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**MODELING OF TRITIUM BEHAVIOR IN
CERAMIC BREEDER MATERIALS**

by

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ABSTRACT

Computer models are being developed to predict tritium release from candidate ceramic breeder materials for fusion reactors. Early models regarded the complex process of tritium release as being rate limited by a single slow step, usually taken to be tritium diffusion. These models were unable to explain much of the experimental data. We have developed a more comprehensive model which considers diffusion and desorption from the grain surface. In developing this model we found that it was necessary to include the details of the surface phenomena in order to explain the results from recent tritium release experiments. A diffusion-desorption model with a desorption activation energy which is dependent on the surface coverage was developed. This model provided excellent agreement with the results from the CRITIC tritium release experiment. Since evidence suggests that other ceramic breeder materials have desorption activation energies which are dependent on surface coverage, it is important that these variations in activation energy be included in a model for tritium release.

1. INTRODUCTION

Computer models are being developed to predict tritium behavior in candidate ceramic breeding materials for fusion reactors. Tritium transport and release from a solid tritium breeder material are complex processes

involving trapping, diffusion in the grain, diffusion in the grain boundary, surface reactions, desorption, adsorption, and percolation in the gas phase. Initially, most researchers assumed that diffusion in the grain would be the slowest of these processes and would control the tritium release.^{1,2,3} However, the use of a diffusion-controlled tritium release model has led to a wide range of values for the diffusion coefficients for several candidate breeder materials. This inability to obtain agreement for what should be constant values suggests that a process other than diffusion or a combination of two or more processes control the tritium release.

Additional tritium release experiments have given recognition to the need to consider desorption in the kinetics of tritium release.^{4,5} Desorption-controlled kinetics has been observed for some experiments; however, others clearly do not follow desorption-controlled release. It appears that a single mechanism for tritium release may be applicable over a limited range of experimental conditions. However, 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. As a ceramic breeder undergoes changes caused by a change in temperature or by a change in the purge gas composition, it may move from a regime dominated by diffusion to a regime dominated by desorption or to a regime where both diffusion and desorption determine the release. A more complex model of tritium release is needed.

We have developed a diffusion-desorption model for tritium release from a ceramic. This model is applicable over a range of conditions and is a significant improvement over the earlier diffusion models for tritium release

from ceramic materials in a pure helium purge stream. Good agreement has been obtained between experimental results and predictions made with our diffusion-desorption model. However, recent tritium release experiments have yielded some unexpected results which cannot be explained by our simple diffusion-desorption model. We have thus developed a more sophisticated model, which includes the details of the surface phenomena involved in the desorption process. This new model can account for the recent data and is consistent with earlier results.

2. THEORY

The models described herein consider diffusion in the grain and desorption as the rate-controlling mechanisms for tritium release from a ceramic breeder material. Grain boundary diffusion and permeation in the gas phase should be much more rapid than bulk diffusion and desorption at the temperatures involved. Trapping has only recently been observed to affect the tritium release from ceramic breeder materials and appears to be of concern only at low temperatures.⁶ Due to the scarcity of data concerning trapping, it is not being considered in the current models.

The problem of tritium transport in a spherical grain appears analogous to that for heat conduction in a sphere. Of particular interest to our application is the problem for heat conduction in a sphere with the radiation boundary condition. The solution to this problem is known.⁷ The boundary condition is given by

$$J = H(V - V_0) \tag{1}$$

and is very similar to that describing desorption from a surface

$$J = K_{des} C_s - K_{ads} C_0 \tag{2}$$

where

J = flux
 K_{des} = desorption rate constant
 K_{ads} = adsorption rate constant
 C_s = surface concentration
 C_o = concentration in the gas phase
 H = heat transfer coefficient
 V = temperature of sphere
 V_o = temperature of the surrounding media

(Definitions for these symbols and those in the remainder of the report are given in the Appendix.)

The problem is further simplified by taking the reference state (V_o or C_o) to be 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 surface thickness times the ratio of surface area in the sample to 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. The following substitutions were made in the solution provided by Carlsaw and Jaeger⁷ to the heat conduction problem:

$$C = V$$

$$G/D = A_o/K$$

$$D = \kappa$$

These substitutions lead to the solution for the tritium concentration in the grain as a function of the grain radius and time:

$$C = \frac{G}{8\pi D} \{h(a^2 - r^2) + 2a\} - \frac{2ha^2G}{rD} \sum_{n=1}^{\infty} \frac{\sin(ra_n) \exp(-Da_n^2 t)}{a_n^2 [a^2 a_n^2 + ah(ah-1)] \sin(aa_n)} \quad (3)$$

Taking C_o 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 is the effective desorption rate constant (K_d) times the tritium concentration evaluated at the surface ($r=a$) and is given by

$$R_t = \frac{Ga}{3} - 2h aG \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 [a^2 \alpha_n^2 + ah(ah-1)]} \quad (4)$$

R_t = tritium flux

The tritium flux predicted from equation (4) may be dominated by diffusion or desorption, depending on the temperature regime of the breeder material. A second variable, which also has a large effect on tritium release, is the sample grain radius. The dependence of the tritium flux predicted from a diffusion-desorption model on temperature and grain size was investigated for a sphere of Li_2O . The diffusional parameters used were those determined by Guggi et al.,⁸ and the desorption rate constant used was that observed by Okuno and Kudo.⁹

To determine whether diffusion or desorption dominates the tritium release under certain parameter ranges, we plotted the difference between the release calculated from a pure diffusion model and the diffusion-desorption model as a function of time and temperature for a given radius and as a function of time and grain radius at a given temperature. The grain size dependence of this difference is illustrated in Fig. 1 for 400°C and Fig. 2 for 500°C. As can be observed from the figures, the diffusion model overestimates the tritium release for short times for samples with a small grain radius. As the time increases and the release approaches steady-state release, the diffusion model and diffusion-desorption model approach the same

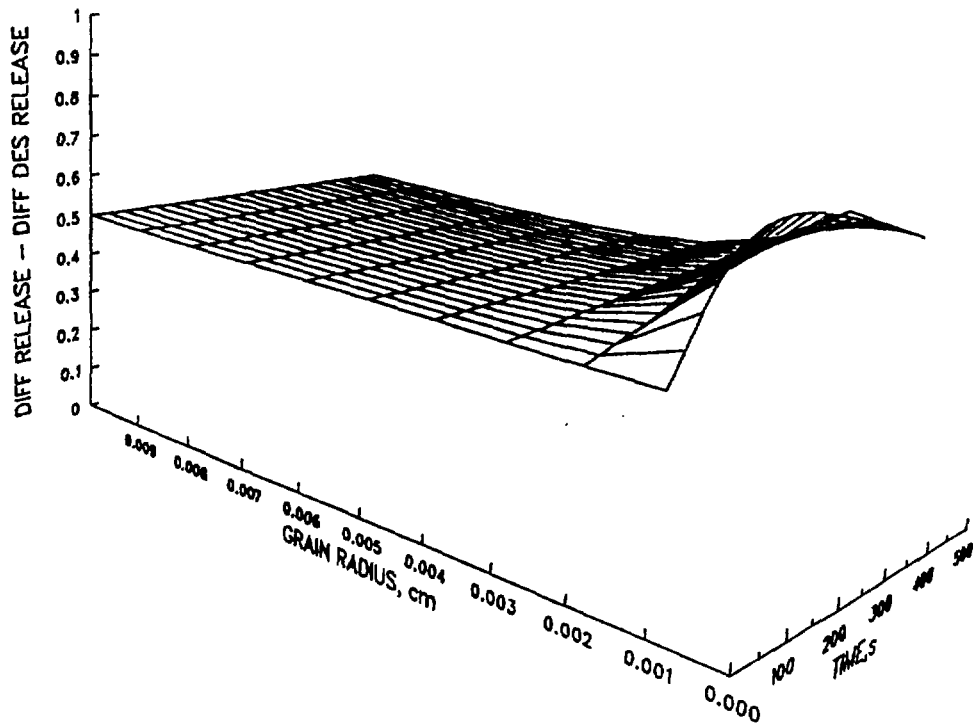


Fig. 1. Difference between Fractional Release Calculated Using a Diffusion Model and a Diffusion-Desorption Model as a Function of Time and Grain Radius for a Sample at 400°C.

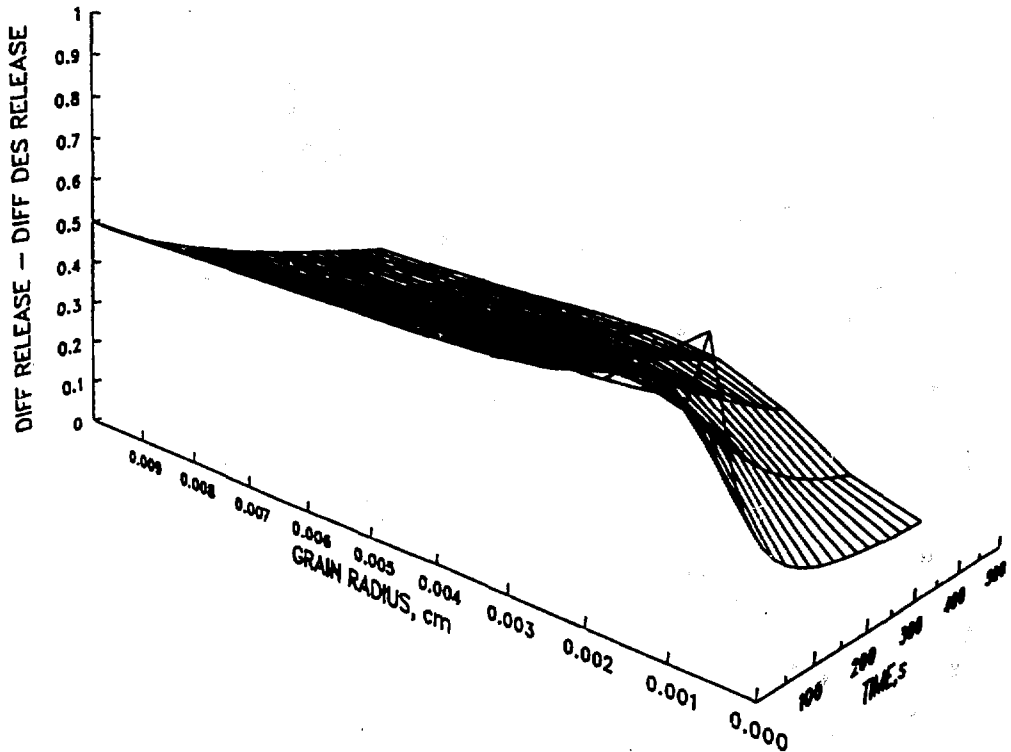


Fig. 2. Difference between Fractional Release Calculated Using a Diffusion Model and a Diffusion-Desorption Model as a Function of Time and Grain Radius for a Sample at 500°C.

value. The diffusion model overestimates the tritium release. The overestimation increases with time until a maximum is reached, then decreases as the release approaches steady state. This maximum difference between the results obtained with the diffusion model and diffusion-desorption model decreases with increasing grain size. This indicates that the rate-controlling mechanism is diffusion for large grains and desorption for small grains.

The temperature dependence of the difference plot of diffusional release and diffusion-desorption release for grains of 10 and 50 micron radii is shown in Figs. 3 and 4, respectively. For the 10 micron grain at low temperature, the diffusion model is a very poor approximation to the diffusion-desorption release. The overestimation increases with time until a maximum is reached, then decreases as steady state is approached. At higher temperatures, the diffusion model is a good approximation to the diffusion-desorption model, except at very short times. There are two distinct regions in this figure: the low-temperature region below 475°C, where the diffusion model does a poor job of estimating the diffusion-desorption release, and the high-temperature region above 500°C, where the diffusion model does a reasonable job of estimating the diffusion-desorption release. For a 50 micron grain, the diffusion time is longer and the diffusional model is a better approximation for the diffusion-desorption release at low temperature than for the 10 micron case. This indicates that tritium release is controlled by diffusion for high temperatures and large grains and by desorption for small grains and low temperature.

For a system which 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 change is that given by equation (3). Using this concentration profile for the initial

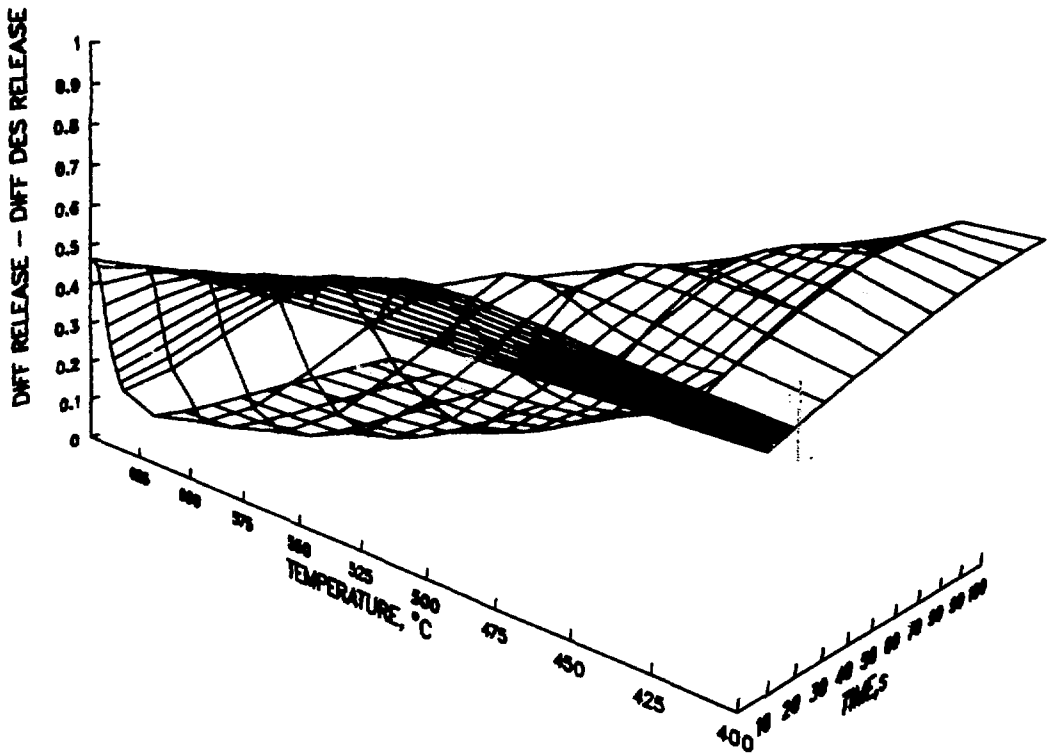


Fig. 3. Difference between Fractional Release Calculated Using a Diffusion Model and a Diffusion-Desorption Model as a Function of Time and Temperature for a 10 Micron Grain.

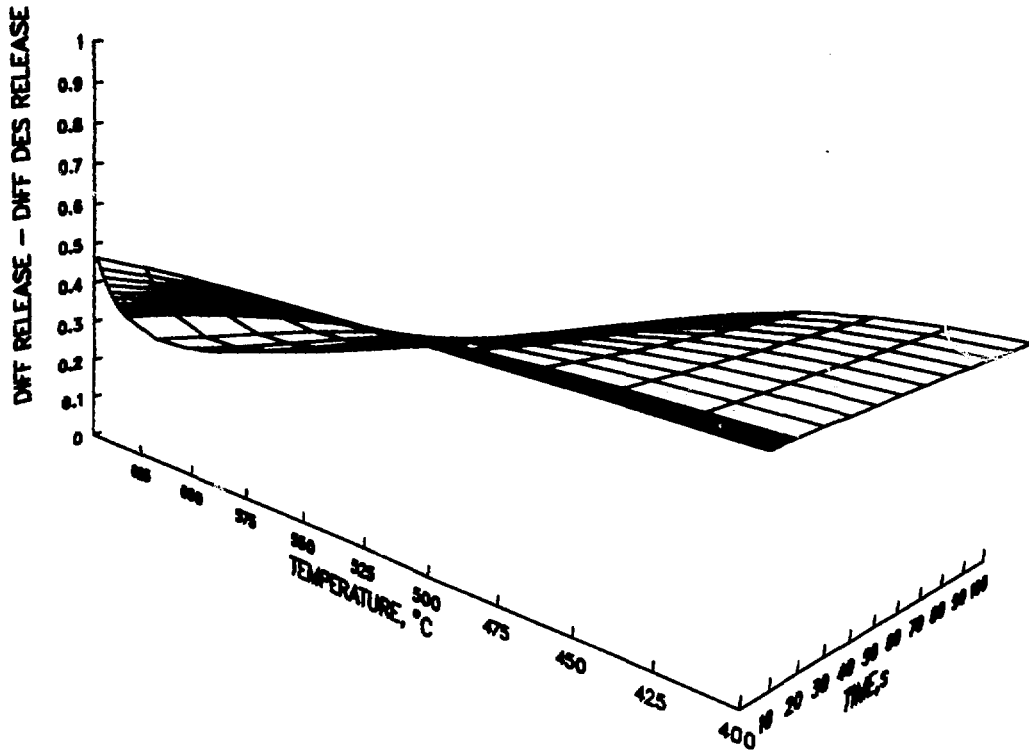


Fig. 4. Difference between Fractional Release Calculated Using a Diffusion Model and a Diffusion-Desorption Model as a Function of Time and Temperature for a 50 Micron Grain.

condition and solving the differential equations governing tritium diffusion in a grain with surface desorption yielded the following solution for the tritium flux after a temperature change:

$$R_t = \left(1 - \frac{3}{G_a} K_d C_1\right) \left(\frac{G_a}{3} - 2h a G \sum_{n=1}^{\infty} \frac{\exp(-D a_n^2 t)}{a_n^2 [a^2 a_n^2 + ah(ah-1)]} \right) + K_d C_1 \quad (5)$$

In arriving at equation (5), we assumed that the desorption rate constant follows a simple Arrhenius dependence. For many materials the desorption activation energy varies as a function of surface coverage. In this case, equation (5) would only be valid over regions where the desorption activation energy remained constant. To treat the cases where the desorption activation energy is a function of surface coverage, we employed the DISPL computer package¹⁰ to solve the set of partial differential equations which describe the tritium transport.

The effect that surface coverage has on the desorption activation energy can be understood by examining more closely the desorption process. In tritium release experiments what we regard as desorption is really two processes: (1) a surface reaction between tritium which has diffused to the surface as T⁺ and chemisorbed hydrogen to form surface bound HTO or HT and (2) desorption of the surface bound HTO or HT. These processes can be expressed as



The activation energy of either the surface reaction (1a or 1b) or the actual desorption of the physisorbed molecule (2a or 2b) may be dependent on the surface coverage. If there are two or more chemisorption sites for hydrogen on lithium oxide (e.g., H⁺ bound to an O on a normal O site, H⁺ bound to an O adjacent to a lithium vacancy), then at high surface coverage both the low

and high energy sites will be occupied. Reaction with T^+ at the surface will occur with the hydrogen which is least tightly bound to the surface, i.e., in the highest energy sites. At low surface coverage, the hydrogen will occupy the surface sites of lowest energy, and the high energy sites will be unoccupied. The T^+ must now react with a hydrogen which is more tightly bound to the surface, so the activation energy for the surface reaction will be higher than that for the high surface coverage case. Alternatively, it is not necessary to have different sites of adsorption for the desorption activation energy to be dependent on surface coverage. The surface coverage dependence of the activation energy may be due to interactions between the adsorbed molecules on the surface. Interactions between adsorbed hydrogen (as OH^- or H^-) will increase as the surface concentration of these species increases. The interaction between the adsorbed hydrogen will affect the binding energy of the hydrogen to the surface and, therefore, will affect the activation energy for the reaction with T^+ at the surface. In addition, interactions of adsorbed hydrogen with surface bound HT or HTO will increase as the surface concentration increases, leading to a possible surface coverage dependence of the activation energy for reactions 2a and 2b above.

3. RESULTS AND DISCUSSION

Equation (5) was applied to data for three samples of Li_2SiO_3 (P1, P3, and P5) and one sample of $LiAlO_2$ (P2) from the LISA experiment, an in situ tritium removal experiment.¹¹ The experimental temperature profiles were used as input, along with a characteristic grain size. Two characteristic grain sizes were used in the case of the silicate samples: the average grain radius and a volume-weighted average of the grain radii. This volume-weighted average was calculated as follows. The number of grains with a radius within

a given radial distribution was multiplied by the average volume for that distribution. This value was summed over the entire radial distribution, then divided by the total volume occupied by the grains. No radial distribution was available for the aluminate sample; thus the reported average grain radius was used.

The diffusion and desorption rate constants were assumed to have a simple Arrhenius temperature dependence, characterized by a temperature-independent preexponential term and an activation energy. Initially, the values for the diffusion preexponential and diffusion activation energy were obtained using a pure diffusion model and data from two sources: Werle et al.¹¹ (LISA experiment with hydrogen added to the purge gas) for LiAlO_2 , and Kudo and Okuno¹² for Li_2SiO_3 . Values of the desorption activation energy were varied between 75 and 145 kJ (18 and 35 kcal), characteristic values for chemisorption, and the best fit was obtained by varying the desorption preexponential and by making slight adjustments in the diffusion preexponential term. For samples P3 and P5 of Li_2SiO_3 , similar fits to the experimental data were obtained using either the average radii or the volume-weighted average radii. The best fits to the experimental data for Li_2SiO_3 samples P3 and P5 with pure helium purge gas and average radii of 51.4 and 97.3 microns, respectively, are shown in Figs. 5 and 6. The equations for the rate constants used in calculating the tritium release are shown on the graphs, with the activation energies given in units of kJ/mol. A good fit could not be obtained using the volume-weighted average radius for sample P1. The distribution of grain sizes for this sample showed a small number of grains with grain radii of over 250 microns.¹¹ The large volume of these grains means a few of them dominate the volume of the sample. In samples containing these very large grains, the use of the volume-weighted average radius as the characteristic radius is a

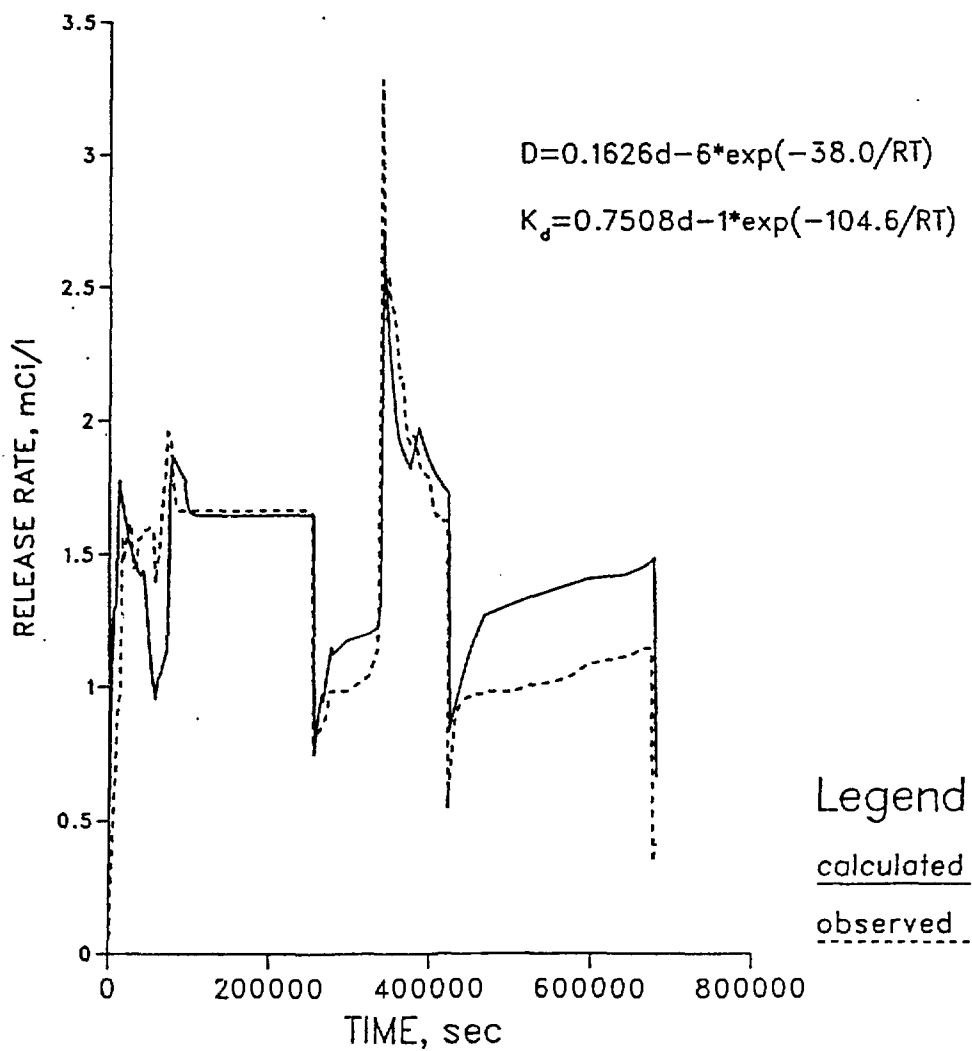


Fig. 5. Calculated and Observed Tritium Release from Metasilicate Sample P3. Activation energy (exponential term) given in kJ/mol.

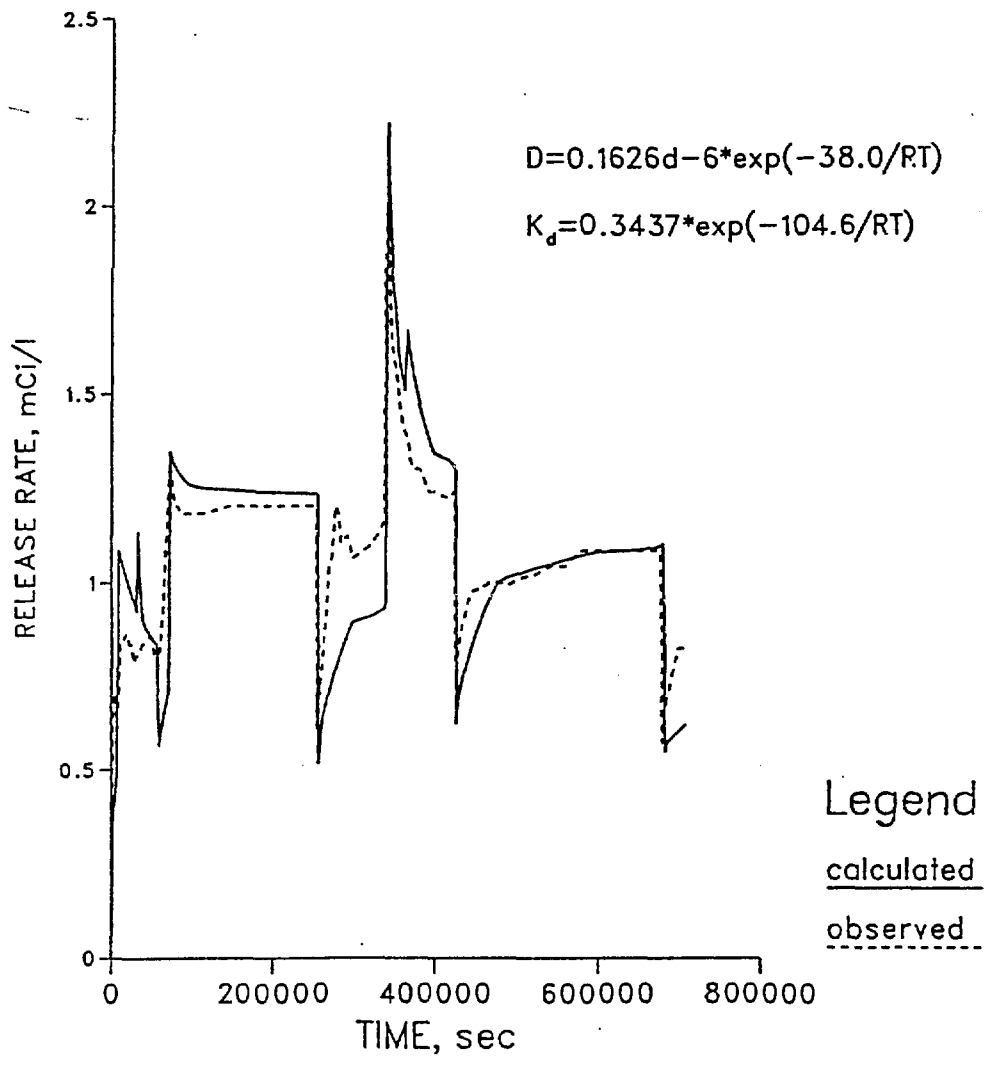


Fig. 6. Calculated and Observed Tritium Release from Metasilicate Sample P5. Activation energy (exponential term) given in kJ/mol.

poor choice. It results in an underestimation of the surface area of the grains. If a smaller effective grain radius of 97.3 microns is used (the volume-weighted average radius for sample P5, which was the same material as sample P1¹¹), the diffusion-desorption model does a good job of predicting the tritium release of sample P1. The fit obtained using the average grain radius for sample P1 was good (see Fig. 7). This suggests that the average grain radius is a better characteristic distance to use for the diffusion-desorption model than the volume-weighted average grain radius.

The temperature history of the samples was similar. They were initially brought up to temperature (650-700°C) with fluctuations in temperature occurring during the temperature increase. At approximately 250,000 sec, the temperature was decreased by ~50°, then increased by ~50° at 350,000 sec. At ~425,000 sec, the temperature was decreased by ~50°, and decreased again by ~50° at 700,000 sec. Sharp rises occur in the tritium release rate after a temperature increase, while a sharp drop occurs when the temperature falls.

The desorption activation energies for the Li_2SiO_3 samples are all about 105 kJ/mol (25 kcal/mol), a value in relatively good agreement with the desorption activation energy of HTO from lithium oxide of 120 kJ/mol (28.7 kcal/mol) found by Kudo and Okuno.¹³ The activation energy for Li_2SiO_3 is expected to vary slightly from that of Li_2O . The difference in the preexponentials is probably due to differences in the effective grain radius and surface characteristics of the samples.

The best fit obtained for the lithium aluminate sample is shown in Fig. 8. The activation energy of desorption used was 83.7 kJ/mol (20.0 kcal/mol), which is larger than the 61.5 kJ/mol observed by Fischer for LiAlO_2 .¹⁴ This discrepancy indicates that we did not use the true diffusion coefficients for LiAlO_2 or that we used an oversimplified equation for the

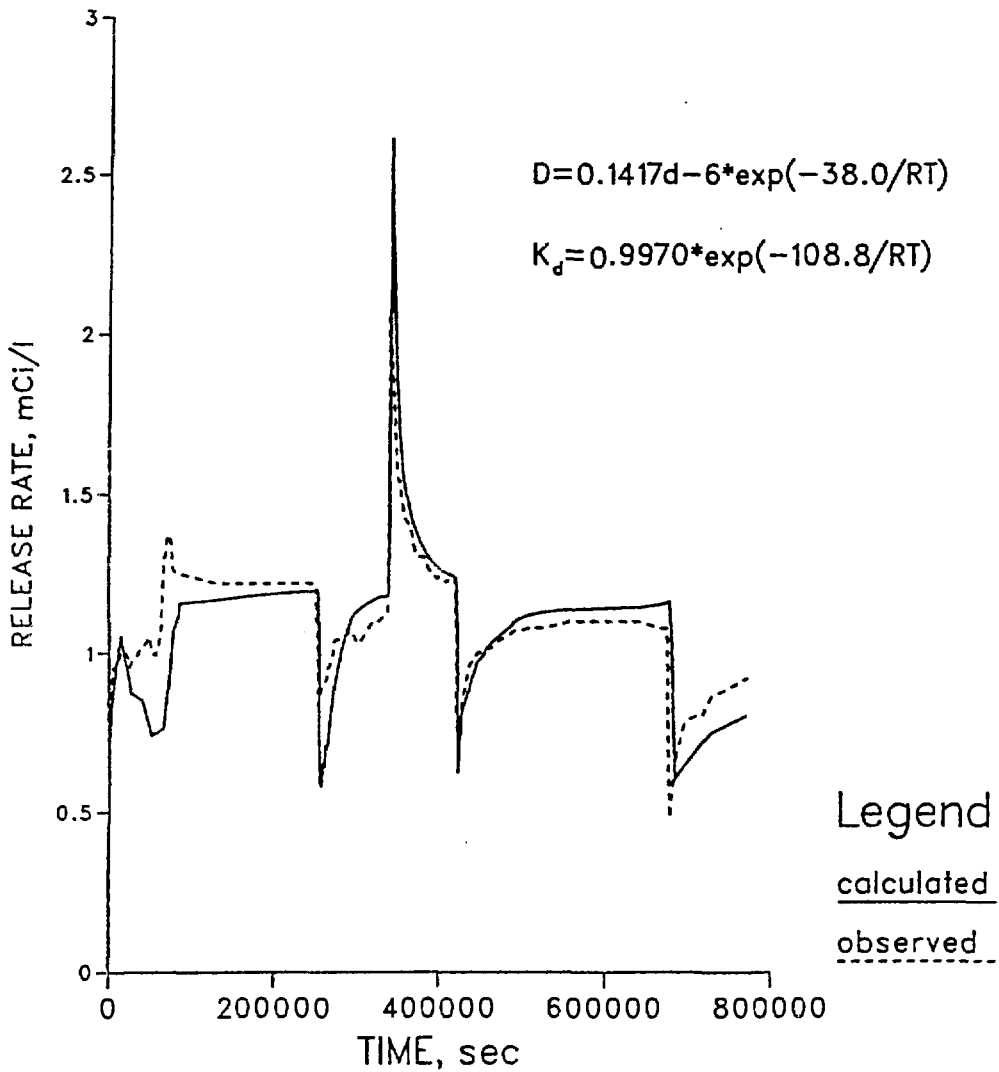


Fig. 7. Calculated and Observed Tritium Release from Metasilicate Sample P1. Activation energy (exponential term) given in kJ/mol.

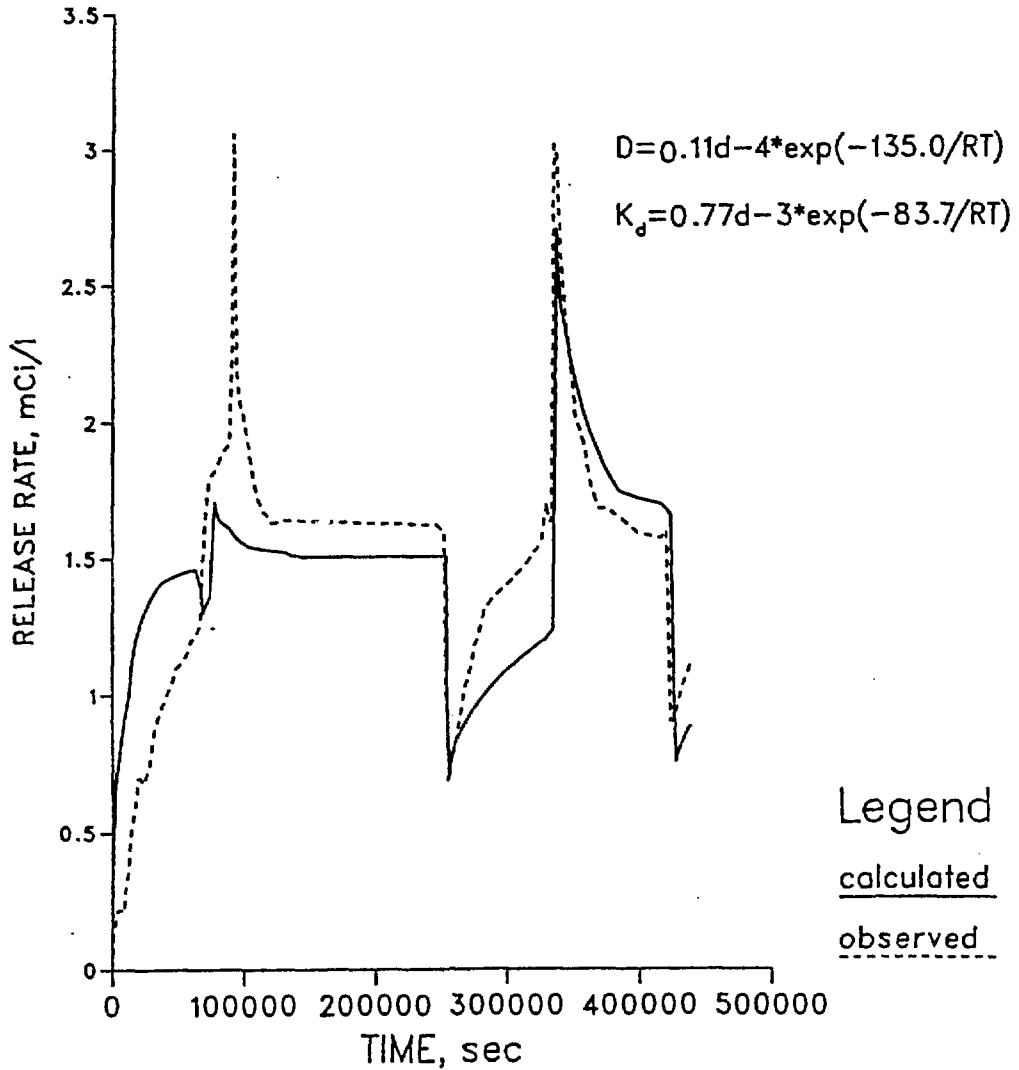


Fig. 8. Calculated and Observed Tritium Release from Aluminate Sample P2. Activation energy (exponential term) given in kJ/mol.

desorption rate constant. This will be discussed later in this section. One feature of the tritium release curve for the aluminate sample could not be reproduced with the current diffusion-desorption model. This was the sharp increase in the release rate starting at 100,000 sec. Apart from this, the model did a good job of reproducing the tritium release profile. The sharp increase in tritium release at 100,000 sec could be due to tritium trapping, which is not taken into account in our model.

The diffusion-desorption model is a significant improvement over the pure diffusion model, although there is still some deviation from the observed tritium release. To get a reasonable agreement with the release rate calculated by the diffusion-controlled model, we used an activation energy of diffusion which does not agree with that from other data obtained on the same samples. The deviation from observed release suggests either that another aspect of tritium transport is a factor in determining the tritium release or that there is some error in the form of the equation used to calculate the effective desorption rate constant or diffusion rate constant. In several systems, it has been shown that the activation energies of adsorption and desorption are dependent on the amount of surface coverage.¹⁵ The dependence of the desorption rate constant on the surface coverage was not included in these calculations. In addition, this model neglects the effects of adsorption of tritium from the gas phase.

The necessity for a more sophisticated tritium release model became apparent when data were obtained from the CRITIC in-pile tritium release experiment.¹⁶ In this experiment under certain conditions of temperature and purge gas composition, an increase in the sample temperature resulted in a sudden decrease in the tritium release. In some cases, the decrease was followed by a rapid increase to a maximum release above the steady-state

release, then a gradual decline to steady state (see Fig. 9). In other cases, the decrease was followed by a gradual increase back to steady state. This behavior could not be described using the simple diffusion-desorption model. The dependence of this behavior on purge gas composition led us to surmise that it was associated with surface phenomena. We thus sought to develop a diffusion-desorption tritium release model which incorporates a desorption activation energy that is dependent on surface coverage.

The dependence of the desorption activation energy on surface coverage would be expected to resemble that shown in Fig. 10. The slope of the plot is proportional to the desorption activation energy. This plot would be expected to be applicable for the cases where the dependence is either due to different adsorption sites or due to interactions between adsorbed species. In the region which corresponds to high surface coverage (θ), reaction of T^+ occurs with hydrogen from the highest energy sites (those with the lowest activation energy). As the coverage decreases, the coverage approaches the point where reaction of T^+ with hydrogen from the lower energy sites begins, and the desorption activation energy changes (region II). As the coverage decreases further, only the low energy sites are occupied; the T^+ reacts with the hydrogen in these sites and the activation energy observed is just that for reaction of T^+ with hydrogen in the low energy site. Alternatively, in the high coverage region, repulsive interactions between surface species lower the activation energy for surface reaction or desorption of the surface species into the gas phase. As the coverage decreases, these interactions decrease and the activation energy begins to change (region II). As coverage decreases further, the concentration gets to the point where the interactions between surface species are no longer important and the activation energy becomes constant (region of low θ). One would expect that the activation energy would

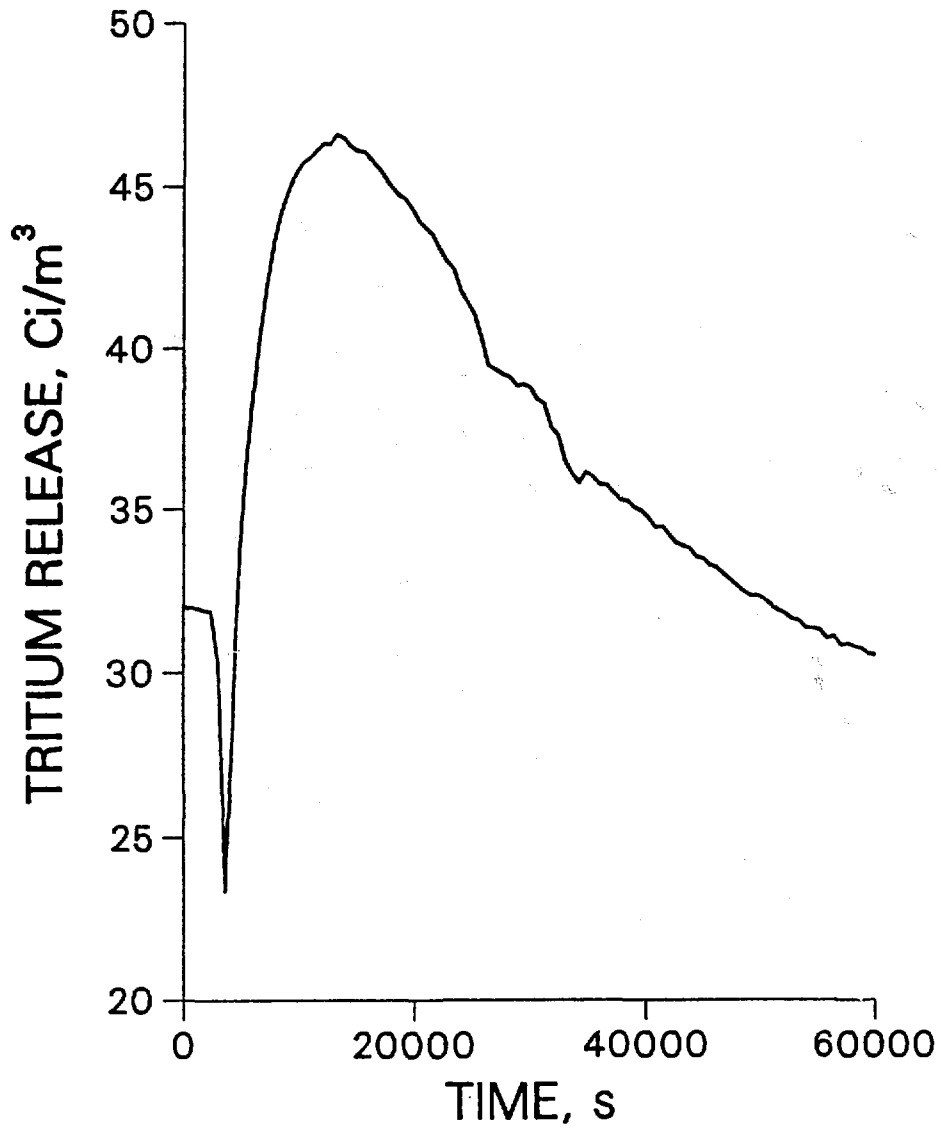


Fig. 9. Observed Tritium Release for a Temperature Increase from 455 to 549°C.

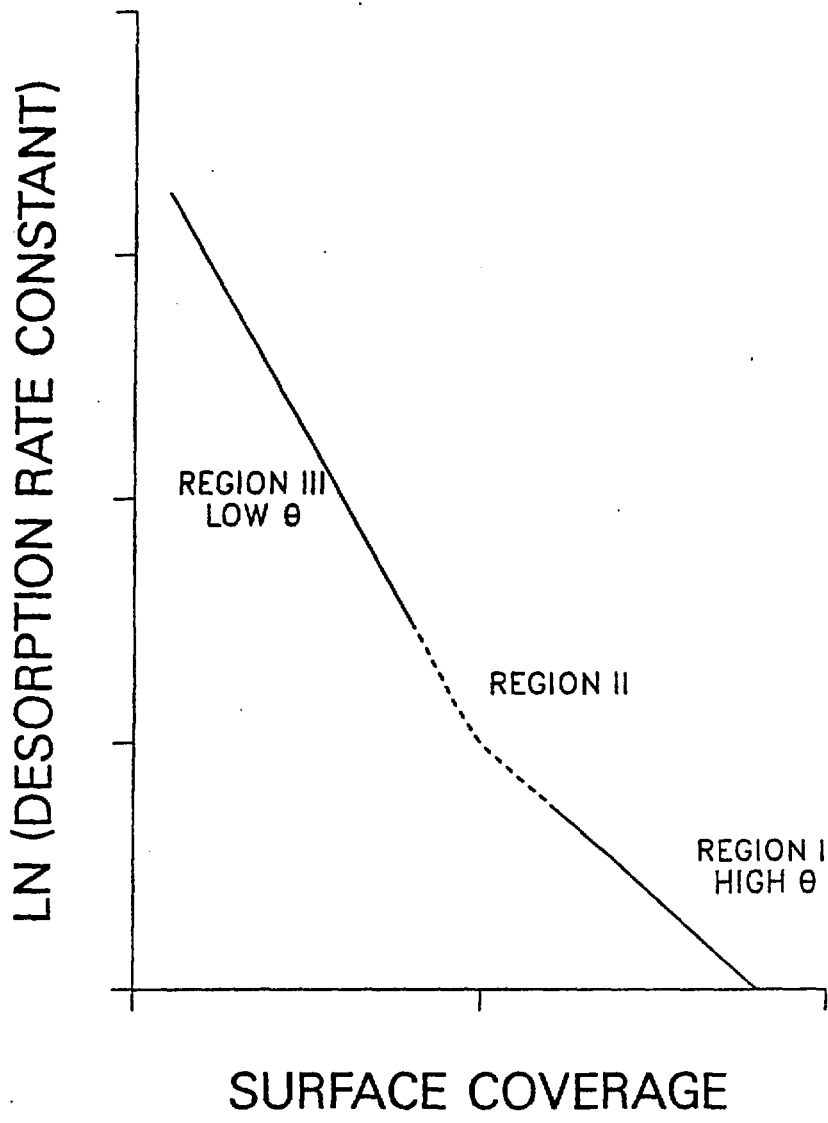


Fig. 10. Dependence of Desorption Rate Constant on Surface Coverage.

change smoothly in region II for the case where the dependence on surface coverage is due to interactions between adsorbed species, while it would change less smoothly if the dependence is due to different adsorption sites.

Tritium release behavior from a material in which desorption activation energy depends upon surface coverage will be different in region II compared with I and III. Temperature transient experiments performed at a constant hydrogen pressure correspond to changes in surface coverage. If the temperature changes correspond to changes in surface coverage confined to region I or III in Fig. 10, then a normal tritium release curve would be obtained and equation (5) would hold. However, if the temperature transient corresponds to surface coverages in region II, one would expect to see an abnormal tritium release curve due to the change in activation energy taking place over this range of surface coverage. This would depend on how drastically the desorption rate constant changes over this region and on the interrelation between diffusion and desorption in this regime. If the desorption rate constant decreases drastically and desorption is the rate-controlling process, one would expect to see the tritium release decrease then gradually increase back to steady-state release after a temperature increase. Parametric studies using a diffusion-desorption model with a surface-coverage-dependent desorption activation energy have predicted this type of tritium release.¹⁷ When the desorption activation energy changes less drastically in region II, this model predicts that the tritium release will decrease, then increase to a maximum above the steady-state release, then gradually decrease back to steady state after an increase in the sample temperature.¹⁷

Surface coverage is also dependent on the hydrogen partial pressure, increasing with increasing pressure. To maintain a constant coverage when the pressure is increased, the temperature must be increased. These effects are

illustrated in Fig. 11 in which surface coverage is plotted against temperature for two different pressures. Region II, the critical region in surface coverage where the activation energy of desorption changes, is indicated in the figure. When the hydrogen pressure is increased, the temperature range for region II will be shifted to higher temperature.

The diffusion-desorption model with a surface-coverage-dependent desorption activation energy was used to model the tritium release for several of the temperature transients from the CRITIC experiment which displayed unusual tritium release behavior. As illustrated in Fig. 12, model calculations fit the release curves obtained in the CRITIC experiment. The validity of the model can be tested further by performing surface studies on Li_2O to determine if the activation energy of desorption is dependent on the surface coverage. Such experiments with CRITIC are planned. If the model is accurate, then the unusual tritium release behavior observed upon a temperature increase when the helium purge gas contains 0.1% hydrogen should occur at higher temperatures when the purge gas is changed to 1.0% hydrogen and at lower temperatures when the purge gas is changed to 0.01% hydrogen. Temperature transients with these purge gas compositions are to be performed in the near future.

One very important aspect of tritium behavior in ceramic breeders is the tritium inventory in the breeder. The steady-state inventory for the diffusion-desorption model is given by the following expression:

$$I = 4/3 \Pi a^3 G (a^2/15D + a/3K_d)$$

The "desorption inventory" term, $4/3 \Pi a^3 G (a/3K_d)$, accounts for the tritium at the surface of the grain and for the tritium within the grain due to a nonzero surface concentration. The transient inventory is most readily calculated graphically. The difference between the area under the curve for

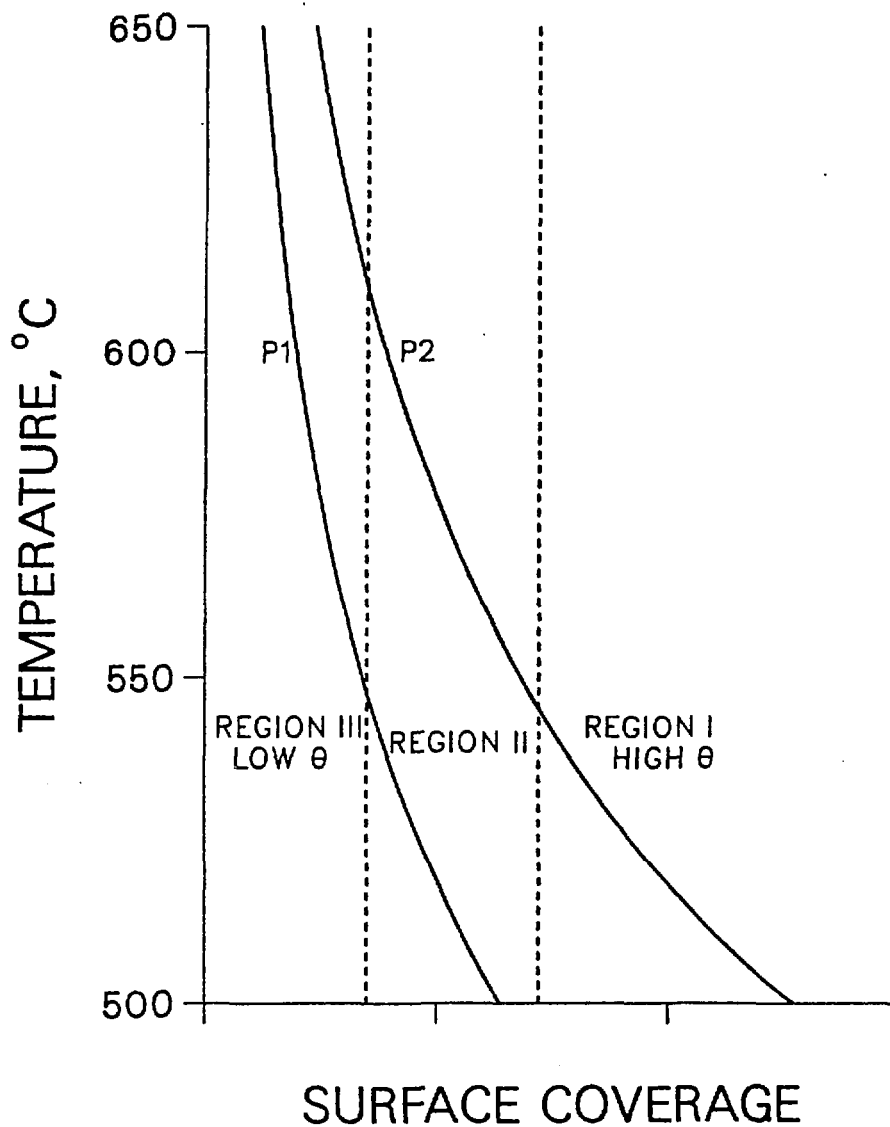


Fig. 11. Relationship between Surface Coverage and Temperature for Two Pressures. $P_2=2 P_1$.

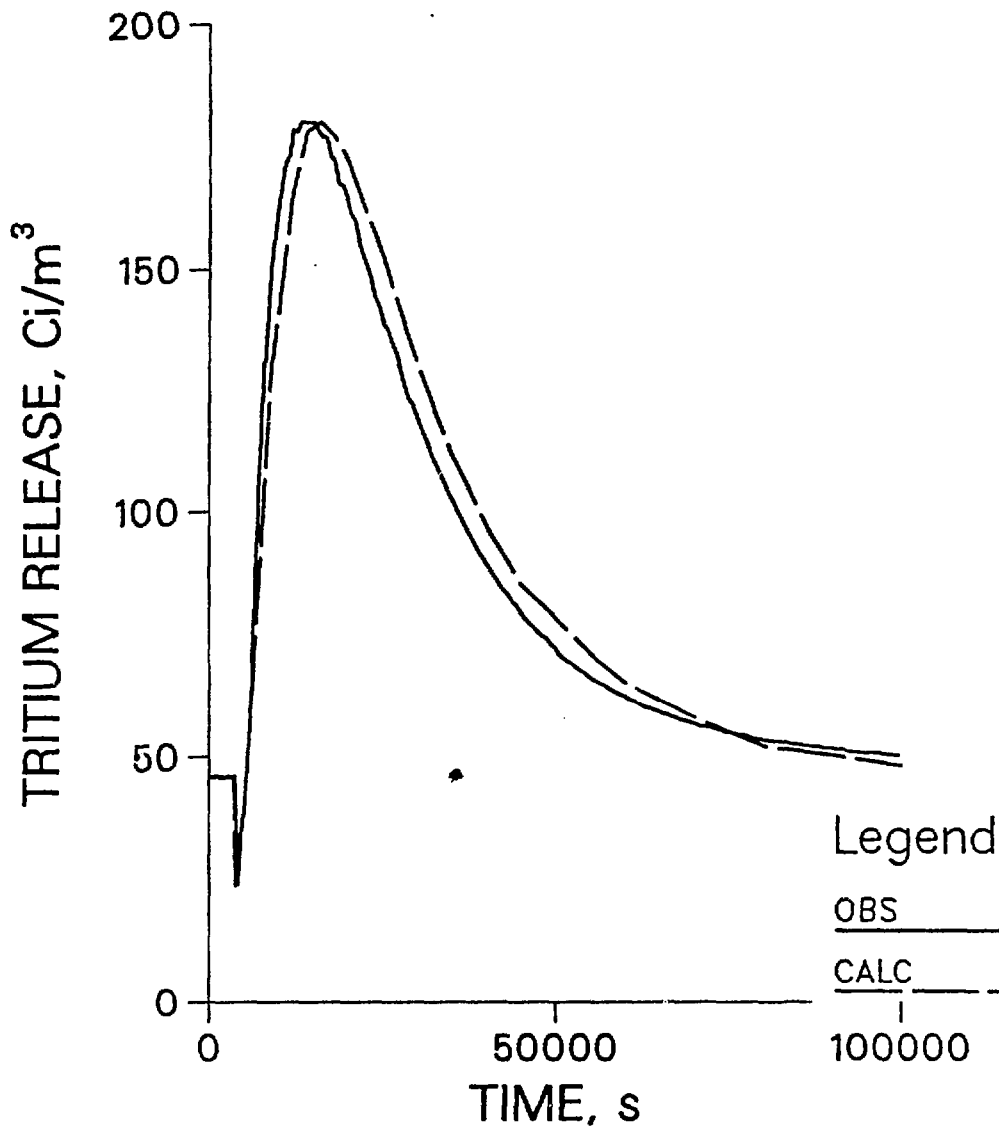


Fig. 12. Calculated and Observed Tritium Release for a Temperature Increase from 435 to 615°C.

the calculated tritium release versus time and the curve for generation rate versus time will be the tritium density in the grains at that time. Converting to the proper units and multiplying by the volume of the grains will give the diffusion-desorption tritium inventory.

4. CONCLUSIONS

Tritium release from a ceramic breeder material is a complex process which cannot be predicted accurately using a simple model. Diffusion models and desorption models have been applicable over a small range of experimental conditions but have failed under slightly different conditions. A combination diffusion-desorption model with a single desorption activation energy is an improvement, but it too is unable to account for some of the experimental data. Experiments suggest that the activation energy for desorption of tritium from the leading solid breeder material candidates is dependent on the surface coverage.^{14,16,17} In order to accurately calculate the tritium release from these materials, the relationship between surface coverage and the desorption activation energy must be known. A diffusion-desorption tritium release model which takes into account this dependence of the desorption activation energy on surface coverage was developed. Calculations performed with this model are in good agreement with tritium release from the CRITIC experiment, whereas models which did not incorporate a dependence of the desorption activation energy on surface coverage gave poor agreement with the experimental data.¹⁷

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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 release rate
t	= time
α_n	= roots of $a \cot(a\alpha) = 1 - ah$
I	= steady-state inventory
H	= heat transfer coefficient
J	= flux
V	= temperature of sphere
V_o	= temperature of surrounding media
C_s	= surface concentration
C_o	= concentration in the gas
κ	= thermal conductivity
K_{ads}	= adsorption rate constant
K_{des}	= desorption rate constant
K	= $\rho C_p \kappa$
ρ	= density
C_p	= heat capacity

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