UCRL- 86038
PREPRINT

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This paper was prepared for presentation at
9th Symposium on Engineering Problems of
Fusion Research
Chicago, Illinois, October 26-29, 1981

October 1, 1981

Lawrence
Livermore
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STUDIES OF MATERIALS EXHIBITING LOW TRITIUM PERMEATION RATES*

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Summary

Tritium permeation is being measured through potential barriers, such as aluminum, copper, various oxides and glasses. The temperature range of the experiments is 300-500 K (25-200 C) to compare such results to extrapolated high temperature data. A physical model is presented that accounts for the non-linear permeability seen at these low temperatures, where surfaces predominate.

Introduction

Tritium penetration through structural materials of nuclear reactors is a continuing problem. The situation will be more acute in a fusion reactor where tritium is a major fuel and millions of Curies will be inventoried. Considerable attention has been directed toward the high-temperature heat exchange system where there is a great likelihood of tritium escape to the environment. Most permeation studies have concentrated on stainless steels in these temperature regimes. Tritium fueling systems will contain most of the tritium near room temperature, however, and little work has addressed other potential structural materials and these lower temperatures.

Most available hydrogen permeation data is for relatively highly permeable metals such as platinum, palladium, and niobium at high temperature. Permeation under these conditions is easily monitored and the scientific interest in high diffusivities is great.

For materials exhibiting low hydrogen and, particularly, tritium permeability, there is little data available. It is the purpose of our research to fill this void and find materials used structurally or as coatings that substantially reduce tritium permeation. Models that explain the large deviations between our results and extrapolating of high temperature data are also being developed.

Experimental Procedures

Sample Preparation

The two centimeter diameter membranes were cut from high-purity 0.1 mm thick sheets. They were then cleaned with sequential washes of detergent, distilled water, acetone, and distilled water again. A heat lamp was used to dry the cleaned discs. No special concern, beyond this simple cleaning, was shown for the surface condition of these first samples. This problem will be addressed later in the project. Components of the permeation fixture were cleaned in a similar way.

Method of Measurement

The classical time-lag permeation method was chosen because it is well understood and experimentally straightforward. Several techniques were examined that could sense the low tritium concentrations in these experiments. These techniques were mass spectroscopy, proportional counting and scintillation counting. Liquid scintillation counting was chosen because it is highly sensitive (1 part in 10^{17}), inexpensive, and avoids background contamination.

Mass spectroscopy requires a continuously pumped vacuum chamber. It and proportional counting require expensive instrumentation, limiting them to serial (one sample at a time) experiments. This is a major handicap in these low temperature experiments, which must run continuously for days and weeks. The counting and vacuum chambers make residual contamination a problem on further experiments. Liquid scintillation counting avoids these problems.

A blow-up of a permeation cell is shown in Figure 1.

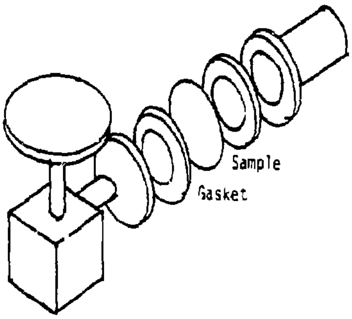

Fig. 1. Sketch of Permeation Cell

The sample membrane, usually 0.125 mm (5 mil) thick, is squeezed by two copper gaskets between Miniconflat-type knife-edge-sealed vacuum flanges, after checking for leaks in the assembly. About two cubic centimeters (STP) of tritium are introduced on the inlet side between the valve seat and the membrane. The tube on the opposite (outlet) side of the membrane is partially filled with a solvent that is regularly sampled. This tube is capped by a teflon-coated silicone (high temperature) septum and is held in place by a Swagelock fitting. This latter seal prevents the solvent from evaporating and allows sampling with a syringe.

This design has several advantages. All of the components are inexpensive and can be used only once and discarded to radioactive disposal after each experiment. This avoids a background contamination problem. The design also prevents leakage around the membrane into the counting solvent. Such a gas leak would simply disappear into the exhaust hood. Several samples can be run simulataneously (up to 16 in our ovens).

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*This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Results and Discussion

The experiments that are discussed here were carried out primarily to check the suitability of the scintillation method and detect any unexpected problems in the technique. Additionally, some interesting permeation data were obtained. Permeation measurements on gold, silver, aluminum and platinum at 300K and 400K were completed. Platinum was selected because of the wealth of published data available that could be used to evaluate the technique.

Classic permeation through a membrane is described by the following equation:

$$\frac{dQ}{dt} = \frac{KA}{L} \cdot (\Delta P)^{1/2} \qquad (1)$$

where dQ/dt is the rate of gas through the membrane, K, the temperature dependent permeability constant, A and L, the membrane area and thickness, respectively, and ΔP is the gas pressure differential across the membrane. SI units have been used to avoid the chaos resulting from permeabilities being given in so many different units.

The diffusion coefficient, D, can be determined from the time lag, τ, which is the extrapolated gas breakthrough time. The relationship is:

$$\tau = \frac{L^2}{6D} \qquad (2)$$

Results for the gold and silver samples at both 300 and 400 K show that after several weeks only a few picrocuries of tritium have penetrated the membrane and that steady-state permeation has not been achieved. Results for the aluminum and platinum membranes are shown in Table 1.

From Table 1 it can be seen that, for both metals at the two temperatures, the permeabilities are less than reported in the literature. The diffusion constants, calculated from the time-lag, are several orders of magnitude less. Since permeability is a product of diffusion and solubility, the resultant solubilities are greater than the published one. A possible explanation for these discrepancies can be advanced by assuming the diffusion rate is hindered by a surface barrier, but once in the bulk metal, the tritium is trapped at impurity sites, leading to an abnormally high solubility. Such an explanation is

Table 1. Comparison of Current Results with Extrapolated Values from the Literature

	300 K	400 K
Permeation Coefficient (K in $mol/m \cdot s \cdot Pa^{1/2}$)		
Platinum (1)	8.03×10^{-23} $[1 \times 10^{-19}]$*	3.93×10^{-18} $[1.42 \times 10^{-16}]$
Aluminum (2)	-	2.48×10^{-15} $[4.9 \times 10^{-21}]$
Diffusion Coefficient (D in m^2/s)		
Platinum	7.37×10^{-16} $[3.0 \times 10^{-11}]$	3.45×10^{-15} $[3.57 \times 10^{-10}]$
Aluminum	-	3.07×10^{-14} $[5.0 \times 10^{-11}]$
Solubility (mol T_2/m^3 metal)		
Platinum	3.46×10^{-5} $[7.18 \times 10^{-7}]$	0.362 $[7.0 \times 10^{-5}]$
Aluminum	-	25.6 $[2.7 \times 10^{-6}]$

*Literature values are in brackets.

very uncertain in light of the repeatedly large differences between this and previous work. We are in the process of carefully characterizing our samples, and examining the mechanical integrity of the cells to determine if any defects may be allowing tritium to escape through the membrane, indicating high permeation or escape from inlet side, reducing the driving pressure. Effects of the ethylene glycol on the membrane are being considered.

Many further experiments are planned or in progress. These include measurements on more metals such as iridium, zinc, and beryllium; oxides, such as alumina or silica, amorphous metals, and ion-implanted materials.

Permeation Model

The following model provides a rationale for the observation that the experimental time-lag is greater than expected from extrapolated high temperature data. Three possible explanations for such a result exist. They are: 1) the gas concentration just inside the gas-metal interface is not at equilibrium with the gas phase; 2) permeation occurs through a multilaminate (oxide-metal-oxide); or 3) a combination of the two.

The model allows calculation of the diffusion constants through the oxide and metal, the gas-solid equilibrium constant at the interface, and the tritium concentrations just inside the metal and oxide. The variables are defined in Fig. 2. Layers A and C are the oxide; layer B is the metal. The gas concentration just inside each layer are the C's. The diffusion constant in each layer is labeled D, and the layer thickness is L.

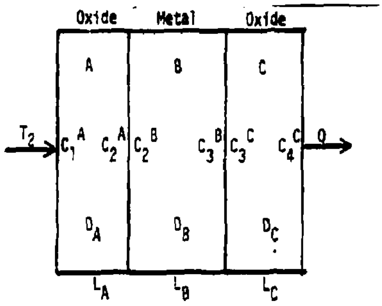

Fig. 2. Diagram of oxide-covered metal used in permeation model.

If we measure sample and oxide thickness, plot gas quantity permeated with time, and measure gas dissolved in sample, the permeability and time-lag can be calculated. If M is the amount absorbed at steady-state, and κ is the T (ads)/OH(ads) equilibrium constant, the following relationship exists:

$$M = \frac{\alpha\, C_1^A}{2\left[\frac{1}{L_A} + \frac{1}{L_C} - \frac{1}{\kappa_1 L_B}\right]}, \tag{3}$$

From experiment:

$$\kappa_1 = \frac{\frac{1}{L_B}\left[3Q_S - 3\phi t_S - 4\,\frac{M}{\alpha}\right]}{3Q_S\left(\frac{1}{2L_C} + \frac{2}{L_A}\right) - 3\phi t_s\left(\frac{1}{2L_C} - \frac{1}{L_A}\right) - \frac{4M}{\alpha}\left(\frac{1}{L_A} + \frac{1}{L_C}\right)} \tag{4}$$

From the slope of the Q vs. t plot, we obtain ϕ_S, the steady-state permeability where,

$$\phi_S = \frac{\alpha C_1^A}{\frac{L_B}{\kappa_1 D_B} + \left(\frac{L_A + L_C}{D_A}\right)} \tag{5}$$

From the time-lag intercept, τ, we obtain:

$$\tau = \frac{2\alpha C_1^A}{3\phi_S\left[\frac{1}{\kappa_1 L_B} - \frac{1}{2L_C} - \frac{2}{L_A}\right]} \tag{6}$$

After we evaluate K, experimentally D_A, D_B, and C_1^A can be evaluated from these three independent equations. This model will be used to evaluate the surface effects in our experiments.

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