TRITIUM TRANSPORT AND RELEASE FROM LITHIUM CERAMIC BREEDER MATERIALS

by

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Tritium Transport and Release from Lithium Ceramic Breeder Materials

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Abstract

In an operating fusion reactor, the tritium breeding blanket will reach a condition in which the tritium release rate equals the production rate. The tritium release rate must be fast enough that the tritium inventory in the blanket does not become excessive. Slow tritium release will result in a large tritium inventory, which is unacceptable from both economic and safety viewpoints. As a consequence, considerable effort has been devoted to understanding the tritium release mechanism from ceramic breeders and beryllium neutron multipliers through theoretical, laboratory, and in-reactor studies. This information is being applied to the development of models for predicting tritium release for various blanket operating conditions.

1. Introduction

The principle functions of a tritium breeder blanket in a fusion reactor are to convert the kinetic energy of the deuterium-tritium (DT) neutrons to recoverable heat and produce adequate tritium breeding to supply the tritium fuel requirement during the reactor lifetime as well as generate enough surplus tritium to start another reactor within a reasonable period of time. From the reactor design point of view, it is desirable to maximize the recoverable heat produced in the blanket which is defined as the energy deposited in the first wall, breeder, reflector, and plenum per fusion neutron. Another important function of the blanket is to perform as a part of the reactor bulk shield. While the blanket does perform many functions the critical feature is to recover the bred tritium so this fuel can be used to continue the process. The element lithium, in some form, appears to be the only material suitable for breeding tritium in a commercial fusion reactor. The most promising breeder materials are liquid lithium and lithium containing ceramics. This paper will focus on tritium behavior in lithium ceramics.
Tritium transport and release from a lithium ceramic tritium breeder material are complex processes involving diffusion in the grain, trapping, grain boundary diffusion, surface reactions, desorption, adsorption, and percolation in the gas phase. However, until recently, tritium release from ceramic materials was interpreted as either diffusion controlled [1,2] or desorption controlled [3,4]. The inappropriate use of diffusion models has led to a wide range of values for the diffusion coefficients for several candidate breeder materials. Care must be taken in applying a diffusion or desorption model to make certain that the data warrant using such a simple interpretation over the whole range of conditions. If a tritium breeding system undergoes changes, such as a change in temperature or purge gas composition, it may move from a regime where a simple diffusion model applies to a regime where desorption dominates to a regime where a simple diffusion or desorption model is inadequate. Our efforts have focused on developing a model that more effectively deals with changes in operating conditions and material characteristics.

2. Results and Discussion

A. Mathematical Background

The mathematical basis for understanding tritium transport in a lithium ceramic (thought of as a spherical grain), is analogous to that for heat conduction in a sphere. Of particular interest is the problem for heat conduction in a sphere with the radiation boundary condition. The solution to this problem is known [5]. The boundary condition is given by

\[ J = H(V - V_o), \]  

where \( J \) = Flux of tritium, \( H \) = heat transfer coefficient, \( V \) = temperature of sphere, and \( V_o \) = temperature of the surrounding media, and is very similar to that describing desorption from a surface

\[ J = K_{des} C_s - K_{ads} C_o, \]  

where \( J \) = flux, \( K_{des} \) = desorption rate constant, \( K_{ads} \) = adsorption rate constant, \( C_s \) = surface concentration, and \( C_o \) = concentration in the gas phase. The problem is simplified by taking the reference state (\( V_o \) or \( C_o \)) as zero and converting the surface concentration, \( C_s \), to a volume concentration. A new desorption rate constant \( K_d \) is defined as \( K_{des} \) times the effective surface layer times the ratio of the surface area of the sample to the surface area of the grains. This converts the problem of desorption from the surface of the sample into the gas pores to the easier problem of desorption from the surface of the grains. Making the following substitutions in the solution provided by Carslaw and Jaeger [5] to the heat conduction problem leads to the solution for the tritium concentration in the grain as a function of the grain size and time:

\[ C = V, \ G/D = A_o/K, \ D = \kappa. \]  

Definitions for all symbols are given in the appendix.
\[ C = \frac{G}{6hD}[h(a^2 - r^2) + 2a] - \frac{2h^2G}{rD} \sum_{n=1}^{\infty} \frac{\sin(r\alpha_n)\exp(-D\alpha_n^2t)}{\alpha_n^2[a^2\alpha_n^2 + ah(ah - 1)]\sin(a\alpha_n)} \]  

(3)

Taking \( C_0 \) equal to zero is equivalent to assuming that the gas phase concentration above the surface is zero. This is believed to be a good first approximation since the gas phase diffusion is orders of magnitude more rapid than diffusion in the bulk. Since desorption from the surface is, in this model, believed to be the same magnitude as bulk diffusion, gas phase diffusion will also be orders of magnitude more rapid than desorption. The tritium release rate by desorption, \( R_t \), is the effective desorption rate constant, \( K_d \), times the tritium concentration evaluated at the surface \( (r = a) \) and is given by

\[ R_t = \frac{Ga}{3} - 2h^2aG \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2t)}{\alpha_n^2[a^2\alpha_n^2 + ah(ah - 1)]} \]  

(4)

For a system that undergoes a change in temperature, the boundary conditions are changed due to the Arrhenius behavior of the desorption rate constant. The initial concentration profile after the temperature is that given by eq. (3). Using this concentration profile for the initial condition and solving the differential equations governing tritium diffusion in a grain with surface desorption provides the following solution for the tritium release rate after a temperature change.

\[ R_t = (1 - \frac{3}{Ga} K_d C_t)[(\frac{Ga}{3} - 2h^2aG \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2nt)}{\alpha_n^2[a^2\alpha_n^2 + ah(ah - 1)]}) + K_d C_t] \]  

(5)

B. Theoretical Studies

The solid state defect structure of the lithium ceramic (lithium vacancy, defects, traps, etc.) can strongly influence the tritium transport and release process. The origin of the lithium vacancy \( (V_{Li}) \) can arise from: (1) the \( ^6\text{Li}(n,a)^3\text{H} \) reaction, which generates many defects in transforming \(^6\text{Li}\) into \(^3\text{H}\) and \(^4\text{He}\) atoms; (2) defects created by displacement damage, i.e., fast neutron scattering and recoil of energetic \(^3\text{H}\) and \(^4\text{He}\) atoms; (3) the extrinsic impurity-induced defects that control lithium diffusion, and (4) the intrinsic defects due to thermal equilibrium. We find that tritium release is controlled primarily by two processes: bulk diffusion in the grains and desorption from the grain surface. Also, hydrogen in the helium purge gas is known to promote the release of tritium from candidate lithium ceramic breeder materials.
To better understand the role of hydrogen in the release process, calculations have been initiated to directly simulate the processes through which hydrogen can interact with lithium oxide surfaces. The methods that have been employed include a combination of ab-initio techniques in both crystalline and cluster environments. The method uses no adjustable parameters and may more accurately be described as computer experiments rather than calculations. Initially, attention is being given to examination of the interaction of the hydrogen molecule with the lithium oxide surface [6,7]. The nature of the surface sites that may participate in the adsorption process are described in terms of Terrace-Ledge-Kink (TLK) terminology. Terrace sites are associated with the regular planar locations on the flat atomic surfaces, and kinks with the corners. The terrace sites have been examined and found to be energetically unfavorable with respect to hydrogen adsorption because of their relatively high coordination and, therefore, the small number of unsaturated bonds surrounding the sites. Early simulations suggest that hydrogen undergoes dissociative chemisorption to low coordination sites.

The concepts outlined above have been developed into computer models [8-14] that include the phenomena of bulk diffusion and desorption from the grain surface [8], bulk and grain boundary diffusion, desorption and solubility [9-13], and tritium transport through open porosity [9,14]. Surface heterogeneity was modeled using surface sites with different activation energies for tritium desorption [15]. Some success has been achieved in modeling tritium transport and release by assuming only diffusion and desorption processes [8,15]. The desorption activation energy may change with surface coverage because of the existence of multiple sites for adsorption [15]. At high surface coverage, both low and high energy sites will be occupied. However, it is not necessary to have different sites of adsorption for the desorption activation energy to be surface coverage dependent. The measured desorption activation energy may be due to interactions between adsorbed molecules on the surface. The interaction between the adsorbed hydrogen species (OH\(^-\) or H\(^+\)) will affect the binding energy to the surface and, therefore, the desorption activation energy. While the computer model still needs further refinement, it can predict tritium inventory for end-of-life experiments. However, as yet, it cannot accurately predict tritium release curves from in-pile experiments over the length of an experiment.

C. Laboratory Studies

Tritium release experiments were performed in various laboratories for Li\(_2\)O [16,17], LiAlO\(_2\) [18], Li\(_4\)SiO\(_4\) [19], Li\(_2\)ZrO\(_3\) [20,21], and Li\(_2\)TiO\(_3\) [22]. These experiments have focused on determining the tritium extraction parameters, identifying the chemical form of the released tritium, and characterizing the rate-limiting process. For some materials, the tritium release rates have shown significant variance under test conditions. The reason for these variances is not fully understood but may involve any, or all, of the following: poorly controlled experimental conditions, different sample characteristics, or unknown mechanistic effects. What has been understood is that surfaces play an extremely important role in the tritium release process. Studies [17] have demonstrated that limiting mechanisms are very dependent upon grain size in that
desorption is limiting for small grain materials (<200um dia) and diffusion is limiting for large grain materials (>2000 um dia). Desorption has been determined to be the rate-limiting step in several cases [23,24].

Adsorption / desorption experiments of water or hydrogen on lithium ceramics have examined the surface release mechanisms. Experimental data on water desorption from LiAlO$_2$ and Li$_4$SiO$_4$ have been analyzed [25] and it was concluded that the process involved multiple desorption sites exhibiting different activation energies. The desorption of water from LiAlO$_2$ has been studied and sites with different activation energies have been identified [26,27]. Studies [28-30] using FTIR spectroscopy have reported several different OH (OD) species on a lithium oxide surface and identified surface exchange reactions using hydrogen isotopes. HT and HTO were the chemical forms of the desorbed tritium; the fraction of HT increased with increasing hydrogen concentration in the helium sweep gas. The reaction rate for HT release was proportional to the residual tritium concentration and to the square root of the hydrogen concentration. This implies that the dissociation of hydrogen occurs on the ceramic surface, in agreement with the above theoretical calculations.

D. In-reactor Experiments

In-reactor experiments combine the effects of neutrons, temperature, and purge gas chemistry in a single test. To date, tritium release experiments have been conducted for the candidate materials: Li$_2$O [31,32], LiAlO$_2$ [31,33], Li$_2$ZrO$_3$ [31,33-35], and Li$_4$SiO$_4$ [28,31]. One of the capsules in the BEATRIX II experiment [32] contained an Li$_2$O ceramic pellet stack experiencing a large temperature gradient that provided valuable engineering performance data. In the in-situ tritium release experiments, tritium residence times of one day were found in helium with 0.1% H$_2$ purge gas at ~310-320°C for Li$_2$O and Li$_2$ZrO$_3$, 390°C for Li$_4$SiO$_4$, and ~450°C for LiAlO$_2$. The chemical form of the tritium collected downstream was both HT and HTO, the fraction of each depending on the oxygen potential of the system. Tritium diffusion in the grain was measured for some of the ceramic breeders. Tritium diffusivity in the grain boundary was also estimated [37,38]. In most experiments tritium release was not controlled by bulk diffusion, but rather by desorption. Recent experiments [39,40] have shown that desorption is a first-order reaction, and the activation energy for desorption depends on surface coverage. The surface reaction was also studied by varying the H$_2$ pressure. A one-half power dependence of the surface desorption rate constant for single-crystal Li$_2$O and unity power dependence for sintered Li$_2$O pellets has been reported [41]. Tritium inventories were measured at the end-of-life for several experiments and found to be well within current safety design criteria.

E. Testing of the Mathematical Model

Several experiments have been used to test the diffusion/desorption hypothesis contained in the mathematical models. These include: tritium release experiments coupled with sample sectioning to determine concentration profiles within the samples [24], experiments studying grain size-tritium release correlations [17], and...
experiments investigating the effects of different purge gas compositions [17,41]. These studies have demonstrated the importance of surface processes in the release process and have been used to test individual aspects of the model.

In-pile tritium recovery experiments have investigated the effects of tritium generation rate, microstructure of the ceramic, composition of the purge gas, and temperature on tritium release kinetics [42]. The results have led to a qualitative understanding of the dependence of tritium inventory and release on these factors. However, a detailed interpretation of the results leading to an understanding of the rate controlling mechanisms is not always straightforward. The diffusion-desorption model described above treats desorption as pseudo first order in tritium and generally considers desorption occurring with a single activation energy. Other work has suggested that the desorption step is second order in tritium or that the desorption may be occurring with different activation energies [43]. The tritium residence time (defined here as the ratio of the tritium inventory to the tritium generation rate) is a convenient indicator of the release kinetics. The tritium residence time should be independent of the tritium generation rate if a diffusion or first order desorption mechanism is the rate controlling step while the tritium residence time will be dependent on the generation rate if a second order desorption mechanism is rate controlling.

In an effort to clarify the kinetic order of the desorption reaction, tests were performed with different neutron fluxes and therefore, different tritium generation rates. For a desorption mechanism which is first order in tritium, the tritium residence time will be independent of the generation rate while for a desorption mechanism which is second order in tritium, the tritium residence time will be inversely proportional to the square root of the generation rate. Transient temperature changes were performed on orthosilicate samples with He + 0.1% H₂ as the purge gas for two thermal neutron fluxes of 0.4 and 0.93 x 10¹⁷ n/m²s. The residence times obtained are shown in Table 1. Within experimental error, the values at a given temperature are identical for the two fluxes indicating that the rate determining step is not second order in tritium. Other factors indicate that tritium desorption is rate controlling for these samples so we can conclude the desorption is first order in tritium under these conditions.

Table 1

<table>
<thead>
<tr>
<th>Neutron Flux 10¹⁷ n/m²s</th>
<th>Temperature °C</th>
<th>Tritium Residence Time, h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.93</td>
<td>450</td>
<td>17.5 &lt; τ &lt; 27</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>4 &lt; τ &lt; 4.2</td>
</tr>
<tr>
<td>0.40</td>
<td>450</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Tritium Residence Time (in hours) versus Thermal Neutron Flux for a Li₄SiO₄ Sample. Purge Gas was He + 0.1% H₂
The sample microstructure may also be a crucial factor affecting tritium release kinetics. For a diffusion mechanism the tritium residence time is given by:

$$t = a^2/15D$$  \hspace{1cm} (6)

and the inventory increases as the square of the grain radius. For a desorption mechanism, the tritium residence time is given by the sample volume divided by the product of the surface area times the desorption rate constant. For a sphere this leads to:

$$t = a/3h$$  \hspace{1cm} (7)

For other configurational geometry, an effective radius, $a^*$, defined as three times the ratio of the sample volume to the specific surface area, can be used to calculate the residence time. If desorption is the rate controlling mechanism, the residence time will be proportional to the effective radius.

The effect of sample microstructure on tritium inventory was examined in a temperature transient experiment in which there were samples of lithium aluminate of differing microstructure. These results indicated that tritium residence time decreased with decreasing grain size. It follows from equation (6) that for diffusion controlled release, the tritium residence time will increase in proportion to the square root of the grain size which means that a ratio of 600 is expected for tritium residence times of two samples with 6 and 0.15 \( \mu \)m grain sizes. The observed ratios of >10.8 at 670°C, 16.3 at 620°C >26.6 at 560°C, and >14.4 at 510°C are much lower indicating that diffusion is not rate limiting for these temperatures and grain sizes. Likewise, if the desorption rate is limiting, the tritium residence time will increase in proportion to the effective grain radius calculated from the specific surface area which means that a ratio of 13.3 is expected for the tritium residence times of the two samples with 6 and 0.45 \( \mu \)m effective grain radii. The observed values are of the same order of magnitude as expected for the desorption controlled release suggesting that desorption is the controlling factor determining tritium residence time. Any variation from the expected ratios suggests other processes may be playing a role in determining the tritium residence time.

The surface processes, desorption of tritium or tritiated water, are influenced by the purge gas chemistry. It has been shown repeatedly that the addition of hydrogen to the purge gas improves the tritium release rate [31,44,45]. What is also hard to separate from the purge gas composition effect is the flow rate past the sample. There is certainly a minimum flow below which tritiated species are not carried away from the sample. However, there is a broad range of flow rates at which tritium is removed as quickly as it is generated, a truly steady state condition. Also, the composition of the purge gas has been demonstrated to have a substantial effect on the tritium residence time. It is reasonable to think that the surface processes are influenced by the purge gas chemistry. However, the bulk properties may also be affected by the purge gas. For example, water addition to the purge gas may be expected to increase the desorption of tritium from the surface. Addition of water to the
purge gas may also lead to a hydrogen concentration in the bulk which exceeds the solubility limit, causing the precipitation of a second phase of LiOH/LiOT, thereby changing the bulk properties including diffusivity.

The importance of temperature was assessed in a series of temperature transient experiments. Generally the tritium inventory and the tritium time constant decreases with increasing temperature. For a pure first order desorption process or a pure diffusion process, the time constant is independent of the previous temperatures while for a second order desorption process, the time constant will depend on the previous temperature. In the case of mixed diffusion-desorption, the mathematics are less straightforward and it is not obvious whether the time constant is dependent on or independent of the previous conditions. However, it does appear that for the mixed diffusion-desorption regime the time constant is dependent on the previous conditions, but as the ratio $\alpha h/D$ increases toward diffusion controlled release or decreases toward desorption controlled release this dependence disappears. This suggests that tritium release is in the mixed diffusion-desorption regime at the temperature when the time constant for temperature increases and temperature decreases are unequal or desorption is second order in tritium.

For tests of the integrated model, we have looked at comparison of model predictions with results from in-pile tests. Model predictions for the inventory at the end-of-life tests are in general agreement with the observed tritium inventory [46,47]. Time dependent behavior can be accurately modeled for some individual temperature change tests, however, correlations between the predicted and observed time dependence of tritium release for temperature transients over the duration of the experiment are not as good. The agreement between model predictions and the measured tritium inventory at end-of-life suggest that we have correctly stated the fundamental basis of the model, but the inability of the present models to predict all the time dependent tritium release behavior suggests that some critical details are still missing.

F. Tritium Release from Beryllium Multiplier

Current ceramic breeder blanket designs include beryllium for neutron multiplication. Small quantities of tritium are generated in the beryllium via a $^9\text{Be}$ neutron reaction producing tritium and helium. Because the buildup of the tritium could become a safety issue, there is strong interest in tritium removal. Initial tritium release studies on beryllium have been on material that has served as a reflector in a nuclear reactor. Generally, these reflector materials have remained in place for several years at low temperature, e.g., <100°C. When these reflector materials have been examined under isothermal anneal conditions, they have exhibited burst release of tritium at high temperatures. Experiments on lower density beryllium show significant tritium release at lower temperatures. Anneals of high density (~100% TD) beryllium discs from the SIBELIUS experiment [48,49] have shown that the bulk of the generated tritium was retained in the beryllium, and when the discs were heated to 650°C and above, the tritium was readily released. The results indicate that tritium release from the beryllium...
did not exhibit burst release behavior, as previously reported, but rather an orderly release dependent solely upon temperature. Generally, ~99% of the tritium was released by 850°C. In comparison with literature information on tritium release from ~100% dense beryllium, the SIBELIUS data for tritium release vs. temperature show a steeper slope. Also, the literature information shows that for lower density beryllium (80.9% TD), tritium release is considerably enhanced. Tritium release from the ceramic discs in the SIBELIUS experiment was quite similar to the behavior shown in other dynamic tritium release experiments on lithium ceramics.

3. Conclusion

Predictions of tritium release obtained from the diffusion-desorption model are in good agreement with observed tritium release from lithium ceramics with an average grain size of up to 100 μm. The diffusion-desorption model is a significant improvement over a pure diffusion model for predicting tritium release under pure helium purge gas. The diffusion-desorption model does not predict all the variations in the tritium release observed experimentally; however, it is a useful model and gives good prediction of tritium release over a wide range of temperature.

Appendix: List of Symbols

- \( a \) = grain radius
- \( r \) = radial distance
- \( C \) = tritium concentration
- \( C_1 \) = surface concentration of tritium before temperature change
- \( D \) = diffusivity
- \( K_d \) = effective desorption rate constant
- \( G \) = volume generation rate
- \( h \) = \( K_d/D \)
- \( R_t \) = tritium flux
- \( t \) = time
- \( \alpha_n \) = roots of \( a \alpha \cot(a \alpha) = 1 - ah \)
- \( I \) = steady state inventory
- \( H \) = heat transfer coefficient
- \( V \) = temperature of sphere
- \( V_o \) = temperature of surrounding media
- \( C_s \) = surface concentration
- \( C_o \) = concentration in the gas
- \( \kappa \) = thermal diffusivity
- \( K_{ads} \) = adsorption rate constant
- \( K_{des} \) = desorption rate constant
- \( K \) = \( \rho C_p \kappa \)
- \( \rho \) = density
- \( C_p \) = heat capacity
- \( A_o \) = heat production rate
4. References


