SIMPLIFIED ESTIMATION OF TRITIUM INVENTORY IN STAINLESS STEEL

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An important part of tritium facility waste management is estimating the residual tritium inventory in stainless steel. This was needed as part of the decontamination and decommissioning associated with the Tritium Systems Test Assembly at Los Alamos National Laboratory. In particular, the disposal path for three, large tanks would vary substantially depending on the tritium inventory in the stainless steel walls. For this purpose the time-dependant diffusion equation was solved using previously measured parameters. These results were compared to previous work that measured the tritium inventory in the stainless steel wall of a 50-L tritium container. Good agreement was observed. These results are reduced to a simple algebraic equation that can readily be used to estimate tritium inventories in room temperature stainless steel based on tritium partial pressure and exposure time. Results are available for both constant partial pressure exposures and for varying partial pressures. Movies of the time dependant results were prepared which are particularly helpful for interpreting results and drawing conclusions.

I. INTRODUCTION

There are a variety of reasons for wanting to know the tritium inventory in stainless steel--probably the most common material used to contain tritium. And often the tritium is in contact with stainless steel at room temperature. This was recently the case as part of the Tritium Systems Test Assembly shutdown project. Three stainless steel (austenitic) tanks had been in tritium service for many years, and they needed to be disposed of. Two tanks had internal volumes of 265 L and one had an internal volume of 600 L. For this project a relatively inexpensive tritiated waste disposal path was available if the overall waste package had a tritium concentration below 10 Ci/m^3 (based on total package volume), while concentrations above this level necessitated relatively expensive waste disposal. Rough estimates of the tritium inventory indicated that the tritium inventory might be near the 10 Ci/m^3 break point. Thus, there was a motivation to attempt to accurately estimate the tritium inventory. Of course, the stainless steel could have been sampled and analyzed, but this would likely have been more expensive than simply packaging the material as

though it were higher level waste. Thus, the strategy was to use model calculations combined with previous experimental work to estimate the tritium inventory. This strategy was quite successful and revealed a very simple relationship for determining these estimates that may be useful for future projects. This valuable experience prompted the preparation of this paper.

II. THEORY

It is well-known that time-dependant diffusion of non-radioactive material into a semi-infinite slab is described by:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} \qquad (1)$$

With boundary conditions:

$C_A = C_{A0}$, at $t = 0$, for all z
$C_A = C_{A,S}$, at $z = 0$, for all t
$C_A = C_{A0}$, as $z \rightarrow \infty$, for all t

The analytical solution is:

$$\frac{C_A - C_{A0}}{C_{A,S} - C_{A0}} = 1 - erf\left(\frac{z}{2\sqrt{D_{AB}t}}\right) \qquad (2)$$

However, if the diffusing material is radioactive, it disappears over time and this, of course, can affect the concentration profile and the diffusion rate. This effect can be accounted for by adding a radioactive decay term to equation (1) resulting in:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2} - k_R C_A \qquad (3)$$

An analytical solution to this equation has not been identified, but numerical solutions can, of course, be obtained. For tritium to enter the stainless steel surface, the diatomic molecule must dissociate, and likewise for tritium to leave the surface it must recombine. For this paper it is assumed that these processes are fast compared to diffusion, so dissociation/recombination terms to not appear in equations. It is recognized that surface properties can have a strong effect on the overall transport process. Indeed this has been observed by Louthan and Derrick[1] and others. For example, surface oxidation can act as a permeation barrier which can prevent tritium from entering or leaving a material. This model does not include surface barrier effects. The validity of leaving

this effect out of this simplified analysis will be considered later in this paper by comparing model results to long-term experiments. Finally, when accounting for the overall tritium inventory associated with a material, it is recognized that tritium can not only be in the bulk material, but it can also be captured as part of a contaminant on the material's surface. Tritiated oil is a common example of this. This model does not account for tritium contained in surface contamination.

III. COMPUTER MODEL RESULTS

The model needs physical properties (diffusion coefficient and solubility) and a number of papers have addressed these [2,3,4,5,6,7,8]. Considerable variation in physical properties is reported. For the present work, the diffusion coefficient at 298K for tritium in stainless steel was taken from Louthan and Derrick [1] as 1.37×10^{-12} cm^2/s. From the same reference the solubility for deuterium at 298 K is reported as 0.121 $scc/cm^3/atm^{0.5}$. This value will be used for the solubility of tritium. All calculations assume that exposure begins with uncontaminated stainless steel, so $C_{A0} = 0$ at all z. The radioactive decay constant, k_R, for tritium is 1.79×10^{-9}/s

Concentration Profiles: Using these parameters, equation (3) was solved numerically. Stainless steel with a thickness of 1651 microns (0.065 in.) was exposed to 1 atm of tritium for 0.1, 1, 3, 8, 20, 100 and 500 years, and the results are shown on figure 1. The concentration falls off from the surface as the tritium moves into the stainless steel. As shown by the exposure times on the first five curves, it takes an increasing amount of time to move the tritium comparable distances into the steel. Finally at 100 years the tritium has not moved much beyond the 20 year profile. And, the 500 year curve is identical to the 100 year curve. Thus, at some point between 20 and 100 years, the concentration profile reaches steady state. Without decay, the steady state profile would be a straight line, but, as shown, with decay the steady state profile is strongly curved.

Effect of Decay: Radioactive decay of tritium will decrease the amount of tritium in the stainless steel. However, this decrease will result in a sharper concentration gradient which will increase the flux of tritium into the material. To examine these competing effects, the model was run with and without radioactive decay. As in the previous section, for these runs the thickness was 1651 microns, and the stainless steel was continuously exposed to 1 atm of tritium. Exposure times were 1, 8 and 20 years. The results are shown on figure 2. The solid curves show results with radioactive decay and the dashed curve show the hypothetical profiles that would develop without radioactive decay. At 1 year both curves are identical, so radioactive decay has little effect.

At 8 years the curves are close to each other, but noticeably different. At 20 years the difference becomes quite pronounced. Thus, radioactive decay does not have a large effect on the concentration profiles until about one half life (i.e. 12.3 years).
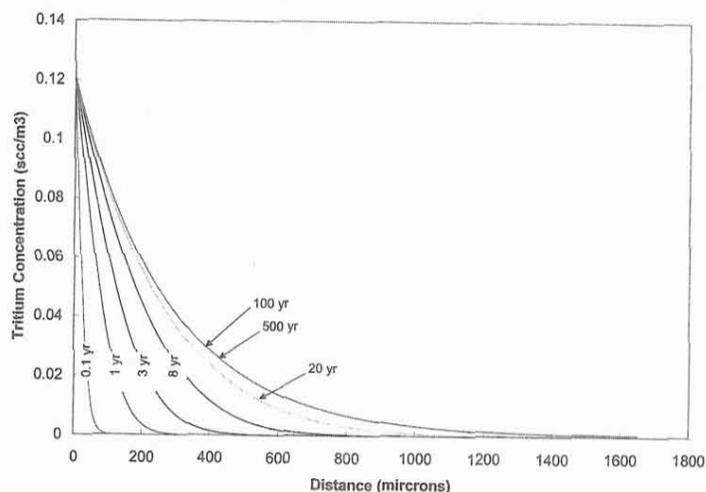

Fig. 1. Concentration profiles developed in stainless steel exposed to 1 atm. of tritium at various times.
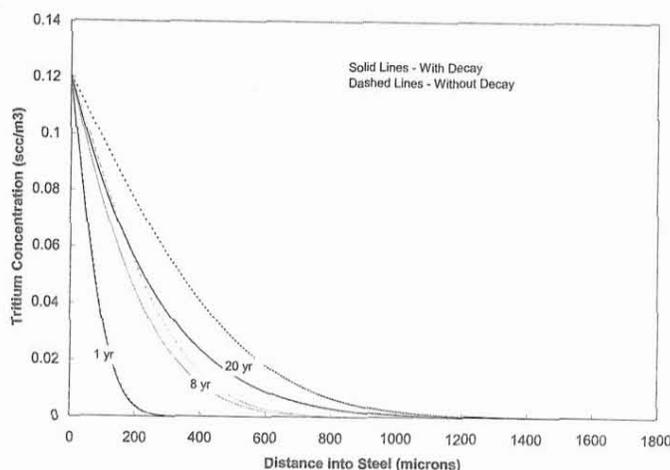

Fig. 2. Concentration profiles for tritium in stainless steel resulting from model runs with and without radioactive decay

Tritium Inventory: The tritium inventory associated with a concentration profile can be determined by integration. Model runs were made with 1651 microns of stainless steel at 298 K exposed to various tritium partial pressures. The tritium inventory was determined as a function of time, and the results are summarized with figure 3. As expected higher partial pressures result in higher tritium inventories. The inventories increase quite rapidly at the beginning, but then flatten out as exposure continues to longer times.
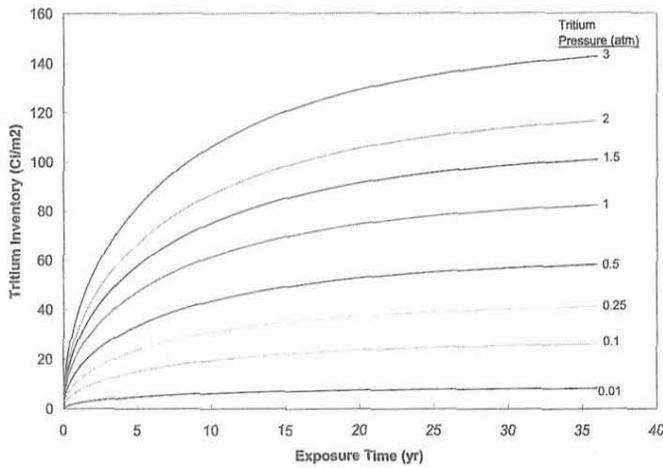
Fig. 3. Tritium inventory as a function of time of stainless steel exposed to various tritium partial pressures

Model Comparison to Experimental Data: In previous work by Wermer [9], it was reported that an approximately 50 L, stainless steel tank, referred to as an "LP50", was exposed to tritium off and on over its service life of 36 years in the normal course of its use as a tritium storage and transportation vessel. At its end-of-life, the amount of tritium in the stainless steel wall was determined to be 71 Ci/m^2. There is no record of the tritium partial pressure exposure history of the vessel. However, generally speaking, the vessel was likely exposed to tritium partial pressures between 0.1 and 1 atm, with possible exposures of 2 atm. And, again generally speaking, the vessel may have contained tritium for about $1/3^{rd}$ of its lifetime, or about 12 years. The tritium inventory values on figure 3 are generally consistent with the measured value of 71 Ci/m^2. This consistency is taken as a tentative confirmation that the model described here can provide reasonable estimates of tritium inventories in stainless steel waste.

Simplified Model: The tritium inventory curves on figure 3 were generated by numerical solution of a partial differential equation. In an effort to simplify the solution for more convenient use, it was found that all the curves on figure 3 can be readily calculated by the following simple equation:

Tritium Inventory (Ci/m2) =

$$\sqrt{503 \cdot p_{T2}(atm) \cdot t(yr)} \cdot \exp(-0.0143\, t(yr)) \qquad (4)$$

Valid for $0 \le t \le 36$ years and $0.01 \le p_{T2} \le 3$ atm

The average difference between the full model results and equation (4) is 0.9%. Roughly speaking the radical term in (4) accounts for diffusion into the stainless steel, and the exponential term accounts for radioactive decay. The favorable comparison between the full model

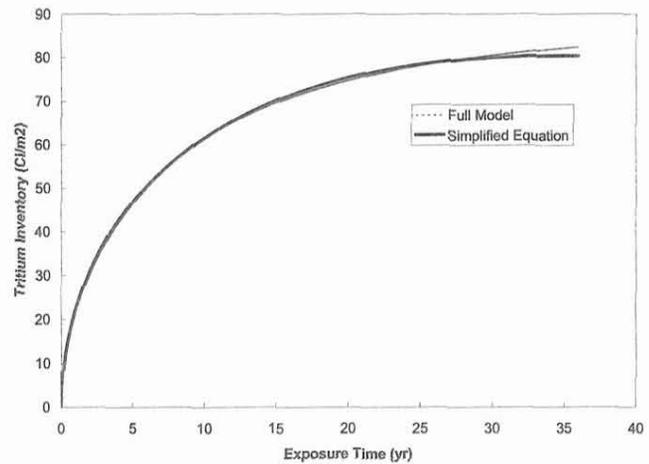and simplified equation results are shown for 1 atm exposure on figure 4.

Fig. 4. Comparison of full model to simplified equation for tritium inventory in stainless steel exposed to 1 atm tritium

Periodic Exposure: Often stainless steel exposure to tritium is periodic, i.e. it is exposed off and on to tritium over a period of time. To investigate the effect of this, the equation (3) model was run, as before, with 1651 micron stainless steel at 298 K. The steel was periodically exposed to 1 atm of tritium and 0 atm of tritium over the course of 36 years. The ratio of exposure time to non-exposure time was varied, and the results are summarized on figure 5. As shown, the tritium inventory increases during periods of exposure and decreases during periods of non-exposure. The decrease results from tritium diffusing back out of the surface and from decay. For reference, the 1 atm constant exposure curve from figure 3 is also included on figure 5. After 36 years all but the uppermost of the periodic exposure curves are observed to reach a quasi-steady state where inventories oscillate between roughly the same values. The longer the period of non-exposure, the quicker the quasi-steady state is reached. It is noted that the LP-50 studied by Wermer was periodically exposed to tritium. Thus, his measurement of 71 Ci/m^2 is best compared with these calculations which include periodic exposure. His measurement falls at the upper end of the curves shown on figure 5 (the 8:1). If the LP-50 spent some time exposed to 2 atm tritium, then the 2:1 curve would likely match Wermer's measurement. The model was used to prepare movies of the development of periodic profiles. Watching these movies, it is observed that a consistent front moves steadily into the stainless steel rather like the profiles on figure 1. However, the surface tritium concentration oscillates between the tritium solubility level during exposure and zero during non-exposure. In response, the profile in the bulk near the surface is observed to flagellate (or whip) back and forth. After a

certain period of time only the near-surface profile changes and the deep bulk tritium becomes constant regardless of surface events.

TSTA Waste: Using the methodology developed here, the tritium inventories in the three TSTA tanks mentioned in the introduction were estimated. They were all found to be below the 10 Ci/m^2 break-point, thus justifying less expensive waste disposal.
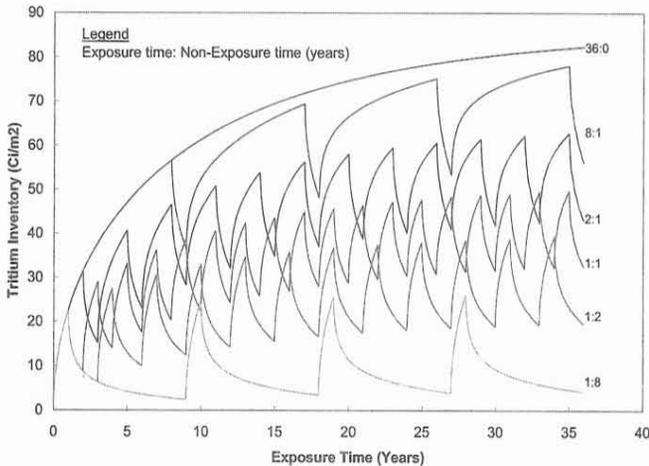

Fig. 5. Tritium inventory versus time for stainless steel periodically exposed to 1 atm of tritium

IV. CONCLUSIONS

- The diffusion equation with decay was used to estimate the tritium inventory in austenitic stainless steel exposed to tritium at 298 K
- Computer modeling using previously reported physical properties showed reasonable agreement with the tritium inventory previously measured for an LP-50 tritium storage container
- For steady exposure, little model error is introduced by simplifying the PDE model to:

Tritium Inventory (Ci/m2) =

$$\sqrt{503 \cdot p_{T2}(atm) \cdot t(yr)} \cdot \exp(-0.0143\, t(yr))$$

Valid for $0 \le t \le 36$ years and $0.01 \le p_{T2} \le 3$ atm

- The PDE model accommodates periodic exposures
- For multi-year, steady exposures tritium initially moves "quickly" into the bulk. However, soon after about 25 years, the profile essentially moves no further into the stainless steel.
- 0.065" stainless steel exposed to 1 atm tritium never has significant tritium on the unexposed surface. In essence, the tritium decays before it can break through the unexposed surface.
- The simplified model may be useful for quick, rough estimates of tritium inventory in stainless steel as may been needed for tritiated waste disposal

NOMENCLATURE

C_A Concentration of component A (i.e. tritium)
C_{A0} Initial concentration of component A
C_{AS} Concentration of component A at the surface
$C_{A,g}$ Concentration of component A in the gas phase
D_{AB} Diffusion coefficient for component A (tritium) in component B (stainless steel)
$erf()$ The error function
k_R Radioactive decay rate constant
t Time
z Distance along the thickness of the stainless steel
scc Standard cubic centimeters (or cm^3 at standard conditions)

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