

Modeling of Tritium Behavior in Ceramic Breeder Materials

by

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Abstract

The model described in this paper considers diffusion and desorption as the rate-controlling mechanisms for tritium release from a ceramic breeder material. This model was used to predict the tritium release from samples of Li_2SiO_3 and LiAlO_2 , given the temperature history of the samples. The diffusion-desorption model did a better job of predicting the tritium release for these samples under pure helium purge gas than did a pure diffusion model using the best values for the diffusivity of these materials available. The activation energies of desorption found from the best fit of the predicted tritium release to the observed release were 105-108 kJ/mol for Li_2SiO_3 and 85.7 kJ/mol for LiAlO_2 . These values are in fair agreement with activation energies reported in the literature.

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1. Introduction

Tritium transport and release from a solid tritium breeder material are complex processes involving diffusion in the grain, trapping, grain boundary diffusion, surface reactions, desorption, adsorption, and intergranular diffusion in the gas phase. However, until recently, tritium release from ceramic materials was interpreted as either diffusion controlled^{1,2,3} or desorption controlled.^{4,5} The inappropriate use of simple 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, it may move from a regime where a simple diffusion model applies to a regime where desorption dominates or to a regime where a simple diffusion or desorption model is inadequate. A more complex model of tritium transport is needed. We have developed a diffusion-desorption model for tritium release from a ceramic which is applicable over a range of conditions and still allows the evaluation of the diffusivity and desorption activation energy from experimental data.

This model is a significant improvement over a pure diffusion model for

tritium release from Li_2SiO_3 samples in a pure He purge stream.

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2. Theory

The model described in this paper considers diffusion and desorption as the rate-controlling mechanisms for tritium release from a ceramic breeder. At the temperatures involved, intergranular gas phase diffusion and grain boundary diffusion should be much more rapid than diffusion in the bulk. Desorption is included as a rate-limiting mechanism based on (1) the observations of desorption-controlled kinetics in some release experiments^{4,5} and (2) the results of experiments in which the importance of surface reactions was identified by changing the composition of the purge gas.^{1,6,7} Diffusion is included based on the observation of diffusion-limited release in other cases.^{1,2,8,9}

The problem of tritium transport in 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.¹⁰ The boundary condition is given by

$$J = H(V - V_0) \quad (1)$$

and is very similar to that describing desorption from a surface

$$J = K_{des} C_s - K_{ads} C_0 \quad (2)$$

where

J = flux

K_{des} = desorption rate constant

K_{ads} = adsorption rate constant

C_s = surface concentration

C_0 = concentration in the gas phase

H = heat transfer coefficient

V = temperature of sphere

and

V_0 = temperature of the surrounding media

The problem is simplified by taking the reference state (V_0 or C_0) 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 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. Making the following substitutions in the solution provided by Carslaw and Jaeger¹⁰ to the heat conduction problem leads to the solution for the tritium concentration in the grain as a function of the grain radius and time:

$$C = V$$

$$G/D = A_0/K$$

$$D = \kappa$$

Definitions for all the symbols are given in the appendix.

$$C = \frac{G}{6hD} \{h(a^2 - r^2) + 2a\} - \frac{2ha^2G}{rD} \sum_{n=1}^{\infty} \frac{\sin(\alpha_n) \exp(-D\alpha_n^2 t)}{\alpha_n^2 [a^2 \alpha_n^2 + ah(ah-1)] \sin(a\alpha_n)} \quad (3)$$

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

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

R_t = tritium release rate

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 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.

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

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.⁶ 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 type 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 the LISA experiment with hydrogen added to the purge gas.⁶ Values of the desorption activation energy were varied between 75 and 145 kJ (18-35 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. The best fits to the experimental data were obtained when the diffusion preexponential was increased only slightly (by up to 15%) from that found by Werle et al.⁶ 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. 1 and 2. The form of 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.⁶ The large volume of these grains means a few of them will 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 poor choice. The use of this radius would result 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 P1⁶), 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. 3), suggesting 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.

For the calculated curves in Figs. 1-3, the diffusion activation energy is identical to that determined using a pure diffusion model (Werle et al.⁶); however, the values for the preexponential terms are about 12% larger. 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 activation energy of desorption of HTO from lithium oxide of 120 kJ/mol (28.7 kcal/mol) found by Kudo and Okuno.¹¹ 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. 4. The activation energy of desorption used was 85.7 kJ/mol (20.5 kcal/mol), which is larger than the 61.5 kJ/mol observed by Fischer for

LiAlO_2 .¹² This discrepancy indicates that we did not use the true diffusion coefficients for LiAlO_2 or that we used an oversimplified form of the 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.

In Figs. 5 and 6 the pure diffusion model was used to calculate the release rate for sample P3 of the LISA experiment. In Fig. 5, the diffusivity calculated by Werle et al. was used.⁶ In Fig. 6, the diffusional parameters were optimized to give the best fit to the observed data. As can be seen by comparing Fig. 1 with Figs. 5 and 6, 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 this reasonable agreement with the observed release rate using 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 values or the form of 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.¹³ This dependence of the desorption rate constant on the surface coverage is not included in our model. In addition our model neglects the effects of

adsorption of tritium from the gas phase. Including these effects should improve our model.

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 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

Predictions of tritium release obtained from the diffusion-desorption model are in good agreement with the observed tritium release from samples of Li_2SiO_3 and LiAlO_2 with average grain radii of up to 100 microns. For these samples the diffusion-desorption model was a significant improvement over a pure diffusion model for predicting tritium release under pure helium purge gas. For a sample with a volume-weighted average radius of 220 microns, the model failed when this radius was used as the characteristic size. This failure may be due to the underestimation of the surface area for such a system. When the average radius was chosen, the diffusion-desorption model prediction was in good agreement with the observed data. Analysis of the release rate data with the diffusion desorption model leads to an activation

energy of desorption of HTO from Li_2SiO_3 of 106 kJ/mol (25 kcal/mol), which is slightly lower than that of HTO from Li_2O of 120 kJ/mol (28.7 kcal/mol) observed by Kudo and Okuno.¹¹ In addition, the release data yielded an activation energy of desorption of HTO from LiAlO_2 of 85.7 kJ/mol (20.5 kcal/mol), which is larger than the value for H_2O of 61.5 kJ/mol found by Fischer¹². The diffusion-desorption model does not predict all the variations in the tritium release observed experimentally; however, it is a useful model and gives a good prediction of tritium release over a wide range of temperatures.

5. References

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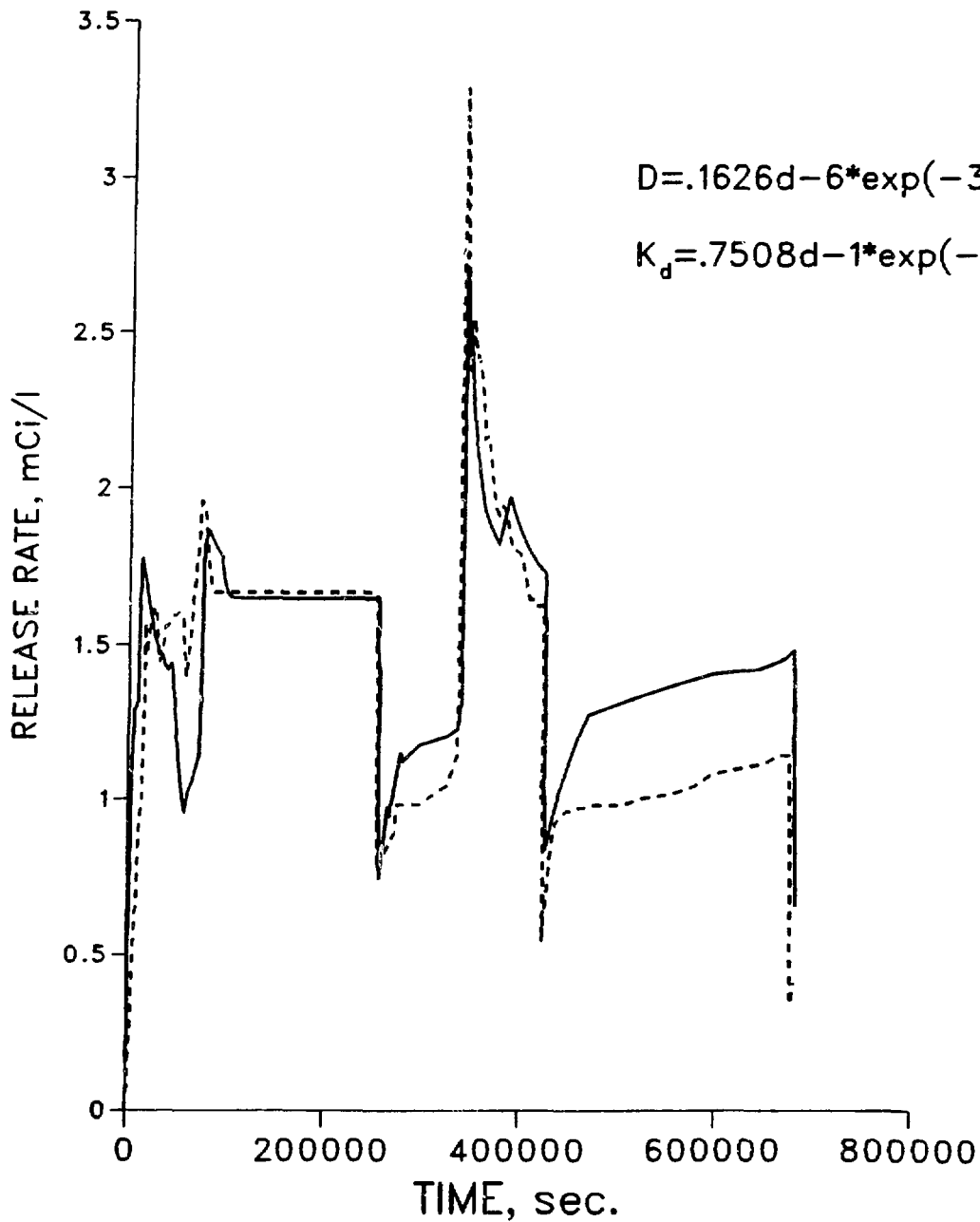
APPENDIX

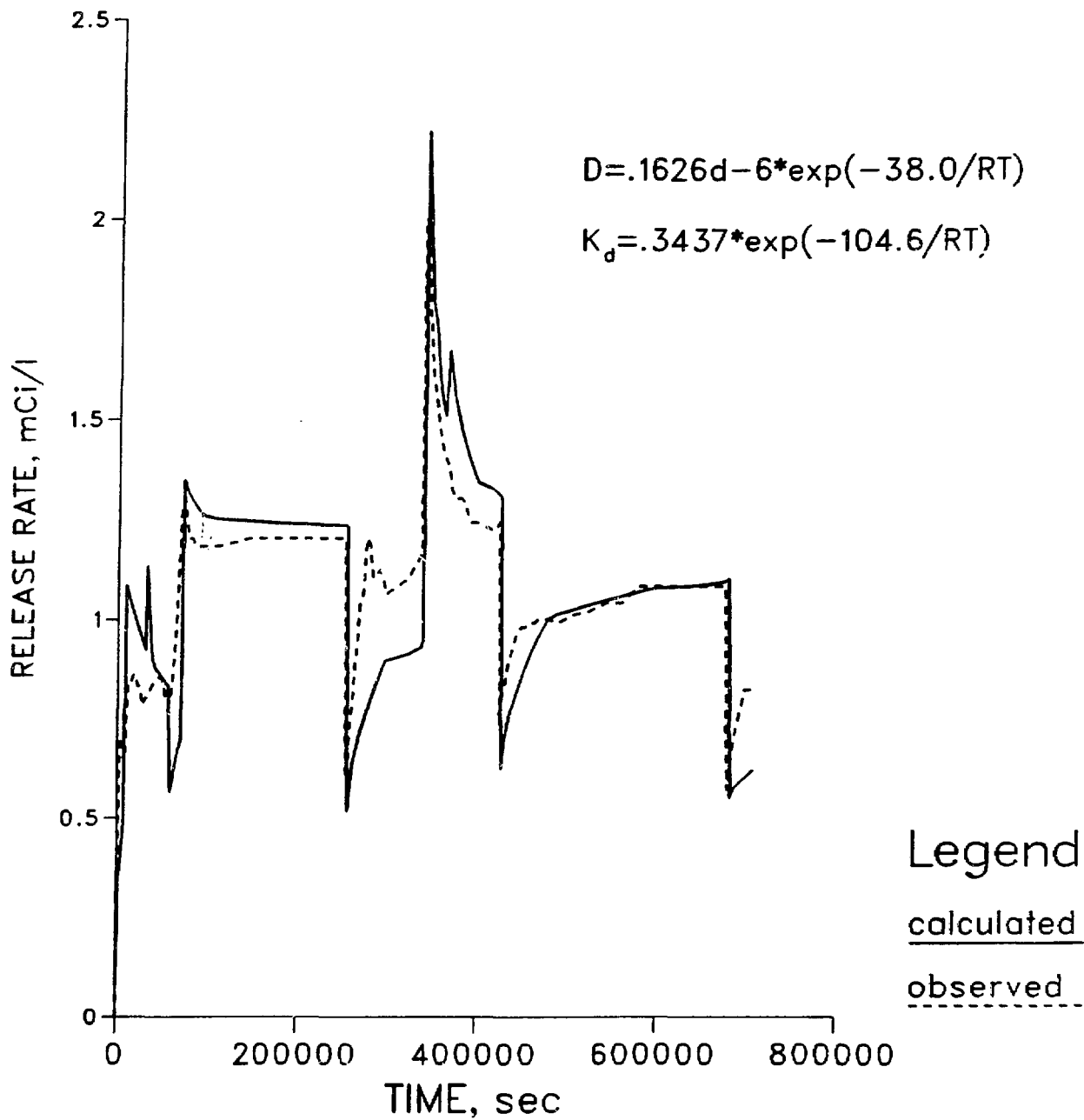
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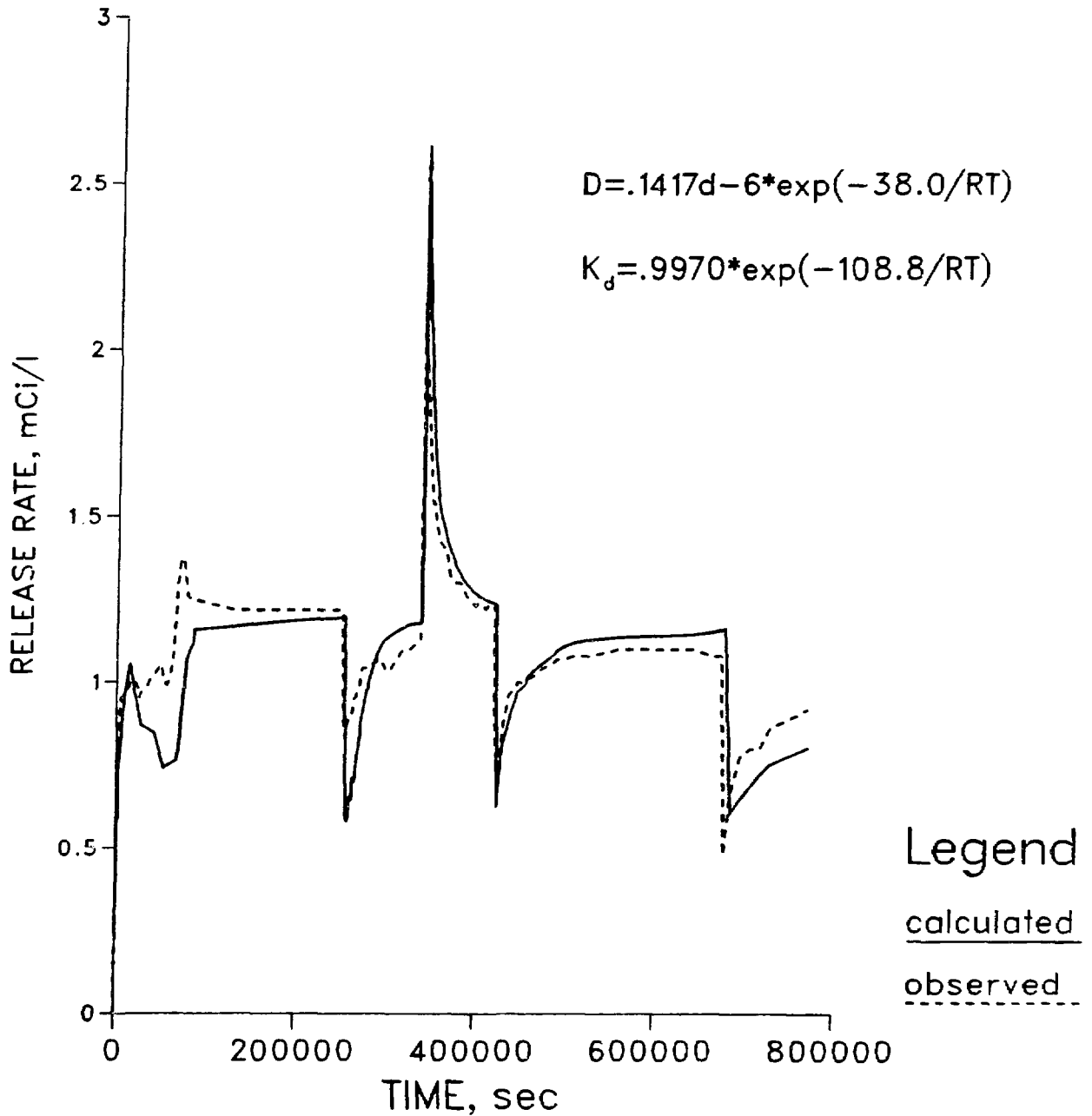
a	= grain radius
r	= radial distance
C	= tritium concentration
C ₁	= surface concentration of tritium before temperature change
D	= diffusivity
K _d	= effective desorption rate constant
G	= volume generation rate
h	= K _d /D
R _t	= tritium release rate
t	= time
α _n	= roots of $\text{arccot}(\alpha) = 1 - a \cdot h$
I	= steady-state inventory
H	= heat transfer coefficient
V	= temperature of sphere
V ₀	= temperature of surrounding media
C _s	= surface concentration
C ₀	= 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

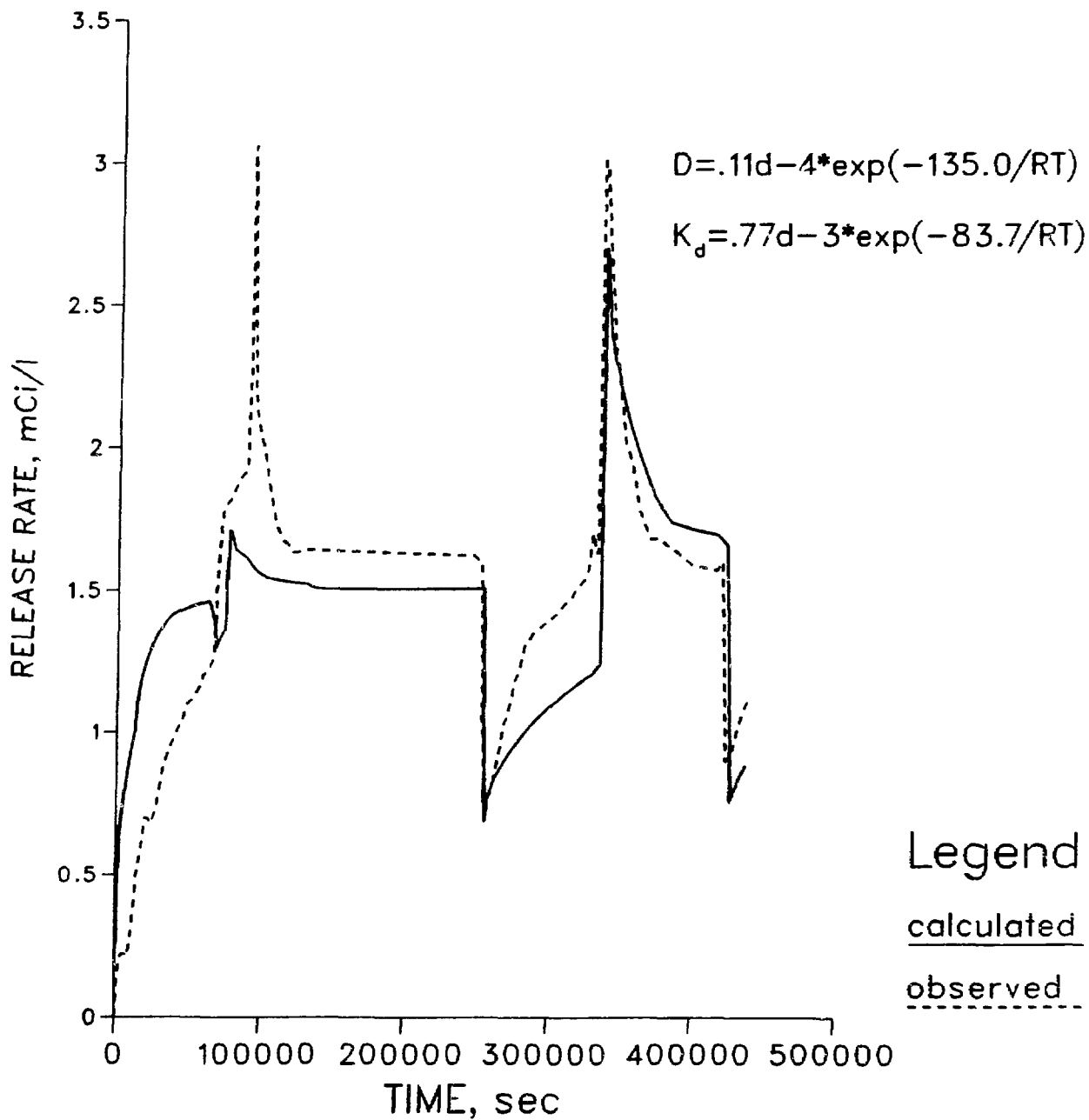
Caption for Figures

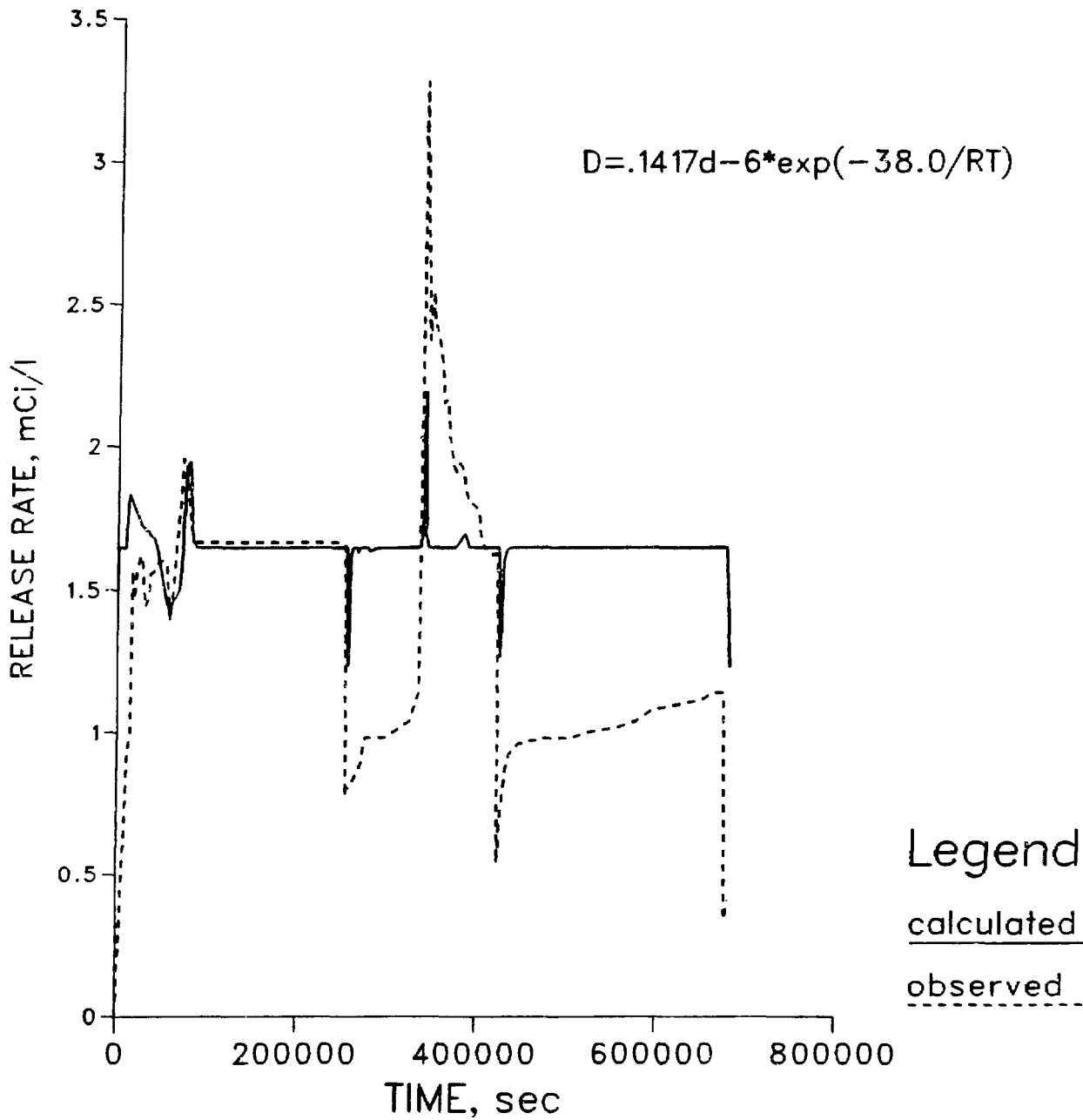
- Fig. 1. Calculated and observed tritium release from metasilicate sample P3.
- Fig. 2. Calculated and observed tritium release from metasilicate sample P5.
- Fig. 3. Calculated and observed tritium release from metasilicate sample P1.
- Fig. 4. Calculated and observed tritium release from aluminate sample P2.
- Fig. 5. Calculated and observed tritium release from sample P3, calculated curve obtained with pure diffusion model and diffusivity in ref. 6.
- Fig. 6. Calculated and observed tritium release from sample P3, calculated curve obtained with pure diffusion model and optimized diffusional parameters.

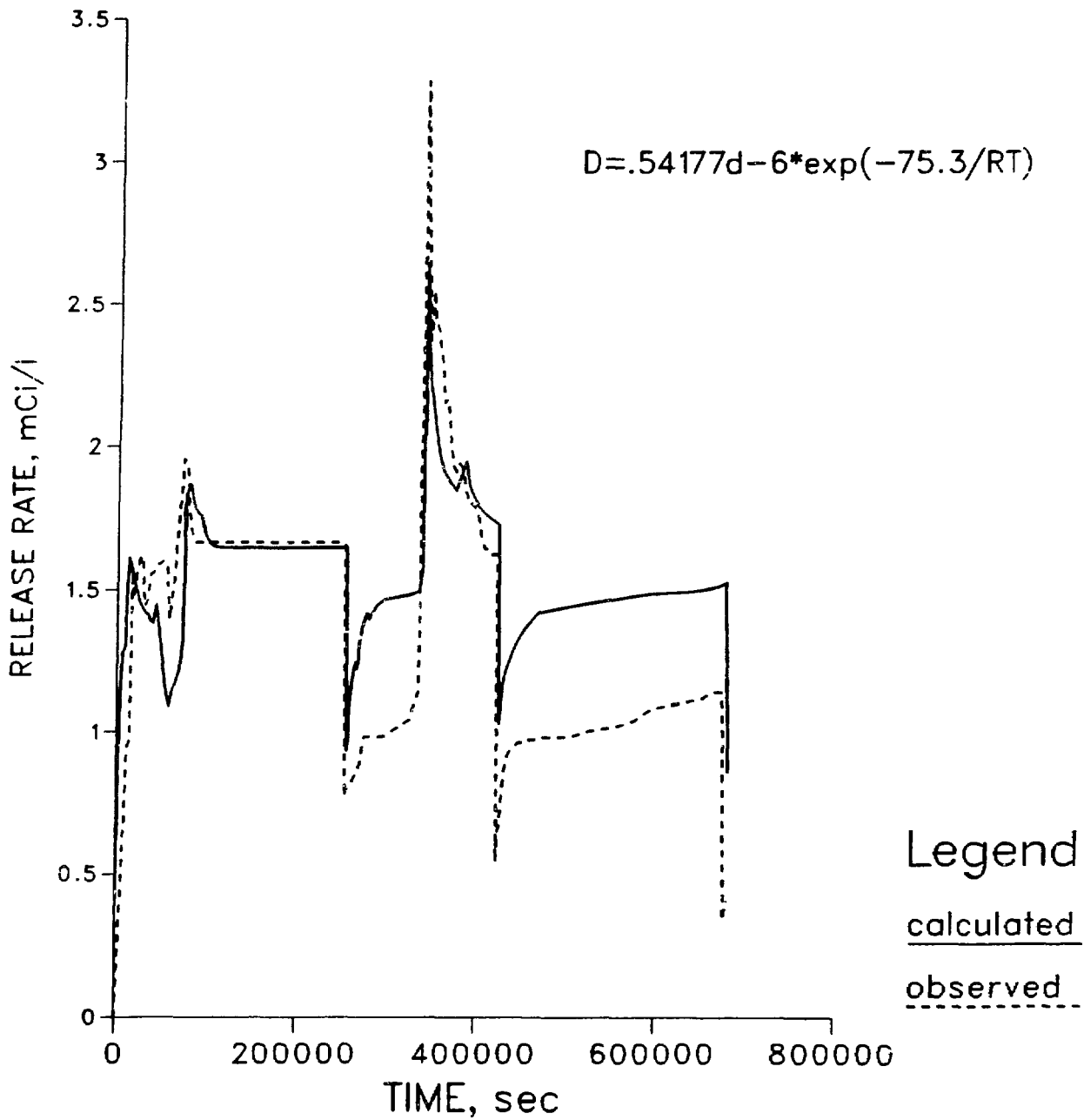












$$D = .54177d^{-6} \exp(-75.3/RT)$$

Legend
calculated
observed