Modeling Tritium Removal from Metal Surfaces

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Abstract

A program was written to numerically model the diffusion of tritons throughout a metal bulk. The program uses Fick's diffusion equation to follow the time evolution of a concentration profile. It has been used to accurately model how particles will flow out of a system with a concentration of zero at the surface. It has also been used to model how a change in diffusion constant, such as the one between the metal oxide layer and the metal bulk, affects the diffusion of particles. Using this model for the concentration profiles within a substance, the outgassing rate of tritons from a surface as a function of time has also been modeled. The outgassing rate model accurately models the outgassing rate from experiments at longer times, but at earlier times it is less accurate. This is believed to be due to the fact that only diffusion through the solid is accounted for in the outgassing rate model, and surface equations are ignored. This would suggest that at earlier times, the removal of tritons is governed by surface equations, while at later times it is governed by diffusion. Work on a more complex program to model the removal of tritons from the surface of the metal has been started, and will be used in conjunction with the diffusion model.

Introduction

Tritium, (H-3) is a radioactive isotope of hydrogen that occurs naturally, and has a half life of 12.32 years. It can often replace hydrogen in a molecule containing hydrogen. For example, a hydrogen atom in water (H_2O) can be replaced by a tritium, forming tritiated water (*HTO*). Due to this characteristic and its small atomic size, tritium can often remain in a substance after multiple swabs to remove it.

Tritium has many applications. Due to its radioactive nature, it is often used as a tracer in biological, chemical and environmental studies. Tritium is used in radio-luminescent sources relying on decay betas to make scintillant deposited on the inner surfaces of tubes to fluoresce. Tritium is a fuel in the production of fusion energy. Tritiated water is also useful for studying the effects of water absorption to surfaces.

The removal of tritium from metal surfaces is important because the tritium can diffuse through the metal that is used to handle it or that comes in contact with it. Removing this radioactivity is important in insuring safety. Due to the composition of the metal substrate, the removal of tritium is not uniform and consists of a number of different movements, as seen in Figure 1.

T H Desorption from Surface	Figure 1. Removal of
Т Н Н Н Н Н – Water Monolayers	bulk
H H H H H H H H H H H H H H H H H H H H	Tritium from the bulk diffuses through the metal lattice, undergoes isotopic exchange within the hydroxide layer and water monolayers, and is desorbed from the surface into the gas stream

Figure 1 shows that tritium undergoes a multi-step removal process; it must diffuse through the metal lattice, undergo isotopic exchange into the hydroxide layer and the water monolayers forming the oxide layers, diffuse through the oxide, and then desorb from the surface or be removed from the surface by a flow of helium over the surface of the metal. As tritiated water is removed from the surface by the gas stream, new particles will diffuse through the oxide layer under a concentration gradient, causing more particles to diffuse to the oxide layer from the metal lattice under a concentration.

Experimental Setup

In testing my model for accuracy, we will use data from collected in experiments performed at the Laboratory for Laser Energetics over the past 2 years. The experimental setup of these experiments has been described in the reports written by these experimentalists $^{(1,2,3)}$. The setup is illustrated in Figure 2.



Metal coupons that are contaminated with tritium are placed within the decontamination chamber. Helium is decompressed from the helium tank with the regulator, purified to remove trace contaminants, and split into two streams. Both streams are metered. One

stream flows directly towards the chamber; the second stream is humidified by bubbling the gas through water. The two streams are combined before entering the decontamination chamber. The relative humidity of the combined streams is adjusted by adjusting the ratio of the wet stream to the dry stream. The gas stream then flows through a dew point sensor (DP) to verify that the relative humidity is consistent with calculations. The decontamination chamber can be set to various temperatures to study the removal rate dependence on temperature and stream humidity. Tritium is removed from the surface of the metal as tritiated water. This water is collected in the liquid scintillation cocktail in the first bubbler (B1), where activity is counted by the liquid scintillation counter (LSC) as the tritiated water is collected. The gas then moves to the second bubbler (B2), where tritium that is not captured in the first bubbler can be removed. Two bubblers are used in series to confirm that the liquid scintillation cocktail in the first bubbler is removing at least 95% of the incoming tritiated water. Between the two bubblers, over 99.5% of the tritium transported to the bubblers is removed from the gas stream. Data from a number of previous experiments have been compiled, with variables including the type of metal, the relative humidity, and the temperature of the coupon. The liquid scintillation counter collects data in the form of activity, which can then be converted to an outgassing rate, which is what we will be using for our purposes.

Theory

Fick's laws of diffusion⁽⁴⁾ state the following;

$$\frac{\partial c}{\partial t} = -\frac{\partial F}{\partial x} \tag{1}$$

$$F = -D\frac{\partial c}{\partial x} \tag{2}$$

where c is concentration, t is time, F is flux, x is distance into the metal, and D is the hydrogen diffusion coefficient in the medium of interest. Equations 1 and 2 lead us to equation 3.

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial c}{\partial x}$$
(3)

Since we are searching for a numerical solution, we must construct a numerical grid dividing the distance into N cells. If we define x_L as the left boundary and x_R as the right boundary, we can define the space between cells, Δx , as in the equation 4.

$$\Delta x = \frac{(x_R - x_L)}{N} \tag{4}$$

Using equation 4, we can define x_i , or the value of distance at the center of the "*ith*" cell.

$$x_i = x_L + (i - \frac{1}{2})\Delta x \tag{5}$$

It is important to note that for our purposes, x_L will be 0 for all equations and models. The next step is to define the diffusion coefficients. In our model, there will be two diffusion coefficients. One defines diffusion through the bulk and the other diffusion through the oxide layers. However, there are two layers of oxide; one on the left and one on the right. The left oxide layer will have diffusion constant D_A , the bulk D_B , and the right oxide layer D_C . We will then define the distance at which the diffusion constants change as x_s and x_t respectively. If we consider D_i as the diffusion constant within the "*ith*" cell, we have

$$D_i = D_A \text{ if } x_i < x_s \tag{6}$$

$$D_i = D_B \text{ if } x_s \le x_i \le x_t \tag{7}$$

$$D_i = D_B \text{ if } x_i < x_i \tag{8}$$

We can then define the diffusion constant at the interfaces between cells. With $D_{i+\frac{1}{2}}$ being the diffusion constant at the interface between the "*ith*" and the "*i*+1"th cell.

$$D_{i+\frac{1}{2}} = \frac{D_i + D_{i+!}}{2} \tag{9}$$

The next step is to solve Fick's equations. The subscript notation denotes the cell the value refers to. The next equations are equation 2 recast in finite difference form. $F_{i+\frac{1}{2}}$ is the flux at the interface between the "*ith*" and the "*i*+1"th cell. c_i refers to the concentration within cell *i*.

$$F_{i+\frac{1}{2}} = -D_{i+\frac{1}{2}} \frac{c_{i+1} - c_i}{\Delta x}$$
(10)

$$F_{i-\frac{1}{2}} = -D_{i-\frac{1}{2}} \frac{c_i - c_{i-1}}{\Delta x}$$
(11)

The next step is to write equation 1 in finite difference form⁽⁵⁾. Δt refers to the time-step to be used between each concentration profile that the program generates; i.e., assuming that the concentration c_i within cell *i* is known at time *t*, we need to find c'_i the concentration at a time $t + \Delta t$.

$$\frac{c'_{i} - c_{i}}{\Delta t} = \frac{-(F_{i+\frac{1}{2}} - F_{i-\frac{1}{2}})}{\Delta x}$$
(12)

Combining equation 11 and equation 12, we find equation 13.

$$\frac{c'_{i} - c_{i}}{\Delta t} = \frac{-1}{\Delta x} \left(-D_{i+\frac{1}{2}} \frac{c_{i+1} - c_{i}}{\Delta x} + D_{i-\frac{1}{2}} \frac{c_{i} - c_{i-1}}{\Delta x} \right)$$
(13)

The only problem with this equation is that it uses past values of F to generate future values of c. By including F', or the flux at the new time, in our equation, we can make it more stable and more accurate. We also include a degree of implicitness, θ , to control the amount of weight that is given to the two times. The degree of implicitness must be between 0 and 1, inclusive. We therefore replace equation 12 with

$$\frac{C'_{i} - C_{i}}{\Delta t} = -\theta(\frac{F'_{i+\frac{1}{2}} - F'_{i-\frac{1}{2}}}{\Delta x}) - (1 - \theta)(\frac{F_{i+\frac{1}{2}} - F_{i-\frac{1}{2}}}{\Delta x})$$
(14)

Expressing F' in a similar way of expression as equation 13, we find equation 15;

$$\frac{c'_{i}-c_{i}}{\Delta t} = -\theta(-D_{i+\frac{1}{2}}\frac{c'_{i+1}-c'_{i}}{\Delta x^{2}} + D_{i-\frac{1}{2}}\frac{c'_{i}-c'_{i-1}}{\Delta x^{2}}) - (1-\theta)(-D_{i+\frac{1}{2}}\frac{c_{i+1}-c_{i}}{\Delta x^{2}} + D_{i-\frac{1}{2}}\frac{c_{i}-c_{i-1}}{\Delta x^{2}})$$
(15)

To simplify the notation;

$$\alpha_{i} = \frac{D_{i-\frac{1}{2}}}{\Delta x^{2}}$$
$$\beta_{i} = \frac{D_{i+\frac{1}{2}}}{\Delta x^{2}}$$
$$P_{i} = -\theta\alpha_{i}$$
$$Q_{i} = \theta\alpha_{i} + \theta\beta_{i} + \frac{1}{\Delta t}$$

$$S_{i} = (1 - \theta)\alpha_{i}c_{i-1} + (-(1 - \theta)(\alpha_{i} + \beta_{i}) + \frac{1}{\Delta t})c_{i} + (1 - \theta)\beta_{i}c_{i+1}$$

$$P_{i}c'_{i-1} + Q_{i}c'_{i} + R_{i}c'_{i+1} = S_{i}$$
(16)

It is important to remember that these equations are only being applied for the interior points of the concentration profile. For cells 1 and N, different boundary conditions will be used and applied. If we compile these equations into a matrix, we find that we have an almost complete tridiagonal matrix.

 $R_i = -\theta \beta_i$

To complete the matrix equation, we must consider the boundary conditions. The boundary condition used in the model is one of specified concentration. A concentration is specified, and the program uses a linear extrapolation between c'_2 and the specified concentration to solve for c'_1 . c_L is the specified concentration at the left boundary.

$$\frac{c'_{1}-c_{L}}{x_{1}-x_{L}} = \frac{c'_{2}-c_{L}}{x_{2}-x_{L}}$$
(18)

$$Q_{1} = \frac{1}{x_{1}-x_{L}}$$

$$R_{1} = \frac{-1}{x_{2}-x_{L}}$$

$$S_{1} = C_{L}(\frac{1}{x_{1}-x_{L}} - \frac{1}{x_{2}-x_{L}})$$

$$Q_{1}c'_{1}+R_{1}c'_{1} = S_{1}$$
(19)

Similarly, we can arrive for the boundary condition on the right, where c_R is the specified concentration at the right boundary.

$$\frac{c'_{N} - c_{R}}{x_{R} - x_{N}} = \frac{c'_{N-1} - c_{R}}{x_{R} - x_{N-1}}$$

$$P_{N} = \frac{-1}{x_{R} - x_{N-1}}$$
(20)

$$Q_{N} = \frac{1}{x_{R} - x_{N}}$$

$$S_{N} = C_{R} \left(\frac{1}{x_{R} - x_{N}} - \frac{1}{x_{R} - x_{N-1}}\right)$$

$$P_{N} c'_{N-1} + Q_{N} c'_{N} = S_{N}$$
(21)

By using the coefficients from these boundary conditions, we now have a completed tridiagonal matrix equation. We do this by attempting to satisfy equation 22 for values of i between one and N-1, and by setting equations 23 and 24.

$$c'_{i} + X_{i}c'_{i+1} = Y_{i}$$
(22)

$$X_1 = \frac{R_1}{Q_1} \tag{23}$$

$$Y_1 = \frac{S_1}{Q_1}$$
(24)

Matrix algebra yields equations 25 and 26, for values of *I* between 2 and *N*.

$$X_{i} = \frac{R_{i}}{Q_{i} - P_{i}X_{i-1}}$$
(25)

$$Y_{i} = \frac{S_{i} - P_{i}Y_{i-1}}{Q_{i} - P_{i}X_{i-1}}$$
(26)

After solving through each row of the matrix, we solve for c'_N , which is equal to Y_N . We then use this to substitute backwards in equation 22, solving for c' along the way. After solving for all c'_i , these are then treated as c_i and the process is repeated to solve for the concentration profile at the next time-step. Using equation 2 again, these concentration profiles can then be used to solve for the flux exiting the system from both sides.

Results and Discussion

Concentration profiles were generated to test the validity of the model. Activity was calculated from the experimental data, which was then converted into the number of particles. The diffusion constant was chosen from the literature for the type of metal and the temperature of the coupon in the experiment. The initial concentration was assumed to be constant through the metal.



The profile develops according to expectation; as particles move outward the region of large concentration gradient expands inward. This was a test using constant diffusivity throughout the bulk, and therefore did not account for the oxide layer that is known to develop on the surface. The diffusivity through the oxide was chosen to be 20 times larger than the diffusivity through the bulk and another set of concentration profiles were

generated, as can be seen in Figure 4. The actual diffusivity through the oxide is unknown.



Due to the higher diffusivity in the oxide layer, particles are removed at a quicker rate and the concentration gradient is therefore lower, as we see on the graph.

Concentration profiles were then developed at parameters to reflect an experimental run of a stainless steel coupon at 150°C. The diffusion coefficient in the oxide layer was varied, and the data⁽¹⁾, converted from outgassing rate to flux, was compared to the model as seen in Figure 5.



The comparison between the data and the model suggests that the outgassing rate of tritium is determined by diffusion at later times, but that the initial peak in outgassing rate is due to surface processes not modelled. The actual concentration profile of a metal coupon is not entirely uniform; within the oxide layers, concentrations actually tend to build to higher levels. The model suggests that this happens within the first 25,000 seconds, and that the outgassing rate is then determined by particles diffusing from the bulk outward. The comparison also seems to suggest that the diffusivity within the oxide layer is at least equal to if not greater than the diffusivity in the bulk; this can be seen by the fact that the models for the higher diffusivities come far closer to accurately modeling the curve.

Summary and Future Work

A numerical model was developed to describe the diffusion of particles through a solid, allowing for three regions of distinct diffusivity. The model suggests that while diffusion through the bulk and oxide is what determines the outgassing rate at later times, surface processes account for the removal of tritium at earlier times. It also suggests that the diffusivity within the oxide layer is at least equal to that of the bulk.

Tritium removal is a three-step process, involving desorption from the surface, diffusion through the bulk, and diffusion through the oxide. The last two have been accurately depicted through this model. Future work would involve extending this model to include equations for the surface processes.

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