordingly, the adsorption and desorption rate of water at the surface of various breeder materials are measured in this work, and the effective diffusivity of water in the particle of breeder material is estimated using data obtained as adsorption and desorption rate and is compared with the so to speak tritium diffusivity in the crystal grain.

4.2 Theoretical consideration

The mass transfer process of adsorption is constituted with the process of diffusion of adsorbate in the fluid film, that of diffusion in pore of adsorbent and that of adsorption on the surface of adsorbent[19,20]. When it is assumed that the solid film exists at the surface of particle and the difference of concentration of adsorbate at both end of film acts as the driving force of adsorption, the rate of adsorption per unit volume of packed bed is expressed as

\[ \gamma \frac{dq}{dt} = k_f a_v (c - c_i) = k_s a_v (q_i - q) \]

where
- \( \gamma \) : density of packed bed [g/cm\(^3\)]
- \( q \) : the amount of adsorption [mol/g]
- \( t \) : time [sec]
- \( k_f \) : mass transfer coefficient of fluid film [cm/sec]
- \( a_v \) : surface area of particle per unit volume of packed bed [cm\(^2\)/cm\(^3\)]
- \( c \) : concentration of adsorbate in gas phase [mol/cm\(^3\)]
- \( c_i \) : concentration of adsorbate at the surface of particle [mol/cm\(^3\)]
\( k_s \) : mass transfer coefficient of solid film \([\text{g/cm}^2 \cdot \text{sec}]\)

\( q_i \) : the amount of adsorption at the surface of particle \([\text{mol/g}]\).

The surface area of particle per unit volume of packed bed is approximately expressed as

\[
a_v = \frac{6(1 - \varepsilon)}{d_p},
\]

where \( \varepsilon \) : void fraction of packed bed [-]
\( d_p \) : diameter of particle [cm].

And then, the product with mass transfer coefficient \((k_f \text{ or } k_s)\) and the surface area of particle per unit volume of packed bed \(a_v\) is called the mass transfer capacity coefficient \((k_f a_v \text{ or } k_s a_v)\). However, the concentration of adsorbate at the surface of particle \((c_i)\) and the amount of adsorption at the surface of particle \((q_i)\) are impossible to quantify. And then, when the amount of adsorption equilibrated to the concentration of adsorbate in gas phase \((q^*)\) and the equilibrium concentration of adsorbate given by the amount of adsorption \((c^*)\) are introduced, eq.(4-1) is changed as

\[
\gamma \frac{\partial q}{\partial t} = K_f a_v (c - c^*) = K_s a_v (q^* - q),
\]

where \( K_f \) : over-all mass transfer coefficient of fluid film [cm/sec]
\( K_s \) : over-all mass transfer coefficient of solid film \([\text{g/cm}^2 \cdot \text{sec}]\).

The over-all mass transfer coefficient is expressed as

\[
\frac{1}{K_f} = \frac{1}{k_f} + \frac{1}{\beta k_s},
\]

\[
\frac{1}{K_s} = \frac{\beta}{k_f} + \frac{1}{k_s},
\]

where \( \beta \) means the adsorption coefficient and expressed as

\[
\beta = \frac{q}{c}.
\]
If adsorption progresses following Henry's low, the adsorption coefficient $\beta$ is to be constant.

The mass transfer capacity coefficient of solid film is also expressed as

$$k_s a_v = \frac{60 D_i' \gamma}{d_p^2},$$

(4-6)

where $D_i'$ : the effective diffusivity of adsorbate in the particle

at the standard of the amount of adsorption [cm$^2$/sec].

The correlative equations of mass transfer coefficient of fluid film have been proposed by many authors. Therefore, if $K_f a_v$ or $K_s a_v$ is obtained by curve fitting of breakthrough curve or release curve obtained from experiments, it is possible to estimate $k_s a_v$. And then, $D_i'$ is estimated using eq.(4-6).

4.3 Experiments

4.3.1 Sample

The samples used in this work were LiAlO$_2$, Li$_4$SiO$_4$, Li$_2$ZrO$_3$ made in Mitsubishi Atomic Power Industries Inc. and their specifications are shown in tables 4.1, 4.2 and 4.3, respectively. The chemical composition of LiAlO$_2$ used in this work was analyzed with the ICP method and is shown in table 4.4. To apply the ICP method for LiAlO$_2$, the solid sample is to be dissolved into aqua regia and it takes about several days to dissolve crystal powders of LiAlO$_2$. In case of analysis for the sintered pellet, of which the result is shown in table 4.4, the ICP analysis is made for solution when about 90% of the sintered pellet is dissolved because the main purpose is to check the amount of impurities. The activation analysis using Kyoto University Reactor(KUR) gives similar results to the ICP analysis.

The result of spectrographic analysis of Li$_2$ZrO$_3$ used in this work is also
shown in table 4.5.

4.3.2 Experimental method

Fig. 4.1 shows a schematic diagram of experimental apparatus. Sample of breeder material was charged in a reaction tube. The reaction tube was a quartz tube of 22.8 mm in inner diameter and 500 mm in length, in which a filter plate with several 1 mm holes was mounted at 220 mm from the bottom end.

Helium was used as the carrier gas and its flow rate was kept at 0.2–0.4 l/min by a flow rate adjuster. The water concentration in He was measured with a hygrometer continuously. The hygrometer used in this work was a moisture analyzer type MAH-50 from SHIMADZU Co. A cold trap was attached at the dry gas channel of the hygrometer that was packed with molecular sieves and kept at liquid nitrogen temperature. The calibration of sensitivity of the hygrometer was carried out before and after each experiment by introducing H$_2$O/He gas of which H$_2$O concentration was known, and it was confirmed that the span was not changed during the experiment. The water concentration in He purge gas at the inlet of sample packed bed was controlled by a hydrogen oxidizing method with a spongy CuO bed which was heated to 350°C. The hydrogen was confirmed to be completely oxidized because gas chromatography detected no hydrogen in the outlet gas of the CuO bed. The pressure gradients along the packed bed and that between the bed and the exit end were determined to be negligible by a pressure gauge, so the pressure of the gas flowing over the experimental sample could be taken as 1 atm with negligible error.

The measurement was carried out as follows.

(1) The sample was heated up very slowly to 1073 K for more than several hours under moisture-free helium gas flow to desorb residual water before each experimental measurement. The moisture in the helium gas from a gas cylinder was removed by a cold trap, that is a packed column of molecular sieves 5A at the...
liquid nitrogen temperature, and the moisture content in the outlet gas of the cold trap was determined to be lower than 0.3ppm by a hygrometer.

(2) Then helium gas containing water vapor with a certain partial pressure was passed through the experimental apparatus without the sample bed until the concentration of water in the inlet gas of hygrometer was equal to that in the outlet gas of CuO bed because of elimination of system effect, that is caused by adsorption and desorption of water to the surface of piping materials, from the breakthrough curve. And then, H₂O/He gas was passed through the sample bed after setting it to the experimental temperature, and change of the water vapor concentration in the outlet gas was traced with time by the hygrometer. Helium gas containing water vapor was passed through the sample bed until the equilibrium state was attained.

(3) And then, moisture-free helium gas was passed through the sample bed again to release the adsorbed water changing the bed temperature from the experimental temperature to 1073K stepwisely.

The experimental conditions for LiAlO₂, Li₄SiO₄ and Li₂ZrO₃ are shown in tables 4.6, 4.7 and 4.8, respectively. It have been known that such breakthrough curve as described by Johnson et al. can not be obtained under the experimental conditions as mentioned in chapter 3. Because the mass flow rate and the water concentration in the carrier gas were too large to obtain the desirable breakthrough curve for curve fitting in the case of the experimental conditions as mentioned in chapter 3. Accordingly, experiments were carried out below 100ppm of water concentration in the carrier gas and below 0.4l/min of mass flow rate at the sample bed. However, 0.4l/min of mass flow rate is necessary to operate the hygrometer normally. And then, He gas channel was attached to the outlet of sample bed to keep the flow rate of 0.4l/min at the inlet of hygrometer.

4.4 Results and discussion

Figs.4.2~4.4 show the breakthrough curves of water on LiAlO₂, Li₄SiO₄ and
The over-all mass transfer coefficient clearly changes with the progress of adsorption as shown in figs.4.2~4.4. Generally, the step of diffusion in fluid film is the rate controlling step at the early step of adsorption, and the rate controlling step changes to the step of diffusion in pore with increase of the amount of adsorption. However, it can not be considered that the step of diffusion in fluid film is the rate controlling step at the early step of adsorption in these cases, because the experimental temperature is high enough. Furthermore, the difference of over-all mass transfer coefficient between at early step and at late step is too large to consider that the water concentration dependency of over-all mass transfer coefficient is the basic reason of the change of over-all mass transfer coefficient. And then, present author assumes that two kinds of adsorption having different mass transfer rate (adsorption(1) with a fast rate and adsorption(2) with a slow rate) progress at the same time. Then, the mass balance equation for water in the sample bed is expressed as

\[
\frac{\partial c}{\partial t} + u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + \gamma \frac{\partial q}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2}. \tag{4-7}
\]

The mass flow rate is large enough to ignore the influence of axial diffusion under
the experimental conditions in this work. Accordingly, eq.(4-7) is expressed as

\[ u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + \gamma \frac{\partial q}{\partial t} = 0 \]  

(4-8)

It can be considered that the rate controlling step is any steps progress in the sample particle. Accordingly, it is assumed that the driving force of adsorption is the difference of the amount of adsorption. The mass transfer equation is expressed as

\[ \gamma \frac{\partial q_1}{\partial t} = K_s a_v (q_1^* - q_1) \quad \gamma \frac{\partial q_2}{\partial t} = K_s a_v (q_2^* - q_2) \]  

(4-9)

where

- \( u \): superficial gas velocity [cm/sec]
- \( c \): concentration of water [mol/cm³]
- \( z \): axial distance [cm]
- \( \varepsilon \): void fraction of packed bed [-]
- \( q \): the amount of adsorbed water [mol/g]
- \( q_1, q_2 \): the amount of adsorbed water by adsorption(1) or (2) [mol/g]
- \( q_1^*, q_2^* \): the amount of water adsorption equilibrate to the concentration of water in gas phase for adsorption(1) or(2) [mol/g]
- \( K_s a_v \): the over-all mass transfer capacity coefficient of adsorption(1) at the standard of the amount of adsorbed water [g/cm³•sec]
- \( K_s a_v' \): the over-all mass transfer capacity coefficient of adsorption(2) at the standard of the amount of adsorbed water [g/cm³•sec].

The adsorption isotherms of water vapor on LiAlO₂, Li₄SiO₄ and Li₂ZrO₃ are expressed as eqs.(3-3), (3-7) and (3-10), respectively. These equations are the Freundlich equation of which exponent is 1/2:

\[ q_0 = a c_0^{1/2} \quad (a = \text{constant}) \]  

(4-10)

And then, the relation of adsorption(1) and (2) are expressed as
\[ q_0 = q_{1,0} + q_{2,0} = \alpha q_0 + (1 - \alpha) q_0 = \alpha a c_0^{1/2} + (1 - \alpha) a c_0^{1/2} \]
\[ q^* = q_{1}^* + q_{2}^* = \alpha q^* + (1 - \alpha) q^* = \alpha a c_1^{1/2} + (1 - \alpha) a c_1^{1/2} \]
\[ q = q_1 + q_2 = \alpha q + (1 - \alpha) q = \alpha a c_1^{1/2} + (1 - \alpha) a c_2^{1/2} \], \quad (4-11)

where
- \( c_0 \): inlet concentration of water \([\text{mol/cm}^3]\)
- \( q_{1,0} \): capacity of adsorption for adsorption(1) \([\text{mol/g}]\)
- \( q_{2,0} \): capacity of adsorption for adsorption(2) \([\text{mol/g}]\)
- \( \alpha \): ratio of capacity of adsorption for adsorption(1) to total capacity \([-]\)
- \( c_{1,2}^* \): equilibrium concentration of water correlated to adsorption(1) or (2) \([\text{mol/cm}^3]\).

The initial and boundary conditions are expressed as
\[
\begin{align*}
  t = 0, z > 0 \rightarrow q = 0 \\
  z = 0, t \geq 0 \rightarrow c = c_0.
\end{align*}
\]
\quad (4-12)

The curve fittings of breakthrough curves were carried out solving eqs. (4-8-12) numerically with the over-all mass transfer capacity coefficients \((K_5a_p, K_7a_p)\) and the ratio of adsorption capacity \((\alpha)\) as the parameters. Figs.4.5-4.7 show examples of the curve fitting for the breakthrough curve of water on various breeder materials. The calculation values almost agree with the data obtained. Figs.4.8-4.10 show the over-all mass transfer capacity coefficients for adsorption(1) and (2) and the ratio of the amount of adsorption(1) to the total amount of adsorption for \(\text{LiAlO}_2\), \(\text{Li}_4\text{SiO}_4\) and \(\text{Li}_2\text{ZrO}_3\), respectively. The over-all mass transfer capacity coefficient for adsorption(1) is about one order magnitude larger than that for adsorption(2) for each material. But the
temperature dependence of the over-all mass transfer capacity coefficient for adsorption(2) is larger than that for adsorption(1). Then, the ratio of the amount of adsorption(1) to the total amount of adsorption without Li₂ZrO₃ increases with the rise of temperature. Accordingly, the influence of adsorption(2) decreases with the rise of temperature. Following equations were obtained from figs.4.8~4.10.

\[
K_\text{a}_v = 0.208 \exp\left(-\frac{14650}{RT}\right) \quad \text{(LiAlO₂)}
\]
\[
= 5.22 \times 10^{-2} \exp\left(-\frac{4380}{RT}\right) \quad \text{(Li₄SiO₄)}
\]
\[
= 8.39 \times 10^{-2} \exp\left(-\frac{3110}{RT}\right) \quad \text{(Li₂ZrO₃)}
\]

(4-13)

\[
K'_\text{a}_v = 0.102 \exp\left(-\frac{24090}{RT}\right) \quad \text{(LiAlO₂)}
\]
\[
= 1.32 \times 10^{-2} \exp\left(-\frac{7860}{RT}\right) \quad \text{(Li₄SiO₄)}
\]
\[
= 4.44 \times 10^{-2} \exp\left(-\frac{10580}{RT}\right) \quad \text{(Li₂ZrO₃)}
\]

(4-14)

\[
\alpha = 1.93 \exp\left(-\frac{5400}{RT}\right) \quad \text{(LiAlO₂)}
\]
\[
= 1.18 \exp\left(-\frac{1420}{RT}\right) \quad \text{(Li₄SiO₄)}
\]
\[
= 0.60 \exp\left(-\frac{1460}{RT}\right) \quad \text{(Li₂ZrO₃)}
\]

(4-15)

However, the ratio of the amount of adsorption(1) to the total amount of adsorption for Li₄SiO₄ or Li₂ZrO₃ may be considered to be constant. Figs.4.11 and 4.12 show the comparison of the over-all mass transfer capacity coefficient for adsorption(1) and (2) among various breeder materials, respectively. The over-all mass transfer capacity coefficients of LiAlO₂ are the smallest among various breeder materials. Accordingly, the mass transfer rate of water on LiAlO₂ is the smallest among various breeder materials. The estimation of the breakthrough
curve of water adsorption for LiAlO$_2$, Li$_4$SiO$_4$ or Li$_2$ZrO$_3$ is possible using eqs.(4-13)~(4-15).

The evaluation of the mass transfer rate of water at desorption step is important to estimate the tritium release rate at the blanket. The release curves of water on LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ are shown in figs.4.13~4.15, respectively. The release rate of water at early step of desorption is fairly large, but that at late step is very small. To release all water that is captured on the sample, the sample bed must be heated up from the temperature at the adsorption experiment as shown in figs.3.5~3.7. When the release curves are estimated, the initial and boundary conditions are expressed as

\[
\begin{align*}
  t &= 0, \quad z > 0 \rightarrow q = q_0 \\
  z &= 0, \quad t \geq 0 \rightarrow c = 0.
\end{align*}
\]

(4-16)

The curve fitting of the release curves of water were carried out solving eqs.(4-8)~(4-11) and (4-16) with the over-all mass transfer capacity coefficients and the ratio of the amount of desorption(1) to the total amount of desorption as the parameters. Figs.4.16~4.18 show examples of the curve fitting of the water release curves for LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$, respectively. The amount of water captured on the piping surface was ignored when the estimation of the water release curves were carried out. However, the water release curves obtained in this work include the effect of water captured by the piping surface. Because the water captured by piping surface without the reaction tube was not purged away before the water release experiment. But it is impossible to eliminate the system effect from the release curves even if the water captured by piping surface without the reaction tube is purged away before the water release experiment, because the water released from the sample bed moves downward with the repetition of adsorption on and desorption from the piping surface. Therefore, the over-all mass transfer capacity coefficients and the ratio of the amount of desorption(1) to the total amount of desorption obtained by the curve fittings include not only the
influence of the sample but also the system effect. Figs. 4.19–4.21 show the over-all mass transfer capacity coefficients and the ratio of the amount of desorption (1) to the total amount of desorption. The values of $K_s a_v$ are about two order of magnitude larger than those of $K_s ' a_v$ at each material. The order of $K_s a_v$ at desorption step almost agree with that at adsorption step. The values of $\alpha$ at desorption step is smaller than those at adsorption step. Disagreement of values of $\alpha$ between at adsorption step and at desorption step is due to the system effect and using adsorption isotherm for estimation of the release curve. Whole water captured at adsorption step is not released at desorption step when the bed temperature is kept at the adsorption step. Accordingly, the desorption isotherm must be used for estimation of the real release curve. Following equations are obtained from figs. 4.19–4.21.

\[
K_{sv} = 0.235 \exp \left(-\frac{12600}{RT}\right) (\text{LiAlO}_2)
\]
\[
= 0.293 \exp \left(-\frac{8300}{RT}\right) (\text{Li}_4\text{SiO}_4)
\]
\[
= 0.290 \exp \left(-\frac{7640}{RT}\right) (\text{Li}_2\text{ZrO}_3),
\]  
\[\text{Eq. (4-17)}\]

\[
K_{sv}' = 2.77 \times 10^{-2} \exp \left(-\frac{25200}{RT}\right) (\text{LiAlO}_2)
\]
\[
= 8.99 \times 10^{-3} \exp \left(-\frac{12700}{RT}\right) (\text{Li}_4\text{SiO}_4)
\]
\[
= 4.63 \times 10^{-3} \exp \left(-\frac{9800}{RT}\right) (\text{Li}_2\text{ZrO}_3),
\]  
\[\text{Eq. (4-18)}\]

\[
\alpha = 5.96 \exp \left(-\frac{17200}{RT}\right) (\text{LiAlO}_2)
\]
\[
= 0.426 \exp \left(-\frac{1320}{RT}\right) (\text{Li}_4\text{SiO}_4)
\]
\[
= 0.86 \exp \left(\frac{4200}{RT}\right) (\text{Li}_2\text{ZrO}_3).
\]  
\[\text{Eq. (4-19)}\]

Figs. 4.22 and 4.23 show the comparison of $K_s a_v$ or $K_s ' a_v$ at desorption step among
various breeder materials, respectively. $K_s \alpha_v$ and $K_s' \alpha_v$ for LiAlO$_2$ are the smallest amount various breeder materials. Accordingly, the mass transfer rate of water on LiAlO$_2$ is the smallest among various breeder materials.

The relation between the over-all mass transfer coefficient and the mass transfer coefficient is expressed as eq.(4-4). The mass transfer coefficient in fluid film ($k_f$) can be considered to be much larger than $k_s$ under the experimental conditions in this work. Therefore, it can be considered that the over-all mass transfer coefficient ($K_s$) is equal to the film mass transfer coefficient ($k_f$). It is possible to estimate the effective diffusivity of water in the particle at the standard of the amount of adsorption using eq.(4-6). Figs.4.24–4.26 show the effective diffusivity of water in the particle of LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ at adsorption step, respectively. And figs.4.27–4.29 show the effective diffusivity of water in the particle of LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ at desorption step, respectively. Following equations are obtained from these figures.

(adsorption step)

\[
\begin{align*}
D_{i1}' & = 4.45 \times 10^{-5} \exp \left(- \frac{14650}{RT} \right) \quad \text{(LiAlO$_2$)} \\
& = 1.11 \times 10^{-5} \exp \left(- \frac{4380}{RT} \right) \quad \text{(Li$_4$SiO$_4$)} \\
& = 6.26 \times 10^{-6} \exp \left(- \frac{3000}{RT} \right) \quad \text{(Li$_2$ZrO$_3$)},
\end{align*}
\]

(4-20)

\[
\begin{align*}
D_{i2}' & = 2.18 \times 10^{-5} \exp \left(- \frac{24090}{RT} \right) \quad \text{(LiAlO$_2$)} \\
& = 2.81 \times 10^{-6} \exp \left(- \frac{7860}{RT} \right) \quad \text{(Li$_4$SiO$_4$)} \\
& = 4.75 \times 10^{-6} \exp \left(- \frac{12100}{RT} \right) \quad \text{(Li$_2$ZrO$_3$)},
\end{align*}
\]

(4-21)
(desorption step)

\[ D^{'}_{1,1} = 5.03 \times 10^{-5} \exp \left( \frac{-12600}{RT} \right) (\text{LiAlO}_2) \]
\[ = 6.23 \times 10^{-5} \exp \left( \frac{-8300}{RT} \right) (\text{Li}_4\text{SiO}_4) \]
\[ = 2.32 \times 10^{-5} \exp \left( \frac{-7820}{RT} \right) (\text{Li}_2\text{ZrO}_3), \] (4-22)

\[ D^{'}_{1,2} = 5.92 \times 10^{-6} \exp \left( \frac{-25200}{RT} \right) (\text{LiAlO}_2) \]
\[ = 1.91 \times 10^{-6} \exp \left( \frac{-12700}{RT} \right) (\text{Li}_4\text{SiO}_4) \]
\[ = 3.98 \times 10^{-6} \exp \left( \frac{-10300}{RT} \right) (\text{Li}_2\text{ZrO}_3), \] (4-23)

where \( D^{'}_{1,1,2} \): the effective diffusivity of water in the particle correlated adsorption(1) or (2) (desorption(1) or(2)) \([\text{cm}^2/\text{sec}]\).

Disagreement between the temperature dependence of diffusivity and that of the over-all mass transfer capacity coefficients at \( \text{Li}_2\text{ZrO}_3 \) is due to the difference of the density of packed bed.

Tritium diffusivity in the crystal grain of breeder material have been investigated by Kudo and Okuno[1~5] using measurement of tritiated water release rate. However, it can be considered that the tritium diffusivity obtained by Kudo and Okuno includes the resistance of surface reaction and the system effect. Tritium diffusivity was estimated using eq.(4-6) and the over-all mass transfer capacity coefficient for desorption(2). When the tritium diffusivity was estimated, the grain size was used as \( d_p \) and the density of pellet was used as \( \gamma \), because single crystals were used in their investigation of the tritium diffusivity. Fig.4.30 shows the comparison of the so to speak tritium diffusivity in the crystal grain. Temperature dependence of diffusivity obtained in this work disagree with that investigated by Kudo and Okuno. But, from the view point of order of values, the data obtained in this work almost agree with that investigated by them. Therefore,
it can be considered that tritium diffusivity in the crystal grain obtained by Kudo and Okuno is possible to include the resistance of surface reaction and the system effect and that real tritium diffusivity in the crystal grain is much larger. So much difference in diffusivity by Kudo and Okuno and that by FINESSE for each breeder material may be explained using the same reasons.

4.5 Conclusion

The over-all mass transfer capacity coefficients of water on LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ were obtained. When it was considered that two kinds of adsorption whose rate are different with each other progress at same time, the estimation of the breakthrough curve and the release curve of water were to be possible.

The effective diffusivity of water in the particle of various breeder materials at the standard of the amount of adsorption were obtained from the over-all mass transfer capacity coefficient.

Tritium diffusivity was estimated when it was assumed that the release rate of water adsorbed on the breeder material is equal to the diffusion rate of tritium in the crystal grain of the breeder material, and was compared with the so to speak tritium diffusivity in the crystal grain measured by other investigators. Tritium diffusivity have been obtained is possible to include the resistance of surface reaction and the system effect.

When the water or the tritiated water release experiment from breeder material is carried out, it is impossible to eliminate the system effect without heating the piping system of an experimental apparatus. Accordingly, it is necessary that the amount of water captured on the piping surface and the mass transfer rate of water on the piping surface are quantified.
Nomenclature

\( a_v \): surface area of particle per unit volume of packed bed [cm\(^2/cm^3\)]

\( c \): concentration of water [mol/cm\(^3\)]

\( \cdot c \): concentration of adsorbate in gas phase [mol/cm\(^3\)]

\( c_i \): concentration of adsorbate at the surface of particle [mol/cm\(^3\)]

\( c_0 \): inlet concentration of water [mol/cm\(^3\)]

\( c^{*}_{1,2} \): equilibrium concentration of water correlated to adsorption(1) or (2) [mol/cm\(^3\)].

\( D'_i \): the effective diffusivity of adsorbate in the particle at the standard of the amount of adsorption [cm\(^2/sec\)].

\( D'_{i1,2} \): the effective diffusivity of water in the particle correlated adsorption(1) or (2) [cm\(^2/sec\)].

\( d_p \): diameter of particle [cm].

\( K_f \): over-all mass transfer coefficient of fluid film [cm/sec]

\( K_s \): over-all mass transfer coefficient of solid film [g/cm\(^2\cdot sec\)].

\( K_{sa} \): the over-all mass transfer capacity coefficient of adsorption(1) at the standard of the amount of adsorbed water [g/cm\(^3\cdot sec\)]

\( K'_{sa} \): the over-all mass transfer capacity coefficient of adsorption(2) at the standard of the amount of adsorbed water [g/cm\(^3\cdot sec\)].

\( k_f \): mass transfer coefficient of fluid film [cm/sec]

\( k_s \): mass transfer coefficient of solid film [g/cm\(^2\cdot sec\)]

\( q \): the amount of adsorbed water [mol/g]

\( q_i \): the amount of adsorption at the surface of particle [mol/g].
\( q_{1,2} \) : the amount of adsorbed water by adsorption(1) or (2) [mol/g]

\( q_{1,0} \) : capacity of adsorption for adsorption(1) [mol/g]

\( q_{2,0} \) : capacity of adsorption for adsorption(2) [mol/g]

\( q^*_{1,2} \) : the amount of water adsorption equilibrate to the concentration of water in gas phase for adsorption(1) or(2) [mol/g]

\( t \) : time [sec]

\( u \) : superficial gas velocity [cm/sec]

\( z \) : axial distance [cm]

\( \alpha \) : ratio of capacity of adsorption for adsorption(1) to total capacity [-]

\( \beta \) : adsorption coefficient [cm³/g]

\( \gamma \) : density of packed bed [g/cm³]

\( \varepsilon \) : void fraction of packed bed [-]
References


Table 4.1 The sample specification.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>LiAlO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>2.6g/cm³</td>
</tr>
<tr>
<td>Density</td>
<td>2.21g/cm³ (85%T.D.)</td>
</tr>
<tr>
<td>Grain Size</td>
<td>20µm (diameter)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>12~16mesh</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>0.29m²/g</td>
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</table>
Table 4.2 The sample specification.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li₄SiO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>2.21g/cm³</td>
</tr>
<tr>
<td>Density</td>
<td>1.88g/cm³ (85% T.D.)</td>
</tr>
<tr>
<td>Grain Size</td>
<td>20μm (diameter)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>12~16 mesh</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>0.73m²/g</td>
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</table>
Table 4.3 The sample specification.

<table>
<thead>
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<th>Sample Name</th>
<th>Li$_2$ZrO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>4.15g/cm$^3$</td>
</tr>
<tr>
<td>Density</td>
<td>3.57g/cm$^3$ (86%T.D.)</td>
</tr>
<tr>
<td>Grain Size</td>
<td>13μm (diameter)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>1.0mmΦ</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>0.09m$^2$/g</td>
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</table>
Table 4.4 The chemical composition of LiAlO₂ used in this work.

<table>
<thead>
<tr>
<th>element (detectable limit) (ppm)</th>
<th>sintering pellet (1934.7mg)</th>
<th>measurement (ppm)</th>
<th>content (mg)</th>
<th>content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (&lt;0.018)</td>
<td></td>
<td>7094</td>
<td>709.4</td>
<td>36.66718</td>
</tr>
<tr>
<td>Li (&lt;0.013)</td>
<td></td>
<td>1777.6</td>
<td>177.76</td>
<td>9.18799</td>
</tr>
<tr>
<td>Mo (&lt;1.072)</td>
<td></td>
<td>0.779</td>
<td>0.078</td>
<td>0.00403</td>
</tr>
<tr>
<td>Cr (&lt;0.009)</td>
<td></td>
<td>0.0101</td>
<td>0.001</td>
<td>0.00005</td>
</tr>
<tr>
<td>Fe (&lt;0.008)</td>
<td></td>
<td>0.4580</td>
<td>0.046</td>
<td>0.00237</td>
</tr>
<tr>
<td>Ni (&lt;0.064)</td>
<td></td>
<td>&lt;0.064</td>
<td>&lt;0.006</td>
<td>&lt;0.00033</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td></td>
<td></td>
<td>45.86631</td>
</tr>
</tbody>
</table>

* ICP analysis is made for LiAlO₂ solution in aqua regia when about 90% of sintered pellet is dissolved.
Table 4.5 Spectrographic analysis of $\text{Li}_2\text{ZrO}_3$ used in this work.

<table>
<thead>
<tr>
<th>RESULTS OF SPECTROGRAPHIC ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Cu</td>
</tr>
</tbody>
</table>
Table 4.6 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>LiAlO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>18.02g</td>
</tr>
<tr>
<td>Height of packed bed</td>
<td>3.9cm</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.2-0.4l/min</td>
</tr>
<tr>
<td>Concentration of H₂O</td>
<td>36.0-48.2ppm in atmospheric pressure (3.6-4.9Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>150-600°C (423-873K)</td>
</tr>
</tbody>
</table>
Table 4.7 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_4$SiO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>11.62g</td>
</tr>
<tr>
<td>Height of packed bed</td>
<td>2.5cm</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.2~0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$O</td>
<td>48.2<del>59.4ppm in atmospheric pressure (4.9</del>6.0Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>150~300°C</td>
</tr>
<tr>
<td></td>
<td>(423~573K)</td>
</tr>
</tbody>
</table>
Table 4.8 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_2$ZrO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>70.0g</td>
</tr>
<tr>
<td></td>
<td>99.92g</td>
</tr>
<tr>
<td>Height of packed bed</td>
<td>7.7cm</td>
</tr>
<tr>
<td></td>
<td>11.4cm</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.2~0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$O</td>
<td>36.0<del>59.4ppm in atmospheric pressure (3.6</del>6.0Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>150~400°C</td>
</tr>
<tr>
<td></td>
<td>(423~673K)</td>
</tr>
</tbody>
</table>
Fig.4.1 A schematic diagram of experimental apparatus.
Fig. 4.2  Examples of breakthrough curves of water for LiAlO$_2$. 

LiAlO$_2$ (85% T.D.): 18.02 g  
Inlet Conc. of H$_2$O: 36.0 ppm  
Flow Rate: 0.4 l/min  

- $200^\circ$C  
- $300^\circ$C  
- $400^\circ$C
Fig. 4.3  Examples of breakthrough curves of water for Li$_4$SiO$_4$. 

Li$_4$SiO$_4$ (85% T.D.) : 11.62 g 
Inlet Conc. of H$_2$O : 59.4 ppm
Flow Rate : 0.4 l/min
150 °C  
300 °C
Fig. 4.4 Examples of breakthrough curves of water for Li₂ZrO₃.
Fig. 4.5 An example of curve fitting for the breakthrough curve of water for LiAlO$_2$. 

**Table:**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlO$_2$ (85% T.D.)</td>
<td>18.02 g</td>
</tr>
<tr>
<td>Inlet Conc. of H$_2$O</td>
<td>36.0 ppm</td>
</tr>
<tr>
<td>Temp.</td>
<td>300 °C</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>0.4 l/min.</td>
</tr>
<tr>
<td>$K_s a_v$</td>
<td>$1.0 \times 10^{-2}$ g/cm$^3$/sec</td>
</tr>
<tr>
<td>$K_s a_v'$</td>
<td>$6.0 \times 10^4$ g/cm$^3$/sec</td>
</tr>
</tbody>
</table>

**Graph:**

- The graph shows the relationship between $C_{out}/C_{in}$ and time, where $C_{out}$ is the concentration of water at the outlet and $C_{in}$ is the concentration at the inlet.
- The estimated curve is shown as a dashed line, fitting the breakthrough curve for LiAlO$_2$. 
- The x-axis represents time in minutes, ranging from 0 to 120 minutes.
Fig. 4.6 An example of curve fitting for the breakthrough curve of water for Li4SiO4.
Fig. 4.7 An example of curve fitting for the breakthrough curve of water for Li$_2$ZrO$_3$.  

Li$_2$ZrO$_3$ (86% T.D.): 70.0 g  
Inlet Conc. of H$_2$O: 36.0 ppm  
Temp.: 250 °C  
Flow Rate: 0.19 l/min  
K$_a$ : 0.04 g/cm$^3$·sec  
K$_a'$ : 0.0035 g/cm$^3$·sec
The overall mass transfer capacity coefficients for adsorption(1) and (2) and the ratio of the amount of adsorption(1) to total amount of adsorption for LiAlO₂.

\[ K_{sat} = 0.208 \exp\left(\frac{-14650}{RT}\right) \]

\[ K_{s'at} = 0.102 \exp\left(\frac{-24090}{RT}\right) \]

\[ \alpha = 1.93 \exp\left(\frac{-5400}{RT}\right) \]
Fig. 4.9  The over-all mass transfer capacity coefficients for adsorption (1) and (2) and the ratio of the amount of adsorption (1) to total amount of adsorption for Li$_4$SiO$_4$. 

\[ K_{a,v} = 5.22 \times 10^{-2} \exp \left( \frac{-4380}{RT} \right) \]

\[ K_{a,v}' = 1.32 \times 10^{-2} \exp \left( \frac{-7860}{RT} \right) \]

\[ \alpha = 1.18 \exp \left( \frac{-1420}{RT} \right) \]

The adsorption step for Li$_4$SiO$_4$ (85% T.D.) with water vapor pressure of 4.9 Pa and 6.0 Pa.
The overall mass transfer capacity coefficients for adsorption(1) and (2) and the ratio of the amount of adsorption(1) to total amount of adsorption for Li$_2$ZrO$_3$.

$$\alpha = 0.60 \exp\left(\frac{1460}{RT}\right)$$

$$K_s a_v = 8.39 \times 10^{-2} \exp\left(-\frac{3110}{RT}\right)$$

$$K_s' a_v = 4.44 \times 10^{-2} \exp\left(-\frac{10580}{RT}\right)$$

Fig. 4.10
Fig. 4.11 The comparison of over-all mass transfer capacity coefficient for adsorption(1) among various breeder materials.
Fig. 4.12 The comparison of over-all mass transfer capacity coefficient for adsorption(2) among various breeder materials.
LiAlO₂ (85% T.D.)
Conc. of H₂O (adsorption step) : 36.0 ppm
Flow Rate
- :- 18.02 g
- 0.4 l/min
\(200 °C\)
\(400 °C\)
\(600 °C\)

\(C_{\text{out}}/C_{\text{ad, in}} [-]\)

Time [min]

Fig.4.13  Examples of desorption curves of water for LiAlO₂.
Li$_4$SiO$_4$ (85% T.D.)
Conc. of H$_2$O (adsorption step) : 59.4 ppm
Flow Rate
- : 0.4 l/m
- : 150 °C
- : 300 °C

Fig. 4.14 Examples of desorption curves of water for Li$_4$SiO$_4$. 
Fig. 4.15 Examples of desorption curves of water for Li$_2$ZrO$_3$. 

Li$_2$ZrO$_3$ (86% T.D.)
Conc. of H$_2$O (adsorption step): 36.0 ppm
Flow Rate: 0.4 l/min
- - 200°C
- - 300°C
- - 400°C
LiAlO$_2$ (85% T.D.)
Conc. of H$_2$O (adsorption step) : 36.0 ppm
Temp. : 600 °C
Flow Rate : 0.4 l/min

K$_s$a$_v$ : 3.5×10$^{-2}$ g/cm$^3$•sec
K$_s'$a$_v$ : 5.0×10$^{-4}$ g/cm$^3$•sec

Fig.4.16 An example of curve fitting for desorption curve of water for LiAlO$_2$. 
Fig. 4.17 An example of curve fitting for desorption curve of water for Li₄SiO₄.
An example of curve fitting for desorption curve of water for Li$_2$ZrO$_3$. 

Fig. 4.18
Fig. 4.19 The overall mass transfer capacity coefficients for desorption (1) and (2) and the ratio of the amount of desorption (1) to total amount of desorption for LiAlO$_2$.
Fig. 4.20 The over-all mass transfer capacity coefficients for desorption (1) and (2) and the ratio of the amount of desorption (1) to total amount of desorption for Li$_4$SiO$_4$.

\[ \alpha = 0.426 \exp \left( \frac{-1320}{RT} \right) \]

\[ K'_{s\alpha_v} = 0.293 \exp \left( \frac{-8300}{RT} \right) \]

\[ K'_{s\alpha_v} = 8.99 \times 10^{-3} \exp \left( \frac{-12700}{RT} \right) \]
The over-all mass transfer capacity coefficients for desorption(1) and (2) and the ratio of the amount of desorption(1) to total amount of desorption for Li$_2$ZrO$_3$. 

$$\alpha = 0.86\exp\left(\frac{-4200}{RT}\right)$$

$$K_a = 0.29\exp\left(\frac{-7640}{RT}\right)$$

$$K_s = 4.63\times10^{-3}\exp\left(\frac{-9800}{RT}\right)$$
Fig. 4.22 The comparison of over-all mass transfer capacity coefficient for desorption(1) among various breeder materials.
Fig. 4.23 The comparison of over-all mass transfer capacity coefficient for desorption(2) among various breeder materials.
Fig. 4.24 The effective diffusivity of water in the particle of LiAlO$_2$ at adsorption step.
Fig. 4.25 The effective diffusivity of water in the particle of Li$_4$SiO$_4$ at adsorption step.

\[ D_{i1}' = 1.11 \times 10^{-5} \exp \left(-\frac{4380}{RT}\right) \]

\[ D_{i2}' = 2.81 \times 10^{-6} \exp \left(-\frac{7860}{RT}\right) \]
Fig. 4.26 The effective diffusivity of water in the particle of Li₂ZrO₃ at adsorption step.

\[ D'_{i1} = 6.26 \times 10^{-6} \exp \left( \frac{-3000}{RT} \right) \]

\[ D'_{i2} = 4.75 \times 10^{-6} \exp \left( \frac{-12100}{RT} \right) \]
Fig. 4.27 The effective diffusivity of water in the particle of LiAlO$_2$ at desorption step.

\[ D_{i1} = 5.03 \times 10^{-5} \exp \left( -\frac{12600}{RT} \right) \]

\[ D_{i2} = 5.92 \times 10^{-6} \exp \left( -\frac{25200}{RT} \right) \]
Fig. 4.28 The effective diffusivity of water in the particle of Li$_4$SiO$_4$ at desorption step.
$D_{i1} = 2.32 \times 10^{-5} \exp \left(-\frac{7820}{RT}\right)$

$D_{i2} = 3.98 \times 10^{-7} \exp \left(-\frac{10300}{RT}\right)$

Fig. 4.29 The effective diffusivity of water in the particle of Li$_2$ZrO$_3$ at desorption step.
Fig. 4.30 The comparison of the so to speak tritium diffusivity in the crystal grain with other reports.
5. Study on Formation of Water in Lithium Ceramics Bed at Hydrogen Addition to Purge Gas

5.1. Introduction

It has been proposed to make use of isotope exchange reaction for the enhancement of tritium release rate from the blanket material. Following this idea, hydrogen or deuterium is added to the He sweep gas, and it is reported that the tritium release rate is enhanced by adding hydrogen isotopes and that the dominant chemical form of release tritium becomes the HT form when a lot of hydrogen is added[1-4]. However, it is found by the present author that formation of water in the lithium oxide bed occurs in the course of the isotope exchange reaction experiments using He sweep gas with hydrogen isotopes.[5] In this study, it is discussed about the formation of water in the lithium ceramics bed.

5.2 Theoretical consideration

If water is formed when hydrogen is introduced to the helium gas purged through the lithium ceramics bed, possibility of a reduction of oxide forming lithium ceramics by hydrogen must be presumed. The redox reaction of metal is expressed as

\[ \text{H}_2 + \frac{1}{n} \text{M}_m \text{O}_n = \frac{m}{n} \text{M} + \text{H}_2 \text{O} \]  \hspace{1cm} (5-1)

where M means any metal[6]. Then, the difference of the standard free energy of the redox reaction is approximately expressed as

\[ \Delta G_r^0 = \frac{1}{n} \Delta G_f^0(\text{M}_m \text{O}_n) - \Delta G_f^0(\text{H}_2 \text{O}) \]  \hspace{1cm} (5-2)

where \( \Delta G_r^0 \) : the difference of standard free energy of redox reaction [J/mol]
\[ \Delta G_f^0(M_{\text{m}O_n}) : \text{the free energy of oxide [J/mol]} \]
\[ \Delta G_f^0(\text{H}_2\text{O}) : \text{the free energy of water [J/mol]}. \]

And then, the equilibrium constant of eq(5-1) is expressed using \( \Delta G_r^0 \) as

\[ K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = \exp \left( - \frac{\Delta G_r^0}{RT} \right), \quad (5-3) \]

where
- \( K \) : the equilibrium constant [-]
- \( P_{\text{H}_2\text{O}} \) : the partial pressure of water vapor [Pa]
- \( P_{\text{H}_2} \) : the partial pressure of hydrogen [Pa]
- \( R \) : gas constant [J/mol\( \cdot \)K]
- \( T \) : absolute temperature [K].

Figs.5.1 and 5.2 show the temperature dependence of the equilibrium constant estimated using eq.(5-3). The difference of the standard free energy of the redox reaction was calculated with the data in JANAF Thermochemical Tables[7]. It is known that the breeder materials are hardly reduced than quartz (SiO\(_2\)). However, as the mention in section 5.3.2, quartz was not reactive with hydrogen. Estimation shown in figs.5.1 and 5.2 suggest that the formation of water at introducing of hydrogen to the ceramic breeder material can not be expected from the thermodynamical consideration.

**5.3 Experimentals**

**5.3.1 Sample**

The samples used in this work were Li\(_2\)O, LiAlO\(_2\), Li\(_4\)SiO\(_4\) and Li\(_2\)ZrO\(_3\) made in Mitsubishi Atomic Power Industries Inc. and their specifications are shown in tables 5.1~5.4. The chemical compositions of Li\(_2\)O and LiAlO\(_2\) shown in table 5.5 were analyzed with the activation analysis using Kyoto University Reactor
The result of spectrographic analysis of Li$_2$ZrO$_3$ is also shown in table 5.6.

5.3.2 Experimental method

Fig. 5.3 shows a schematic diagram of experimental apparatus. The sample was charged in a reaction tube. The reaction tube was a quartz tube of 22.8mm in inner diameter and 500mm in length, in which a filter plate with several 1mm holes was mounted at 220mm from the bottom end. Helium was used as the carrier gas and the flow rate was kept at 0.4l/min by a flow rate adjuster. He gas was passed through the spongy Cu bed that was heated up to 350°C to remove residual O$_2$ in the gas. Hydrogen and Helium mixed gas (H$_2$/He gas) was initially passed through the Platinum-Molecular Sieves 5A (Pt-MS 5A) catalyst bed to change residual O$_2$ in the gas to water. He or H$_2$/He gas was passed through the cold trap immersed in liquid nitrogen to exclude water before the process gas was introduced to the sample bed. The cold trap placed at the channel of He gas flow is a packed column of Molecular Sieves 5A (MS 5A), and that at the channel of H$_2$/He gas flow is a packed bed of glass beads.

The experiments were carried out as follows. He gas was passed through the sample bed, and the sample bed was heated up stepwisely to 1073K to release water. When Li$_2$O was used as the sample, the sample bed was heated up stepwisely to 973K. Because the amount of water captured in Li$_2$O used in this study is minimum at 873–973K. The heat treatment was continued until the water concentration in the outlet gas of the sample bed reached 1ppm or less. Then, the temperature of the sample bed was set to the experimental temperature. H$_2$/He gas was passed through the sample bed after He gas was stopped, and the water concentration in the outlet gas of the sample bed was measured with a hygrometer.
and the hydrogen concentration with a gas chromatography. The amount of hydrogen consumed and water generated were obtained from the change of \( \text{H}_2 \) and water concentration in the outlet gas of the sample bed with time. Figs.5.4-5.7 show examples of the change of hydrogen and water concentration in the outlet gas of sample bed with time. The blank test was carried out in advance and it was confirmed that a reaction tube made of quartz was inactive with hydrogen at the range of the experimental temperature.

The experimental conditions are shown in tables 5.7-5.10.

### 5.4 Results and discussion

#### 5.4.1 Lithium oxide

Fig.5.8 shows the temperature dependence of the amount of water generated and \( \text{H}_2 \) consumed when He gas containing \( \text{H}_2 \) 20.2Pa of partial pressure is introduced to the \( \text{Li}_2\text{O} \) bed. Both values agree with each other. Though generated water and consumed \( \text{H}_2 \) were negligible below 673K, they were not negligible at higher temperatures. Fig.5.9 shows the change of water concentration in the outlet gas of the \( \text{Li}_2\text{O} \) bed at 973K under various partial pressures of \( \text{H}_2 \). It is known from this figure that the amount of water generated is not depended on the partial pressure of \( \text{H}_2 \) and that the rate controlling step must be in the mass transfer step inside the grain of \( \text{Li}_2\text{O} \). The following equation is obtained from fig.5.8 in range of this experiment.

\[
\Delta_{\text{H}_2\text{O}} = \Delta_{\text{H}_2} = 9.36 \times 10^{-2} \exp \left( -\frac{49400}{RT} \right),
\]  

(5-4)

where

- \( \Delta_{\text{H}_2\text{O}} \): the amount of water generated [mol-\( \text{H}_2\text{O}/\text{mol-}\text{Li}_2\text{O} \)]

- \( \Delta_{\text{H}_2} \): the amount of \( \text{H}_2 \) consumed [mol-\( \text{H}_2/\text{mol-}\text{Li}_2\text{O} \)].

It was also found that the amount of water generated was seemed to have the limited

-187-
capacity at each temperature and that this capacity depended on the temperature and
not depended on the concentration of H\textsubscript{2}.

Various reactions as follows can be postulated in the Li\textsubscript{2}O bed to explain
generation of H\textsubscript{2}O at introduction of H\textsubscript{2}.

Reduction of Li\textsubscript{2}O,
\[ \text{Li}_2\text{O} + \text{H}_2 = 2\text{Li} + \text{H}_2\text{O}. \] (5-5)

Formation and dissociation of LiOH,
\[ \text{Li}_2\text{O} + \text{H}_2 = \text{LiOH} + \text{LiH}, \]
\[ \text{LiOH} = \frac{1}{2}\text{Li}_2\text{O} + \frac{1}{2}\text{H}_2\text{O}. \] (5-6)

Formation of LiH,
\[ \text{Li}_2\text{O} + 2\text{H}_2 = 2\text{LiH} + \text{H}_2\text{O}. \] (5-7)

Dissociation of LiOH remained in Li\textsubscript{2}O,
\[ \text{LiOH} = \frac{1}{2}\text{Li}_2\text{O} + \frac{1}{2}\text{H}_2\text{O}. \] (5-8)

Reaction between LiOH and H\textsubscript{2},
\[ 2\text{LiOH} + \text{H}_2 = 2\text{Li} + 2\text{H}_2\text{O}. \] (5-9)

Competitive sorption of H\textsubscript{2} and H\textsubscript{2}O,
\[ \text{Li}_2\text{O}(\text{H}_2\text{O}) + \text{H}_2 = \text{Li}_2\text{O}(\text{H}_2) + \text{H}_2\text{O}. \] (5-10)

Formation or reduction of non-stoichiometric compound,
\[ \text{Li}_2\text{O} + x\text{H}_2 = \text{Li}_2\text{O}_{1-x} + x\text{H}_2\text{O} \]
\[ \text{Li}_2\text{O}_{1+x} + x\text{H}_2 = \text{Li}_2\text{O} + x\text{H}_2\text{O}. \] (5-11)

When H\textsubscript{2}O/He gas was passed through the Li\textsubscript{2}O bed after H\textsubscript{2}/He gas was
passed through the Li\textsubscript{2}O bed for sufficiently long time to generate H\textsubscript{2}O, generation
of H\textsubscript{2} was detected, and the capacity to generate H\textsubscript{2}O was recovered.

Introduction of O\textsubscript{2}/He gas to the Li\textsubscript{2}O bed after the formation of water was
also effective to recover the capacity to generate H\textsubscript{2}O.
When H₂O/He gas was passed through the Li₂O bed after D₂/He gas was passed through the Li₂O bed for sufficiently long time to generate D₂O, only generation of H₂ was obtained and deuterium was not detected.

From the above experimental results, the present author considers that the formation of non-stoichiometric compound (reaction (5-11)) is most possible. If the reaction is the formation of non-stoichiometric compound, x is correlated as

\[ x = 9.36 \times 10^{-2} \exp \left( \frac{-49400}{RT} \right) \]  

(5-12)

It is not fully deniable, however, that reaction occurs between H₂ and impurity in oxide form which is mixed when the Li₂O pellet is made, though the present author does not think it probable considering from the temperature dependency in H₂O formation.

5.4.2 Lithium meta-zirconate

Fig.5.10 shows the amount of water generated and H₂ consumed in the Li₂ZrO₃ bed at H₂ addition to purge gas at various temperatures, and the values taken by both ways agree with each other. This dependency is also known from that the curve of the change of water in the outlet gas of the Li₂ZrO₃ bed and that of H₂ in the outlet gas of the Li₂ZrO₃ bed are almost axisymmetry with each other at the line of 0.5 of the ratio of the concentration in the outlet gas and that in the inlet gas as shown in fig.5.5. The amount of water generated and H₂ consumed increase with the rise of temperature, and reach the constant value between the temperature range of 973 to 1173K. The amount of water generated and H₂ consumed are not dependent on the partial pressure of H₂ as shown in fig.5.11. It is found that the amount of water generated and H₂ consumed are seemed to have limited capacities at each temperature. This capacity is expressed as
\[
\Delta H_{2O} = 5.42 \times 10^{-3} \left( \frac{2.85 \times 10^{10} \exp \left( -\frac{178000}{RT} \right)}{1 + 2.85 \times 10^{10} \exp \left( -\frac{178000}{RT} \right)} \right) + 1.56 \times 10^{-4}
\]

where \( \Delta H_{2O} \) : the amount of water generated [mol-H\textsubscript{2}O/mol-Li\textsubscript{2}ZrO\textsubscript{3}].

The sample was colored ivory white before the experiment, but it was colored gray after the experiment of water formation at H\textsubscript{2} addition. The color of the sample after the experiment at high temperature was deeper than that at low temperature. As the result of introduction of oxygen or water vapor in Li\textsubscript{2}ZrO\textsubscript{3} bed after the experiment of water formation, the hydrogen oxidizing capacity and the color of Li\textsubscript{2}ZrO\textsubscript{3} returned to the state before the experiment. The time to get the state before the experiment of water formation when the water vapor was introduced to the sample bed after the experiment of water formation was longer than the case of the O\textsubscript{2} gas introduction. Formation of hydrides of the constituent atoms of the sample is considered as the cause of change of color. Table 5.11 shows the color of hydrides of various metals\cite{8}. If hydrides are formed, water must be detected in the outlet gas of the sample bed when O\textsubscript{2} gas is introduced to the sample bed after the experiment of water formation. Indeed, water is detected, however, whose amount is so small as below 1% of the amount of water generated at H\textsubscript{2} addition to purge gas.

From these results and results of the blank test, it may be considered that hydrogen reacts with oxygen existing in Li\textsubscript{2}ZrO\textsubscript{3}. The existing form of oxygen in Li\textsubscript{2}ZrO\textsubscript{3} is not confirmed, but it may be considered that the non-stoichiometric compound is formed. It is not fully deniable, however, that reaction occurs between H\textsubscript{2} and impurity in oxide form which is mixed when the Li\textsubscript{2}ZrO\textsubscript{3} pebble is made, though the present author dose not think it probable considering from the temperature dependency in H\textsubscript{2}O formation.
5.4.3 γ–Lithium meta-aluminate

Fig. 5.12 shows the amount of water generated and $H_2$ consumed in the LiAlO$_2$ bed at $H_2$ addition to purge gas. The values taken by both ways almost agree with each other, and these values increase with the rise of temperature. The amount of water generated and $H_2$ consumed are not dependent on the partial pressure of $H_2$ as shown in fig. 5.13. It was found that the amount of water generated was seemed to have limited capacity at each temperature. The hydrogen oxidizing capacity is expressed as

$$\Delta_{\text{H}_2\text{O}} = 2.03 \times 10^{-1} \exp \left( - \frac{64600}{RT} \right),$$  \hspace{1cm} (5-14)

where $\Delta_{\text{H}_2\text{O}}$ : the amount of water generated [mol-$\text{H}_2\text{O}$/mol-LiAlO$_2$].

As the results of introducing oxygen or water vapor in the LiAlO$_2$ bed after the experiment of water formation, the hydrogen oxidizing capacity returned to the state before the experiment. The time to get the state before the experiment of water formation when the water vapor was introduced to the sample bed after the experiment of water formation was longer than the $O_2$ gas introduction as the case of Li$_2$ZrO$_3$. And then, the color change of the sample was not confirmed.

From these results and results of the blank test, it may be considered that hydrogen reacts with oxygen existing in LiAlO$_2$. The existing form of oxygen in LiAlO$_2$ is not confirmed, but it may be considered that the non-stoichiometric compound is formed. It is not fully deniable, however, that reaction occurs between $H_2$ and impurity in oxide form which is mixed when the LiAlO$_2$ pellet is made, though the present author does not think it probable considering from the temperature dependency in $H_2\text{O}$ formation.
5.4.4 Lithium ortho-silicate

Fig. 5.14 shows the amount of water generated and H\(_2\) consumed in the Li\(_4\)SiO\(_4\) bed at H\(_2\) addition to purge gas. The values taken by both ways almost agree with each other, and these values increase with the rise of temperature. The hydrogen partial pressure dependency of the amount of water generated in the Li\(_4\)SiO\(_4\) bed is not still investigated, but it is expected that the amount of water generated is not dependent on the partial pressure of H\(_2\) considering with the results of other materials. The amount of water generated is tentatively expressed as

\[
\Delta H_{2O} = 2.1 \times 10^{-1} \exp \left( \frac{-40100}{RT} \right),
\]

(5-15)

where \(\Delta H_{2O}\) : the amount of water generated [mol-H\(_2\)O/mol-Li\(_4\)SiO\(_4\)].

The sample was colored bluish white before the experiment, but it was colored gray after the experiment of water formation at H\(_2\) addition. The color of the sample after the experiment at high temperature was deeper than that at low temperature. As the results of introducing oxygen or water vapor in the Li\(_4\)SiO\(_4\) bed after the experiment of water formation, the hydrogen oxidizing capacity and the color of the sample returned to the state before the experiment. When the water vapor was introduced to the sample bed after the experiment of water formation, the time to get the state before the experiment of water formation was longer than the case of introducing O\(_2\) gas.

From these results and results of the blank test, it may be considered that hydrogen reacts with oxygen existing in Li\(_4\)SiO\(_4\). The existing form of oxygen in Li\(_4\)SiO\(_4\) is not confirmed, but it may be considered that the non-stoichiometric compound is formed. It is not fully deniable, however, that reaction occurs between H\(_2\) and impurity in oxide form which is mixed when the Li\(_4\)SiO\(_4\) pellet is made, though the present author does not think it probable considering from the
temperature dependency in $H_2O$ formation.

Fig. 5.15 shows the comparison of the amount of water generated in various breeder material beds at hydrogen addition to purge gas. The amount of water generated per unit mole of LiAlO$_2$ is the smallest among the various breeder materials.

5.4.5 Reaction rate

Fig. 5.16a shows the comparison of the changes of water concentration in the outlet gas of Li$_2$ZrO$_3$ bed at 1073K. These response curves are standardized with the amount of hydrogen passed through the sample bed at 992ppm of $H_2$ concentration as shown in fig.5.16b. These three curves at the difference conditions of the inlet concentration of $H_2$ almost agree with each other by standardizing. If the diffusion of oxygen in Li$_2$ZrO$_3$ crystal grain is the rate controlling step, these three curves must agree with each other without standardizing, because the reaction rate is depended on the supply rate of oxygen that is constant at the same temperature. If the surface reaction is the rate controlling step, these three curves agree with each other by standardizing like fig. 5.16b, because the reaction rate is not equal but the reaction rate constant is to be same value at the same temperature. And then, if the diffusion of oxygen in Li$_2$ZrO$_3$ crystal grain is the rate controlling step, the hydrogen oxidizing capacities are not depended on the temperature. However, as a matter of fact, the hydrogen oxidizing capacities are depended on the temperature as shown in figs. 5.8, 5.10, 5.12 and 5.14. Therefore, it is considered that the surface reaction is the rate controlling step of the mass transfer.

The reaction in the sample bed is assumed to be the second order reaction that is the first order reaction for the concentration of activated point (oxygen) in the sample bed and for the concentration of $H_2$, respectively. Then, the mass
balance equation for H\textsubscript{2} in the sample bed is expressed as

\[ u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + (1 - \varepsilon) \frac{\partial q}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2}. \]  
(5-16)

The mass flow rate is large enough to ignore the influence of axial diffusion under the experimental conditions in this study. Accordingly, eq.(5-16) is expressed as

\[ u \frac{\partial c}{\partial z} + \varepsilon \frac{\partial c}{\partial t} + (1 - \varepsilon) \frac{\partial q}{\partial t} = 0, \]  
(5-17)

and the mass transfer rate equation is expressed as

\[ \frac{\partial q}{\partial t} = k_c (q_0 - q), \]  
(5-18)

and the initial and boundary conditions are expressed as

\[
\begin{cases}
  t = 0, z > 0 \rightarrow q = 0 \\
  z = 0, t \geq 0 \rightarrow c = c_0,
\end{cases}
\]  
(5-19)

where

- \( u \): superficial gas velocity [cm/sec]
- \( c \): concentration of H\textsubscript{2} [mol/cm\textsuperscript{3}]
- \( z \): axial distance [cm]
- \( \varepsilon \): void fraction in the bed [-]
- \( t \): time [sec]
- \( q \): concentration of consumed activated point in bed [mol/cm\textsuperscript{3}]
- \( q_0 \): the hydrogen oxidizing capacity in the bed [mol/cm\textsuperscript{3}]
- \( k \): reaction rate constant [cm\textsuperscript{3}/mol\textperiodcentered sec]
- \( c_0 \): the inlet concentration of H\textsubscript{2} [mol/cm\textsuperscript{3}].

In eq.(5-18), the reverse reaction was ignored, because the rate of the reverse reaction was smaller than that of the forward reaction.

The hydrogen oxidizing capacities of various breeder materials (\( q_0 \)) have been obtained in this study. And then, the analytical solution of eqs.(5-17~5-19) has been obtained by Bohart and Adams[9]. The analytical solution of eqs.(5-17~5-19)
is expressed as

\[
\frac{c}{c_0} = \frac{\exp \left( k c_0 \left( t - \frac{\varepsilon z}{u} \right) \right)}{\exp \left( k c_0 \left( t - \frac{\varepsilon z}{u} \right) \right) + \exp \left[ k \alpha z (1 - \varepsilon) \right] - 1.} \tag{5-20}
\]

The curve fittings of the change of hydrogen concentration in the outlet gas of the sample bed were carried out using eq.(5-20) with the reaction rate constant \(k\) as a parameter. Examples of the curve fitting for various breeder materials are shown in figs.5.17~5.20. The curves obtained at low temperature were impossible to fit, because the reactivity is too small at low temperature. Fig.5.21 shows the reaction rate constant obtained. The reaction rate constant for \(\text{Li}_4\text{SiO}_4 \) or \(\text{Li}_2\text{ZrO}_3\) is expressed as

\[
k = 6.9 \times 10^{11} \exp \left( - \frac{165100}{RT} \right) \quad (\text{Li}_4\text{SiO}_4)
\]

\[
k = 7.9 \times 10^{11} \exp \left( - \frac{148900}{RT} \right) \quad (\text{Li}_2\text{ZrO}_3)
\]

The apparent activation energy of reaction rate constant for \(\text{Li}_4\text{SiO}_4 \) and \(\text{Li}_2\text{ZrO}_3\) were determined to be 165kJ/mol and 149kJ/mol, respectively. The reaction rate constants for \(\text{Li}_2\text{O} \) and \(\text{LiAlO}_2\) were obtained only two values, respectively. Accordingly, the reaction rate constants for \(\text{Li}_2\text{O} \) and \(\text{LiAlO}_2\) can not be expressed as equations, but roughly values of the apparent activation energy of reaction rate constant were determined to be 28.6 and 53.5kJ/mol. Ando et al.[10] have obtained the value of 144kJ/mol as the activation energy of diffusion rate of oxygen in \(\text{Li}_2\text{O}\) crystal grain, and Moriyama et al.[11] have obtained the value of about 150kJ/mol as the activation energy of diffusion of vacancy in \(\text{Li}_2\text{O}\) crystal grain. These values are close to that for \(\text{Li}_4\text{SiO}_4 \) or \(\text{Li}_2\text{ZrO}_3\). However, as mentioned in the opening of this section, it can not be considered that oxygen diffusion is the main mechanism of the water formation phenomenon. The values of activation energy of reaction rate constant for \(\text{Li}_2\text{O} \) and \(\text{LiAlO}_2\) are smaller than those for \(\text{Li}_4\text{SiO}_4 \) and \(\text{Li}_2\text{ZrO}_3\). It
may be considered that the main mechanism of water formation phenomenon in the 
\( \text{Li}_2\text{O} \) or \( \text{LiAlO}_2 \) bed is different from that in the \( \text{Li}_4\text{SiO}_4 \) or \( \text{Li}_2\text{ZrO}_3 \) bed.

5.4.6 Simulation of water formation behavior in blanket

The simulation of the change of hydrogen concentration in the outlet gas of the blanket when \( \text{H}_2 \) is added to the blanket sweep gas to enhance the tritium recovery has been carried out using the hydrogen oxidizing capacity and the reaction rate constant obtained in this study. The blanket condition for the simulation is shown in table 5.12. The blanket is assumed to be cylindrical packed bed and the bed height is 1m. The packed bed weight for each breeder material is considered to be 600ton. The tritium breeding rate is 400g/day at the blanket of fusion reactor that generates 1GW of electric output when tritium breeding ratio is 1.0. The mass flow rate of helium sweep gas is to be \( 1.51 \times 10^5 \text{m}^3/\text{day} \) when the total pressure in the blanket is atmospheric pressure and the partial pressure of tritium in the blanket is 1Pa. It is assumed that hydrogen corresponds to the H/T ratio which equals to 100 is added to He sweep gas for tritium recovery using isotope exchange reaction. Then, the concentration of hydrogen in the blanket sweep gas is estimated to be 987ppm. And then, it is assumed that the temperature distribution in the blanket is uniform. The results of simulation for \( \text{Li}_2\text{O}, \text{LiAlO}_2, \text{Li}_4\text{SiO}_4 \) and \( \text{Li}_2\text{ZrO}_3 \) are shown in figs 5.22~5.25, respectively. In the case of \( \text{Li}_2\text{O} \), the time taken to complete the consumption of \( \text{H}_2 \) in water formation at 700°C is the longest and about 18 hour (0.75day). On the other hand, in case of \( \text{LiAlO}_2, \text{Li}_4\text{SiO}_4 \) or \( \text{Li}_2\text{ZrO}_3 \), the time taken to complete the consumption of hydrogen at 500°C or 600°C is the longest. This behavior is due to the relation between the temperature dependence of the hydrogen oxidizing capacity and that of the reaction rate constant. In the case of \( \text{Li}_2\text{O} \), the activation energy of the hydrogen oxidizing capacity is twice as large as that of reaction rate constant. That
is to say, the difference between the hydrogen oxidizing capacity at 700°C and that at 500°C or 600°C is larger than that of reaction rate constant relatively. Accordingly, the time taken to complete the consumption of H₂ at 700°C is longer than that at 500°C or 600°C. In the case of LiAlO₂, Li₄SiO₄ or Li₂ZrO₃, the activation energy of the hydrogen oxidizing capacity is as large as or smaller than that of reaction rate constant. Accordingly, the time taken to complete the consumption of H₂ at 700°C is shorter than that at 500°C or 600°C. Figs. 5.26 and 5.27 show the change of hydrogen concentration in the outlet gas of the blanket using various blanket materials when the blanket temperature is 600°C and 700°C, respectively. The hydrogen oxidizing capacity is the largest in the case when Li₂ZrO₃ is used as the breeder material, but the time taken to complete the consumption of hydrogen is the longest in the case when Li₄SiO₄ is used. And then, it is known from figs. 5.4~5.7 that the curve of hydrogen concentration in the outlet gas of blanket is axisymmetry with the curve of water vapor concentration in the outlet of blanket at the line of which the ratio of (the outlet gas concentration) / (the inlet gas concentration of hydrogen) is to be 0.5. Therefore, the time taken to complete the release of water generated by oxidizing of hydrogen addition to sweep gas is about 2 weeks in the case of using of Li₄SiO₄ as the blanket material when the blanket temperature is 600°C. As the matter of fact, the time taken to complete the release of water may be longer than 2 weeks because of the influence of reverse reaction shown in eq.(5-11) and sorption or desorption behavior of generated water on the blanket material, especially when the low temperature parts are formed in the blanket. Table 5.13 shows comparison of the amount of water generated at the conditions of this simulation. The amount of water generated is the smallest in the case when LiAlO₂ is used as the blanket material. The amount of generated water simply averaged with time for LiAlO₂ or Li₄SiO₄ is smaller than that for Li₂O or Li₂ZrO₃. However, it is considered that these values are enough to affect the mass
transfer of tritium in the blanket, because the tritium generation rate is only 400g/day (67mol/day) at the blanket of the fusion reactor generating 1GW of electric output.

5.5 Conclusion

It was found that formation of water occurs in lithium ceramics bed at hydrogen addition to purge gas. And the amount of water generated and hydrogen consumed for various breeder materials were quantified. The values taken by both ways agree with each other and were not dependent on the partial pressure of hydrogen. Formation of non-stoichiometric compound of lithium ceramic is most possible.

The reaction rate constant in lithium ceramics bed was estimated from data obtained. The reaction in bed is the second order reaction that is the first order reaction for the concentration of hydrogen and for the concentration of activated point (oxygen) in bed, respectively.

The simulation of hydrogen consumption and water formation was carried out using the cylindrical blanket model. The total amount of water generated was the smallest in case when lithium aluminate was used as the breeder material.
Nomenclature

\( c \) : the concentration of hydrogen \([\text{mol/cm}^3]\)

\( c_0 \) : the inlet concentration of hydrogen \([\text{mol/cm}^3]\)

\( K \) : the equilibrium constant [-]

\( k \) : the reaction rate constant \([\text{cm}^3/\text{mol} \cdot \text{sec}]\)

\( P_{H_2} \) : the partial pressure of hydrogen \([\text{Pa}]\)

\( P_{H_2O} \) : the partial pressure of water vapor \([\text{Pa}]\)

\( q \) : the concentration of consumed activated point in bed \([\text{mol/cm}^3]\)

\( q_0 \) : the hydrogen oxidizing capacity in bed \([\text{mol/cm}^3]\)

\( R \) : gas constant \([\text{J/mol} \cdot \text{K}]\)

\( T \) : absolute temperature \([\text{K}]\)

\( t \) : time \([\text{sec}]\)

\( u \) : the superficial gas velocity \([\text{cm/sec}]\)

\( z \) : the axial distance \([\text{cm}]\)

\( \Delta G_f^0(\text{H}_2\text{O}) \) : the free energy of water \([\text{J/mol}]\)

\( \Delta G_f^0(\text{M} \text{O}_n) \) : the free energy of oxide \([\text{J/mol}]\)

\( \Delta G_r^0 \) : the difference of standard free energy of redox reaction \([\text{J/mol}]\)

\( \Delta_{\text{H}_2} \) : the amount of \( \text{H}_2 \) consumed \([\text{mol-}\text{H}_2/\text{mol-Li compound}]\)

\( \Delta_{\text{H}_2O} \) : the amount of water generated or

the hydrogen oxidizing capacity \([\text{mol-H}_2\text{O}/\text{mol-Li compound}]\)

\( \epsilon \) : the void fraction in the packed bed [-]
References

Table 5.1 The sample specification.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>2.023g/cm³</td>
</tr>
<tr>
<td>Density</td>
<td>1.62g/cm³ (80% T.D.)</td>
</tr>
<tr>
<td>Grain Size</td>
<td>10µm (diameter)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>12~16mesh</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>2.0m²/g</td>
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Table 5.2 The sample specification.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>LiAlO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>2.6g/cm$^3$</td>
</tr>
<tr>
<td>Density</td>
<td>2.21g/cm$^3$ (85% T.D.)</td>
</tr>
<tr>
<td>Grain Size</td>
<td>20µm (diameter)</td>
</tr>
<tr>
<td>Pellet Size</td>
<td>12~16mesh</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>0.29m$^2$/g</td>
</tr>
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</table>
Table 5.3 The sample specification.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_4$SiO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical Density</td>
<td>2.21g/cm$^3$</td>
</tr>
<tr>
<td>Density</td>
<td>1.88g/cm$^3$ (85% T.D.)</td>
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<tr>
<td>Grain Size</td>
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<td>Pellet Size</td>
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<td>BET Surface Area</td>
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Table 5.4  The sample specification.

<table>
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<tr>
<th>Sample Name</th>
<th>Li$_2$ZrO$_3$</th>
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<td>Density</td>
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Table 5.5  Neutron activation analysis of lithium compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li$_2$O</th>
<th>Li$_2$O used</th>
<th>LiAlO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
<td>7.2(0.7)</td>
<td>0.4(0.1)</td>
</tr>
<tr>
<td>Fe</td>
<td>7.6(4.9)</td>
<td>18.5(6.4)</td>
<td>9.9(3.6)</td>
</tr>
<tr>
<td>Co</td>
<td>0.03(0.02)</td>
<td>0.10(0.02)</td>
<td>0.05(0.02)</td>
</tr>
<tr>
<td>Zn</td>
<td>2.7(0.5)</td>
<td>5.2(0.6)</td>
<td>-</td>
</tr>
<tr>
<td>Se</td>
<td>0.4(0.1)</td>
<td>1.9(0.1)</td>
<td>0.8(0.1)</td>
</tr>
<tr>
<td>Sn</td>
<td>636.(30.)</td>
<td>616.(27.)</td>
<td>530.(20.)</td>
</tr>
<tr>
<td>Sb</td>
<td>-</td>
<td>0.06(0.02)</td>
<td>0.05(0.02)</td>
</tr>
<tr>
<td>Eu</td>
<td>-</td>
<td>0.02(0.002)</td>
<td>0.02(0.002)</td>
</tr>
<tr>
<td>Th</td>
<td>0.73(0.03)</td>
<td>0.51(0.02)</td>
<td>0.59(0.02)</td>
</tr>
<tr>
<td>Sc</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr</td>
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<td>-</td>
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<tr>
<td>Hf</td>
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</table>

All values are given in ppm. The values in the parentheses denote in standard deviations.
Table 5.6 Spectrographic analysis of Li$_2$ZrO$_3$.

<table>
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<tr>
<th>Element</th>
<th>Percentage</th>
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</thead>
<tbody>
<tr>
<td>Al</td>
<td>&lt;0.01%</td>
</tr>
<tr>
<td>Ca</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fe</td>
<td>0.04%</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ti</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Table 5.7 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>9.0–21.0g</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$</td>
<td>200–30000ppm in atmospheric pressure (20.3–3039Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>400–700°C (673–973K)</td>
</tr>
</tbody>
</table>
Table 5.8 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_2$ZrO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>10.0–21.0g</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$</td>
<td>200–1600ppm in atmospheric pressure (20.3–162Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>400–900°C</td>
</tr>
<tr>
<td></td>
<td>(673–1173K)</td>
</tr>
</tbody>
</table>
Table 5.9 Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>LiAlO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>12.25g</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$</td>
<td>257<del>1333ppm in atmospheric pressure (26</del>135Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>400~900°C</td>
</tr>
<tr>
<td></td>
<td>(673~1173K)</td>
</tr>
</tbody>
</table>
Table 5.10  Experimental conditions.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Li$_4$SiO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Packed bed weight of sample</td>
<td>10.38g</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>He</td>
</tr>
<tr>
<td>Volumetric gas velocity</td>
<td>0.4l/min</td>
</tr>
<tr>
<td>Concentration of H$_2$</td>
<td>723ppm in atmospheric pressure (73.2Pa)</td>
</tr>
<tr>
<td>Temperature of sample bed</td>
<td>700-900°C (973-1173K)</td>
</tr>
</tbody>
</table>
Table 5.11  Color of hydride.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Compound</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>(colorless)</td>
<td>CuH</td>
<td>reddish blown</td>
</tr>
<tr>
<td></td>
<td>smoke or</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>bluish gray</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrH1.54-1.63</td>
<td>metallic gray</td>
<td>MgH2</td>
<td>light gray</td>
</tr>
<tr>
<td>(δ-phase)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrH1.71-2.0</td>
<td>metallic gray</td>
<td>MgH</td>
<td>–</td>
</tr>
<tr>
<td>(ε-phase)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaH2</td>
<td>white</td>
<td>TiH1.63-2.0</td>
<td>metallic gray</td>
</tr>
<tr>
<td>CaH</td>
<td>–</td>
<td>TiH2</td>
<td>metallic gray</td>
</tr>
<tr>
<td>Shape of blanket</td>
<td>Cylindrical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Breeder material</td>
<td>Li$_2$O (80% T.D.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LiAlO$_2$ (85% T.D.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Li$_4$SiO$_4$ (85% T.D.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Li$_2$ZrO$_3$ (86% T.D.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weight of packed bed</td>
<td>600t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Void fraction of bed</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bed height</td>
<td>1.0m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Generation rate of tritium</td>
<td>67mol/day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Partial pressure of tritium</td>
<td>1.0Pa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sweep gas</td>
<td>Helium at 0.1MPa</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate</td>
<td>1.51×10$^5$m$^3$/day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H/T ratio</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature of blanket</td>
<td>uniform at 500, 600 or 700°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.13 The amount of water generated at the condition for the simulation.

<table>
<thead>
<tr>
<th>Blanket Temp. [°C]</th>
<th>( \text{Li}_2\text{O} ) (mol)</th>
<th>( \text{LiAIO}_2 ) (mol)</th>
<th>( \text{Li}_4\text{SiO}_4 ) (mol)</th>
<th>( \text{Li}_2\text{ZrO}_3 ) (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>86</td>
<td>201</td>
<td>80</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>2075</td>
<td>4150</td>
<td>252</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>4175</td>
<td>5567</td>
<td>629</td>
<td>943</td>
</tr>
<tr>
<td>600</td>
<td>2051</td>
<td>22</td>
<td>2051</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>4190</td>
<td>267</td>
<td>4190</td>
<td>267</td>
</tr>
<tr>
<td></td>
<td>7391</td>
<td>2173</td>
<td>7391</td>
<td>2173</td>
</tr>
<tr>
<td>700</td>
<td>1167</td>
<td>80</td>
<td>1167</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>8903</td>
<td>2775</td>
<td>8903</td>
<td>2775</td>
</tr>
<tr>
<td></td>
<td>19491</td>
<td>6755</td>
<td>19491</td>
<td>6755</td>
</tr>
</tbody>
</table>

The amount of water generated \([\text{mol-H}_2\text{O}]\)

The amount of water generated per unit day \([\text{mol-H}_2\text{O/day}]\)

Packed bed weight = 600tons

Tritium generation rate = 67mol/day
Temperature dependence of the equilibrium constant of various redox reaction (1).
Fig. 5.2  Temperature dependence of the equilibrium constant of various redox reaction (2).
Fig. 5.3 A schematic diagram of experimental apparatus.
Inlet conc. of H$_2$

Li$_2$O (80% T.D.) : 20.21 g
Inlet conc. of H$_2$ : 200 ppm
Temp. : 700 °C
Flow rate : 0.4 l/min

Fig. 5.4  An example of change of hydrogen and water concentration in the outlet gas of Li$_2$O bed with time.
Fig. 5.5 An example of change of hydrogen and water concentration in the outlet gas of Li$_2$ZrO$_3$ bed with time.

Li$_2$ZrO$_3$ (86% T.D.): 10.0g
Inlet conc. of H$_2$: 197ppm
Temp.: 900°C
Flow rate: 0.4l/min
LiAlO$_2$ (85\% T.D.) : 12.25 g  
Inlet conc. of H$_2$ : 550 ppm  
Temp. : 900 $^\circ$C  
Flow rate : 0.4 l/min

Fig. 5.6 An example of change of hydrogen and water concentration in the outlet gas of LiAlO$_2$ bed with time.
Fig. 5.7  An example of change of hydrogen and water concentration in the outlet gas of Li$_4$SiO$_4$ bed with time.
Fig. 5.8  The amount of water generated and H₂ consumed in Li₂O bed at H₂ addition to purge gas.

\[ \Delta \text{H}_2 = 9.36 \times 10^{-2} \exp \left( -\frac{49400}{RT} \right) \]
Fig. 5.9 The change of water concentration in the outlet gas of Li₂O bed at 973K under various partial pressure of H₂.
Fig. 5.10: The amount of water generated and H₂ consumed in Li₂ZrO₃ bed at H₂ addition to purge gas at various temperatures.

$\Delta H_{2O} \text{ [mol-H₂O/mol-Li₂ZrO₃]}$

$\Delta H_{2} \text{ [mol-H₂/mol-Li₂ZrO₃]}$
Fig. 5.11  The hydrogen concentration dependency of the amount of water generated in Li$_2$ZrO$_3$ bed.
Fig. 5.12 The amount of water generated and H₂ consumed in LiAlO₂ bed at H₂ addition to purge gas at various temperature.
Fig. 5.13 The hydrogen concentration dependency of the amount of water generated in LiAlO₂ bed.
Fig. 5.14 The amount of water generated and H₂ consumed in Li₄SiO₄ bed at H₂ addition to purge gas.
Fig. 5.15  The comparison of hydrogen oxidizing capacity among various breeder materials.
Fig. 5.16  The comparison of the changes of water concentration in the outlet gas of Li$_2$ZrO$_3$ bed at 1073K.

- 229 -
Li$_2$O (80%T.D.) : 20.21 g
Inlet conc. of H$_2$ : 200 ppm
Temp. : 700 °C
Flow rate : 0.4 l/min
Rate constant : $1.5 \times 10^4$ cm$^3$/mol·sec

Fig. 5.17 An example of curve fitting for response curve of hydrogen of Li$_2$O.
An example of curve fitting for response curve of hydrogen of Li$_2$ZrO$_3$.

Li$_2$ZrO$_3$ (86\% T.D.): 10.0 g
Inlet Conc. of H$_2$: 197 ppm
Temp.: 900 °C
Flow Rate: 0.4 l/min
Rate Constant: $3.5 \times 10^5$ cm$^3$/mol•sec
Fig. 5.19 An example of curve fitting for response curve of hydrogen of LiAlO₂.

LiAlO₂ (85% T.D.) : 12.25
Inlet conc. of H₂ : 1377 ppm
Temp. : 900 °C
Flow rate : 0.4 l/min
Rate constant : $1.0 \times 10^4 \text{ cm}^3$
Fig. 5.20 An example of curve fitting for response curve of hydrogen of Li$_4$SiO$_4$.
Fig. 5.21  The reaction rate constant of various breeder materials.

\[ k = 7.9 \times 10^{11} \exp \left( \frac{-148900}{RT} \right) \]

\[ k = 6.9 \times 10^{11} \exp \left( \frac{-165100}{RT} \right) \]
Fig. 5.22 Results of simulation for Li$_2$O.

- Blanket: Li$_2$O (80% T.D.)
- Bed weight: 600 t
- Bed height: 1.0 m
- Radius of blanket: 15.36 m
- Void fraction of bed: 0.5
- Flow rate of sweep gas: $1.51 \times 10^5$ m$^3$/day
- Inlet conc. of H$_2$: 987 ppm
- Temp. of blanket:
  - --- 700 °C
  - -- 600 °C
  - ---- 500 °C
Fig. 5.23 Results of simulation for LiAlO₂.

- Blanket: LiAlO₂ (85% T.D.)
- Bed weight: 600 t
- Bed height: 1.0 m
- Radius of blanket: 13.15 m
- Void fraction of bed: 0.5
- Flow rate of sweep gas: $1.51 \times 10^5$ m$^3$/day
- Inlet conc. of H₂: 987 ppm
- Temp. of blanket: 700 °C (---), 600 °C (--), 500 °C (----)
Blanket : Li₄SiO₄ (85% T.D.)
Bed weight : 600 t
Bed height : 1.0 m
Radius of blanket : 14.26 m
Void fraction of bed : 0.5
Flow rate of sweep gas : 1.51×10⁵ m³/day
Inlet conc. of H₂ : 987 ppm
Temp. of blanket : 700 °C

--- 600 °C
----- 500 °C

Fig. 5.24 Results of simulation for Li₄SiO₄.
Fig. 5.25 Results of simulation for Li$_2$ZrO$_3$. 

- Blanket: Li$_2$ZrO$_3$ (86\% T.D.)
- Bed weight: 600 t
- Bed height: 1.0 m
- Radius of blanket: 10.35 m
- Void fraction of bed: 0.5
- Flow rate of sweep gas: $1.51 \times 10^5$ m$^3$/day
- Inlet conc. of H$_2$: 987 ppm
- Temp. of blanket:
  - 700 °C
  - 600 °C
  - 500 °C

$C_{out}/C_{in}$ [-]

Time [day]
The comparison of results of simulation at 600°C among various breeder materials.

**Fig. 5.26**

- **Bed weight**: 600 t
- **Bed height**: 1.0 m
- **Void fraction of bed**: 0.5
- **Flow rate of sweep gas**: \(1.51 \times 10^5 \text{ cm}^3/\text{mol} \cdot \text{sec}\)
- **Inlet conc. of H2**: 987 ppm
- **Temp. of blanket**: 600°C
- **Blanket mater.**:
  - Li2O
  - LiAlO2
  - Li4SiO4
  - Li2ZrO3
Bed weight : 600 t
Bed height : 1.0m
Void fraction of bed : 0.5
Flow rate of sweep gas
: $1.51 \times 10^4 \text{ cm}^3/\text{mol} \cdot \text{sec}$
Inlet conc. of H2 : 987 ppm
Temp. of blanket : 700°C

Li2O

LiAlO2

Li4SiO4

Li2ZrO3

Fig.5.27 The comparison of results of simulation at 700°C among various breeder materials.
6. Estimation of Lithium Ceramics as The Tritium Breeding Blanket Material from The View Point of Tritium Recovery

6.1 Introduction

As mentioned in chapter 1, the data related to the solid breeder material for discussion from the view point of tritium recovery is in shortage. Consequently, the selection of the breeder material is inclined to be carried out basing only the tritium breeding performance. However, if bred tritium in the blanket can not be recovered effectively, the fuel self supplying system of a D-T fusion reactor is not completed even though tritium breeding performance of the breeder material is good. Accordingly, present author has accumulated the data related to the solid breeder material from the view point of tritium recovery. Estimation of performances of breeder materials from the view point of tritium recovery is carried out using data obtained in this study.

6.2 Performance of breeder materials

Table 6.1 shows the performances of breeder materials from the view point of tritium recovery.

6.2.1 Tritium breeding ratio

Tritium breeding ratio (TBR) shown in table 6.1 means the number of tritium generated by one fusion neutron. The comparison of tritium breeding performance should be carried out using the effective tritium breeding ratio defined in chapter 1. However, values of $T_{\text{leak}}$ or $T_{\text{decay}}$ dependent on the size of fusion reactor system and the amount of tritium inventory are not clear at present. Accordingly, estimation of tritium breeding performance of breeder candidate...
materials is carried out using values shown in table 6.1. \( \text{Li}_2\text{O} \) has a potential to give the largest tritium breeding ratio even if \( \text{Li}_2\text{O} \) made with natural lithium is used. However, when the neutron multiplier is used for all candidate materials, all candidate materials are expected to have a potential to give a fair tritium breeding ratio though enrichment of \( \text{Li}^6 \) is required at this time. Therefore, a candidate material showing good performances about tritium recovery is regarded to be the best.

### 6.2.2 Tritium inventory

In chapter 3, the comparison of tritium inventory due to sorption for various candidate materials has been shown. In case when \( \text{Li}_4\text{SiO}_4 \) is used as the breeder blanket material, tritium inventory due to sorption is possible to save at minimum value. Tritium inventory due to diffusion in the crystal grain is very small in comparison with that due to sorption. And then, present author pointed out that tritium diffusivity in the crystal grain is possible to be larger than the reported values at present in chapter 4 considering the effect of adsorption and the system effect. If this is the fact, tritium inventory due to diffusion in the crystal grain is possible to be smaller than that estimated in chapter 3. The ratio of tritium inventory to tritium inventory due to sorption for \( \text{Li}_2\text{O} \) at 600°C is compared in table 6.1 for various breeder materials when the estimation conditions in table 6.1 are equal to that in table 3.9. In case when \( \text{Li}_4\text{SiO}_4 \) is used as the breeder material, tritium inventory is possible to save at minimum value.

### 6.2.3 Lithium transfer

In chapter 2, the amount of lithium transfer for \( \text{Li}_2\text{O} \) was quantified. About the other candidate materials, quantification of lithium transfer was not carried out.
But the amount of lithium transfer for the other material is expected to be smaller than that for Li$_2$O, because LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ do not have corrosiveness like Li$_2$O as mentioned in chapter 3. In case when lithium in ceramics corrodes other materials, it is considered that the formation of lithium hydroxide is the main cause and LiOH is formed by reaction between lithium in ceramics and water. The reactivity of Li$_2$O with water is vary large in comparison with that of other candidate materials. For example, Li$_2$O dissolves in water and to be aqueous. Accordingly, the amount of Li transfer caused by formation of LiOH on LiAlO$_2$, Li$_4$SiO$_4$ or Li$_2$ZrO$_3$ can be expected to be smaller. However, the influence of Li transfer at LiAlO$_2$, Li$_4$SiO$_4$ or Li$_2$ZrO$_3$ on tritium recovery is not clear, because only a small Li transfer is observed for these blanket materials in this study.

6.2.4 Time to get steady state of tritium recovery

In case when only helium is used as the blanket sweep gas, time to get steady state of tritium recovery is larger than the case when sweep gas added with hydrogen or water vapor is used. In chapter 4, the over-all mass transfer capacity coefficients of water on LiAlO$_2$, Li$_4$SiO$_4$ and Li$_2$ZrO$_3$ are obtained. The mass transfer rate of water on LiAlO$_2$ is the smallest among various breeder candidate materials.

6.2.5 Effect of use of the sweep gas added with hydrogen

It have been clear from the results of the in-situ experiments that tritium release rate is enhanced by using sweep gas added with hydrogen. However, the present author found the water generation phenomenon in the solid breeder material bed at hydrogen addition to purge gas. The water generated by swamping
of hydrogen is possible to affect to the equilibrium state between gaseous tritium and oxide form tritium in the blanket, and is possible to increase the load on tritium recovering system. In chapter 5, the hydrogen oxidizing capacity and the reaction rate are quantified. The ratio of hydrogen oxidizing capacity to the amount of water generated for Li₂O at 600°C is compared in table 6.1. The estimation condition is that the blanket contains 70 tons of lithium and hydrogen concentration in sweep gas at the inlet of blanket is 987ppm in atmospheric pressure. The hydrogen oxidizing capacity of Li₂ZrO₃ is the largest among various breeder materials. The hydrogen oxidizing capacity under the irradiative condition is not clear, though discussion based on the defect arisen from irradiation is going to be applied by some authors.

6.2.6 Effect of use of the sweep gas added with water vapor

It have been clear from the results of in-situ experiments that tritium release rate is enhanced by using the sweep gas added with water vapor. This is because that the rate of isotope exchange reaction by water is larger than that by hydrogen. In case when Li₂O is used as breeder material, using of the sweep gas added with water vapor is infeasible due to increasing of lithium transfer. Accordingly, using the sweep gas of this type is effective for such materials as have small reactivity with water vapor, LiAlO₂, Li₄SiO₄ and Li₂ZrO₃.

6.2.7 Compatibility with other structural materials

As mentioned in chapter 1, construction of the blanket must be complex when solid breeder material is used for the blanket because of installing coolant pipings and neutron multiplying zones in the blanket. Accordingly, solid breeder material is required the good compatibility with other structural materials. Li₂O is the most
corrosive material among various solid breeder candidate materials because of formation of a fair amount of lithium hydroxide via reaction with water vapor, and it is impossible to avoid water formation from the solid breeder materials considered in this study.

6.3 Estimation of performances of solid breeder material

If lithium transfer problems can be solved, lithium oxide is the most probable for tritium breeding blanket. However, lithium orthosilicate, Li$_4$SiO$_4$, is considered to be most probable material as the tritium breeder blanket from the view point of tritium extraction and recovery at the present. The reasons are mentioned as follows;

(1) Lithium orthosilicate has the potential to give a fair tritium breeding ratio.
(2) Tritium inventory is possible to be saved at minimum value.
(3) Lithium transfer caused by formation of lithium hydroxide is possible to be smaller.
(4) Release rate of tritium is enhanced by using the sweep gas added with water vapor.

6.4 Subject for study on tritium recovery from solid breeder blanket

(1) Quantifying of the system effect is the most important theme and must be carried out immediately. The data related release behavior of tritium from the blanket obtained by in-situ experiment so far are possible to include the system effect and can not be the true data.

(2) Grasping of surface condition of breeder material is necessary to understand the transfer process of tritium in the pellet of breeder material. The transfer process of water in the pellet of breeder material is considered to be controlled by surface reaction and pore diffusion. However, the pore distribution, the diameter
of pore and so on are not still cleared.

(3) So far, the release behavior of tritium bred in blanket have been studied with the in-situ experiment based on the idea that the investigation of release behavior of tritium from the pellet under the condition of blanket for use is more realistic. Accordingly, reports about the release behavior of bred tritium incline to the discussion based on the data obtained by in-situ experiment. However, the strong point of the in-situ experiment is only the point that experiment can be carried out under the real blanket condition, though the amount of blanket material is too small compared with area of the piping surfaces. From the view point of accumulation of effective data, more simple and more flexible experiments useful to discuss the behavior of tritium at each mass transfer step excluding the system effect should be carried out.
Table 6.1 Performances of solid breeder blanket.

<table>
<thead>
<tr>
<th>Breeder Material</th>
<th>Li₂O</th>
<th>Li₄AlO₂</th>
<th>Li₄SiO₄</th>
<th>Li₂ZrO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tritium Breeding Ratio</td>
<td>1.08</td>
<td>0.9~1.0</td>
<td>0.9~1.0</td>
<td>0.93</td>
</tr>
<tr>
<td>with Multiplier and ⁶Li enrichment</td>
<td>1.2~1.3</td>
<td>1.05~1.12</td>
<td>1.05~1.12</td>
<td>?</td>
</tr>
<tr>
<td>Tritium Inventory ¹)</td>
<td>diffusion</td>
<td>sorption</td>
<td>diffusion</td>
<td>sorption</td>
</tr>
<tr>
<td>Blanket Temp.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>3.5x10⁻⁴</td>
<td>0.60</td>
<td>9.7x10⁻³</td>
<td>3.4</td>
</tr>
<tr>
<td>600°C</td>
<td>8.6x10⁻⁵</td>
<td>1.0</td>
<td>2.0x10⁻³</td>
<td>1.9</td>
</tr>
<tr>
<td>700°C</td>
<td>2.8x10⁻⁵</td>
<td>2.0</td>
<td>5.6x10⁻⁴</td>
<td>1.2</td>
</tr>
<tr>
<td>Li Transfer</td>
<td>yes</td>
<td>possible to be smaller</td>
<td>possible to be smaller</td>
<td>possible to be smaller</td>
</tr>
<tr>
<td>Time to get steady state</td>
<td>large</td>
<td>very large</td>
<td>large</td>
<td>large</td>
</tr>
<tr>
<td>H₂ addition to sweep gas</td>
<td>effective</td>
<td>effective</td>
<td>effective</td>
<td>effective</td>
</tr>
<tr>
<td>Water generation ²)</td>
<td>Blanket Temp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500°C</td>
<td>0.04</td>
<td>0.17</td>
<td>1.98</td>
<td>2.87</td>
</tr>
<tr>
<td>600°C</td>
<td>1.0</td>
<td>0.53</td>
<td>4.04</td>
<td>21.9</td>
</tr>
<tr>
<td>700°C</td>
<td>2.01</td>
<td>1.21</td>
<td>7.12</td>
<td>47.9</td>
</tr>
<tr>
<td>H₂O addition to sweep gas</td>
<td>not be used</td>
<td>effective</td>
<td>effective</td>
<td>effective</td>
</tr>
<tr>
<td>Compatibility with other structural materials</td>
<td>not good</td>
<td>fairly good</td>
<td>fairly good</td>
<td>fairly good</td>
</tr>
</tbody>
</table>

¹) The blanket is assumed to contain 70tons of lithium. Grain size of breeder material is 10μm. The partial pressure of tritiated water vapor in the blanket is 10Pa. Tritium inventory due to sorption for Li₂O at 600°C is 1.0.

²) The blanket is assumed to contain 70tons of lithium. Hydrogen concentration in sweep gas at the inlet of blanket is 987ppm. The amount of water generated for Li₂O at 600°C is 1.0.
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