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TRITIUM PERMEATION THROUGH MATERIALS FOR STEAM GENERATOR SYSTEMS*

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Proposed running head

"Tritium Permeation Through Metals"

ABSTRACT

Mixed isotope techniques and experimental apparatus have been developed for determining the rates of tritium permeation through metals at high temperatures. These methods are used primarily for observing the permeabilities of tritium through materials for steam generator systems. The techniques include the option of an inert gas or a controlled steam oxidizing atmosphere on the downstream side of the sample. Therefore, effects of surface oxidation and the formation of oxide coatings to impede tritium permeation can be determined. The validity of the method was demonstrated by determining the tritium permeability of nickel and comparing the tritium values to established hydrogen and deuterium permeabilities. The methods were applied in a long-term experiment by measuring tritium permeation through Incoloy 800 at 657°C with the downstream side of the sample continuously treated with a 750 torr sweep gas of Ar-H_2O with the H_2O partial pressure at 240 torr. The oxidation of the metal to form an oxide coating on the metal was accompanied by a decrease in the tritium permeation by a factor of 160 over a period of 84 days.

INTRODUCTION

The development of nuclear power stations and the potential loss of tritium to the environment has kindled the interest in hydrogen permeability through metals. The production of tritium by these facilities and the need to restrict losses of tritium to the atmosphere demand that we know the quantities of tritium that can escape by permeation through the construction materials. These factors are particularly significant in the development of deuterium-tritium fusion reactor systems where the plant inventories of tritium will be relatively high, and safety regulations restrict tritium release into the environment. In these future fusion power plants, the tritium that escapes from the plasma and blanket areas can be controlled by secondary containment and then processed and recycled back to the plasma. However, there will be a serious problem if too much tritium escapes from the blanket or coolant into the steam system by permeating through the walls of the steam generator. Removal of tritium from the steam system is not practical; therefore the permeation of tritium into the steam system must be minimized and must be known quantitatively.

The surface oxidation of metals to form oxide coatings on the metal is known to impede the permeation of hydrogen through the metal.[1-3] However, there is little quantitative information on this impedance, and little is known about the chemical and physical character of oxide films formed under steam generator conditions.[4] The best experimental results on this subject will come from studies where the permeation through a sample is measured while the oxidation proceeds and forms an oxide film. Experimental methods are needed for studying steam generator materials to determine the effects of at least four particular factors:

1. The quantitative effects of the oxide film to impede permeation, and the conditions which will produce a film with the greatest impedance. Impedance factors greater than 100 are needed for tritium management in fusion reactors.[5]

2. The pressure dependence of tritium permeation through metal-oxide composites. This will require nearly perfect oxide films so that in the experiment the tritium does not escape through cracks, holes, etc.

3. The chemical composition of the oxide coating. It is likely that particular oxides will have higher impedance factors, and alloys may have oxide coatings composed of several metal oxides. Then the chemical stability and composition of the coating is especially important.

4. The physical character of the oxide coatings and the effects of temperature cycling. There is concern that the physical integrity of effective oxide coatings may be destroyed when the temperature changes more than 100°C.

We have developed a mixed isotope technique and have built an experimental apparatus with a simulated steam generator. With this combination we can measure the permeation of tritium through a metal sample at high temperatures (up to 800°C) and with an oxidizing sweep gas on the downstream side of the sample. This paper describes the mixed isotope technique, the associated apparatus, validity of the methods by application to nickel, and the results of a long-term experiment observing the permeation of tritium through Incoloy 800 while the downstream side of the sample oxidized.

EXPERIMENTAL METHOD AND APPLICATION TO NICKEL

The experimental apparatus in this work is similar to that used earlier in a study of deuterium permeation.[4] The analytical techniques are different, but they can still be considered as tracer techniques. Potential hazards because of the radioactivity of tritium demand that experimental techniques use minimum amounts of tritium. The method basically consists of measuring the tritium that permeates from a T_2-HT-H_2-Ar (or other inert gas) feed gas through a specimen tube into a sweep gas that is predominantly Ar but may contain controlled amounts of H_2 and/or H_2O. The feed gas is prepared by mixing T_2 with a mixture of Ar-4% H_2. The conditions must be such that the hydrogen and tritium are isotopically equilibrated by the reaction

$$H_2 + T_2 \rightleftarrows 2\ HT \tag{1}$$

and the tritium pressure, p_{T_2}, may be expressed as

$$p_{T_2}^{1/2} = \frac{p_{HT}}{p_{H_2}^{1/2}\ K_p^{1/2}} , \tag{2}$$

where K_p is the equilibrium constant which is only slightly temperature dependent above 400°C.[6] Under the present experimental conditions, the ratio H_2/T_2 is large and essentially all of the tritium is present as HT. Hydrogen isotopes diffuse through metals as atoms, and the diffusing tritium atoms should not be influenced by the hydrogen atoms at these low concentrations.

A schematic diagram of the experimental apparatus is shown in Fig. 1. The feed gas flows at a constant rate into a heated quartz chamber maintained

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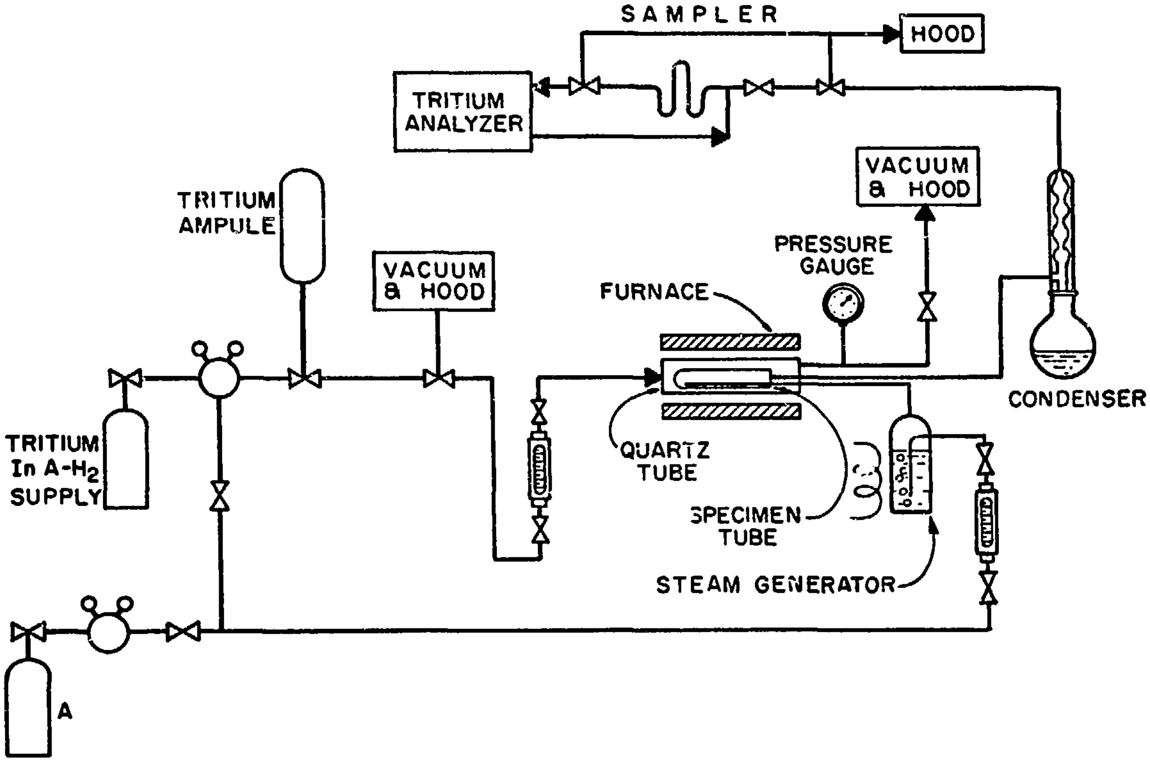

Figure 1. Apparatus for observing tritium permeation through metal samples under controlled oxidizing conditions.

within ± 1°C of a predetermined temperature. The sample temperature is determined from three thermocouples attached at equal intervals on the tube. Both hydrogen and tritium permeate the sample tube and are carried by a sweep gas from inside the tube to the analytical system. The oxidation potential of the sweep gas is controlled by adding H_2 and/or H_2O to Ar. The H_2O is added by passing the Ar through a steam generator which is simply a boiler with a condenser. The temperature of the condenser is controlled by a constant temperature bath and determines the partial pressure of H_2O in the sweep gas. In experiments with H_2O in the sweep gas, the tritium that permeates into the sample tube equilibrates with the H_2O, and the exhaust from the sample tube passes through a second condenser maintained at <15°C. Most of the tritium is trapped as HTO with the condenser, and the condensed sample is analyzed for tritium by liquid scintillation counting. The exhaust from the condenser is analyzed with a Johnson Laboratories Model 1055 B tritium gas analyzer, and the total tritium flux for a given time interval is the sum of the two analyses.

The flux, J, of tritium permeating through a metal sample has been derived[4] from Fick's law of diffusion and Sieverts' law of solubility to be

$$-J = \frac{DK_s}{x} [p_1^{1/2} - p_2^{1/2}] \tag{3}$$

where D is the diffusion constant, K_s is the Sieverts or solubility constant, x is the thickness (mm) of the sample, p_1 and p_2 are the upstream and downstream pressures of T_2, respectively. The product, DK_s, is permeability. Substitution of equation (2) into equation (3) gives

$$-J = \frac{DK_s}{x\, K_p^{1/2}} \left[\left(\frac{p_{HT}}{p_{H_2}^{1/2}} \right)_1 - \left(\frac{p_{HT}}{p_{H_2}^{1/2}} \right)_2 \right]. \tag{4}$$

Equation (4) rather than equation (3) is used with the mixed isotope technique, because the partial pressure of T_2 is too low for an accurate determination. The upstream pressures of HT and H_2 are determined from the factors in preparation of the feed gas, the flow rates, the mass spectrometric analysis of the original Ar-4% H_2, and from tritium analysis of the feed gas. The downstream pressure of HT is calculated from the tritium permeation flux, J, (experimentally determined as cc-atm of T_2 per min cm^2); the log mean area of the sample tube, A; the sweep gas flow rate, Z[cc(NTP)/min]; and a stoichiometry factor of 2 because there will be two times more HT than theoretical T_2. Then

$$p_{HT_2} = \frac{2 \cdot 760 \cdot A \cdot J}{Z} . \qquad (5)$$

Eqn. (4) is then used for converting observed data from the mixed isotope techniques into permeabilities. Values of K_p are taken from Jones' data.[6]

The validity of the mixed isotope techniques and the associated apparatus for permeability studies was proven by determining the tritium permeation through nickel. Nickel is a good standard for permeation measurements, because nickel does not form oxide films at oxidation potentials, p_{H_2O}/p_{H_2}, less than 100, and because the permeabilities of protium and of deuterium are well established.[4] For the first test, mixtures of T_2-He and Ar--3.5% H_2 were blended in several proportions to provide a variety of H_2 and T_2 (HT) pressures. The tritium permeated through the nickel tube into a flowing Ar--3.57% H_2 mixture. The tritium (essentially all present as HT under experimental conditions) was analyzed with a tritium gas analyzer. Table I gives eight values for tritium permeability through nickel at 836°K for various HT driving pressures. The average value of 1.9×10^{-4} [cc(NPT)·mm ·min^{-1}·cm^{-2}·$torr^{-1/2}$] agrees well with the value of 1.5×10^{-4} calculated

Table 1. Tritium Permeability, DK_s, through Nickel at 836°K.[a]

Total Pressure Upstream (torr)	$P_{H_2}^{1/2}$ (torr)$^{1/2}$		$10^3\ P_{HT}$ (torr)		$10^4\ P_{T_2}^{1/2}$ (torr)$^{1/2}$		$10^8\ J$ $\left[\frac{cc(NTP)}{min \cdot cm^2}\right]^b$	$10^4 DK_s$ $\left[\frac{cc(NTP) \cdot mm}{min \cdot cm^2 \cdot torr^{1/2}}\right]^b$
	Upstream	Downstream	Upstream	Downstream	Upstream	Downstream		
101[c]	1.31	5.21	1.56	0.474	6.04	0.472	12.4 ± 0.7	1.97 ± 0.1
225[c]	2.01	5.21	3.47	0.681	8.96	0.678	17.8 ± 0.5	1.91 ± 0.05
322[c]	2.40	5.21	4.96	0.826	10.7	0.823	21.6 ± 0.4	1.94 ± 0.03
484[c]	2.94	5.21	7.45	0.899	13.1	0.895	23.5 ± 0.02	1.70 ± 0.002
719[c]	3.58	5.21	11.0	1.40	15.9	1.39	36.7 ± 1.4	2.24 ± 0.08
263[c]	2.84	5.21	1.13	0.151	2.06	0.150	3.96 ± 0.12	1.84 ± 0.10
5.7[d]	0.3	5.21	0.124	0.0348	2.14	.0346	4.70	1.98
2.5[d]	0.2	5.21	0.0544	0.0162	1.41	.0161	2.19	1.39
							Avg.	1.87 ± 0.3

[a] Sample thickness = 0.889 mm; sample 146 cm^2.

[b] Uncertainty estimate for 95% confidence level.

[c] Downstream flow rate, Z, 58 cc(NTP) min^{-1}.

[d] Downstream flow rate, Z, 300 cc(NTP) min^{-1}.

from data for deuterium permeability through nickel by the equation[4]

$$DK_s = k \exp(-12800/RT), \qquad (6)$$

where k is 0.363, and R is 1.98 cal/mole•degree.

The temperature dependence of tritium permeation through nickel was measured over the 636-910°K range. A plot of log permeability vs T^{-1} is shown in Fig. 2 for 23 data points. The least squares fit of the data gives the equation

$$\ln DK_s \frac{\mathrm{cc(NTP)\cdot mm}}{\mathrm{min\cdot cm^2\cdot torr^{1/2}}} = -0.906 - 6.36 \frac{10^3}{T}, \qquad (7)$$

and the heat of activation for tritium permeation through nickel is 12.6 ± 0.4 kcal mole^{-1}. From these data k in equation (6) is 0.399 for tritium permeability through nickel.

The method was also tested using H_2O in the downstream sweep gas. A final evaluation experiment to determine tritium permeability through Ni at 836°K was conducted with the downstream sweep gas composed of H_2O, H_2, and Ar. Partial pressure ratios of H_2O/H_2 were 8.6 and 175, and corresponding permeabilities of 1.26×10^{-4} and 1.56×10^{-4} $\mathrm{cc(NPT)\cdot mm\cdot min^{-1}\cdot\ cm^{-2}\cdot torr^{-1/2}}$ were determined from the condensate and the exhaust of the condenser.

These evaluation experiments accomplished two feats. (1) The mixed isotope technique and the associated apparatus were shown to be ideal for studying tritium permeation through metals under controlled oxidizing conditions. This technique used with the reducing feed gas is an excellent way to avoid oxidation of the metal on the upstream side of the sample. (2) The first tritium permeation data for nickel were determined.

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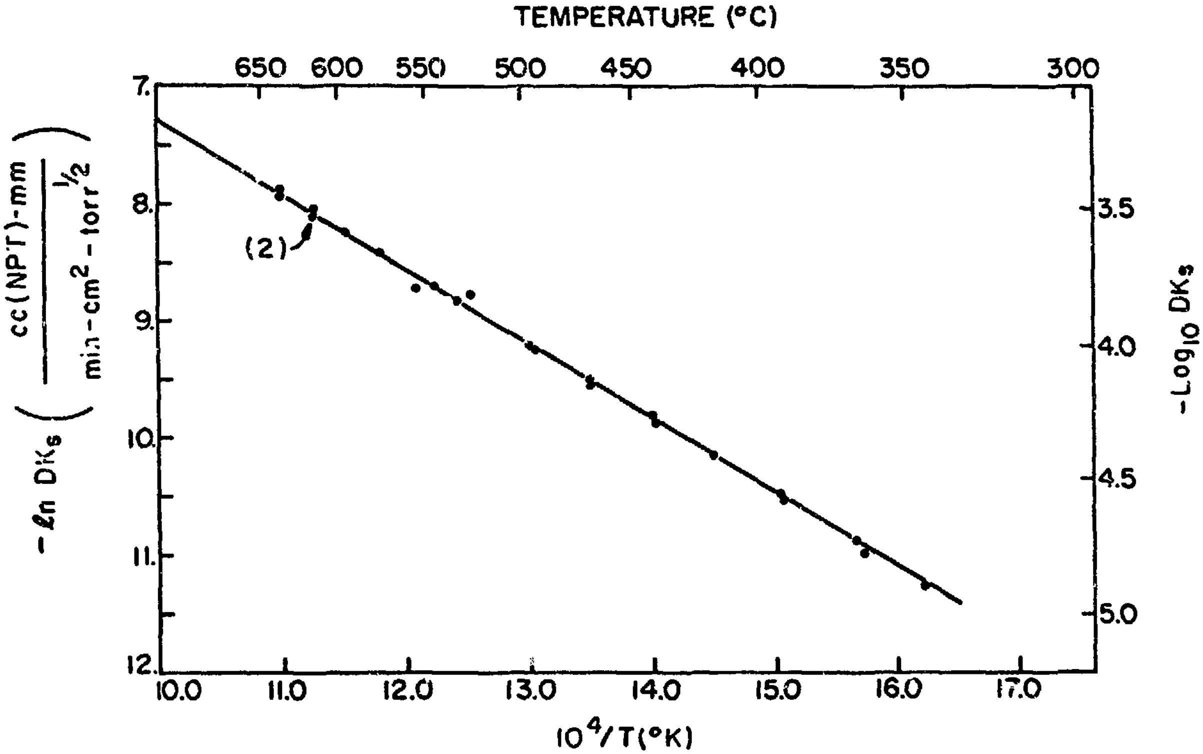

Figure 2. The tritium permeability through nickel over the 636-910°K range.

OXIDE COATINGS TO IMPEDE TRITIUM PERMEATION

The mixed isotope techniques and the associated apparatus with the oxidizing steam-argon sweep gas is being used to determine the effects of surface oxidation to impede tritium permeation through Incoloy 800, henceforth called I800. This alloy is an iron, nickel, chromium alloy with low concentrations of Si, Mn, Cu and C, and it is a candidate material for steam generators in fusion and fission reactor systems. I800 will oxidize, especially at high temperatures, and a feed-gas mixture of 4% H_2 in Ar will have enough H_2O as an impurity to oxidize the surface of an I800 sample. Thermodynamic data for the reaction of Cr with H_2O indicate that I800 will oxidize at 650°C in an atmosphere with the H_2O/H_2 ratio as low as 10^{-6}. It was desirable to oxidize only one side of the sample, so the upstream side of the I800 sample was protected with a layer of nickel. This was accomplished by using a duplex tube of 1/8-in.-thick nickel metallurgically bonded onto 1/8-in.-thick I800 as the sample specimen. Nickel does not oxidize under these upstream conditions and nickel has a higher permeability than I800. The driving pressure at the nickel-I800 interface can be calculated from the permeability of nickel and the upstream pressure. With the above described techniques applied to this sample, we measured the permeation of tritium through I800 at 657°C with a steam partial pressure of 240 torr in the argon sweep gas. The feed gas mixture was Ar-4% H_2 with 1.5 ppm HT. The permeability data for the I800 sample over an 84 day period are shown in Fig. 3.[7] The permeability was 1.6×10^{-4} $cc(NPT) \cdot mm \cdot cm^{-2} \cdot min^{-1} \cdot torr^{-1/2}$ before the steam was added to the argon sweep gas. This value cannot be assumed to be the permeability of clean I800 because there was some surface oxidation of the I800 by the trace amounts of

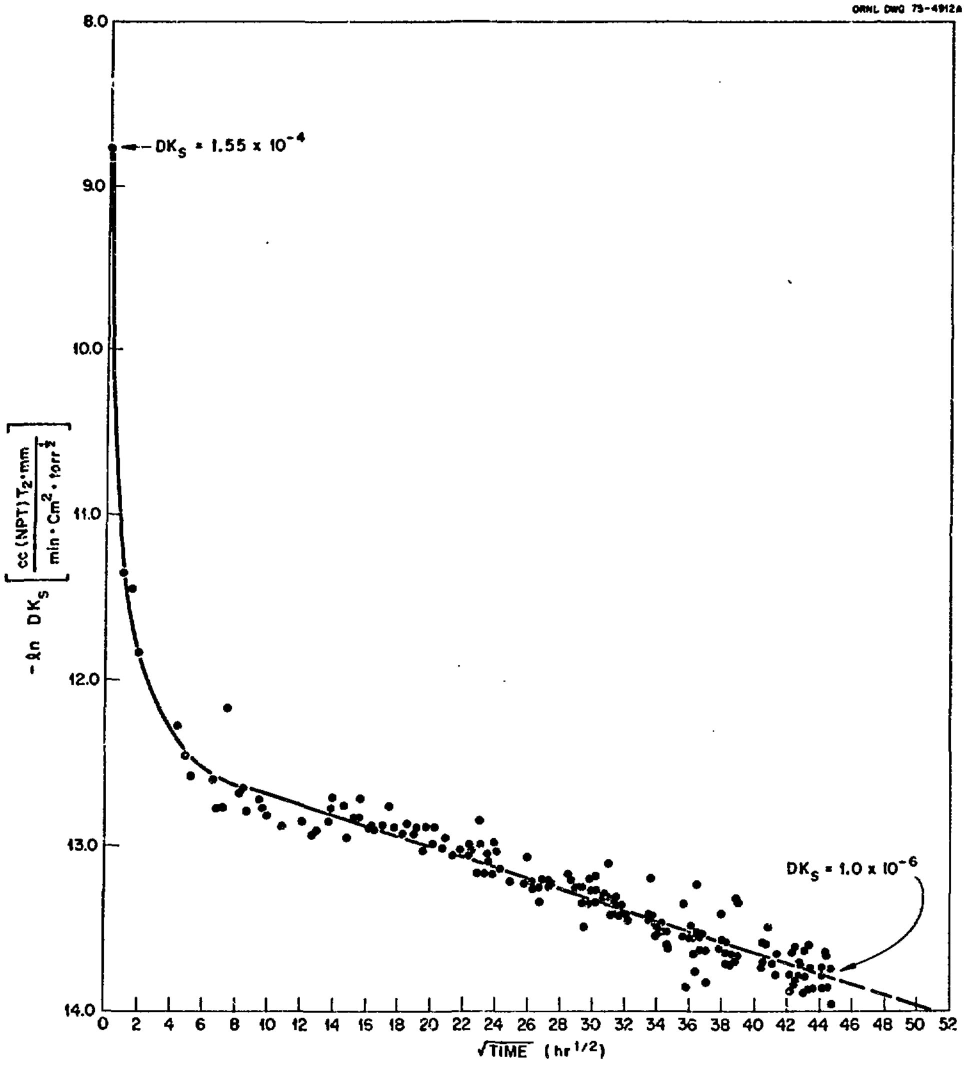

Figure 3. The permeability of tritium through Incoloy 800 at 930°K with 0.32 atm H_2O on the downstream side.

water in the argon before the steam was added. An oxidation potential of $<10^{-2}$ was calculated as the ratio of partial pressures for H_2O/H_2 in the initial sweep gas. Furthermore, the permeability of 1.6×10^{-4} is a factor of 6 greater than the earlier reported permeability of D_2 through I800 at 649°C, and indicates that the I800 sample in the earlier work had more surface oxide. In fact, the earlier sample was somewhat oxidized on both sides, whereas in the present work the upstream side of the specimen tube was protected from oxidation.

The time that steam was added to the sweep gas corresponds to zero time in Fig. 3. Immediately thereafter, the permeability rapidly decreased for 36 hr, and then decreased at a much slower rate linearly with the square root of time, $t^{1/2}$. This indicates that the surface of the I800 sample was completely covered with an oxide layer after 36 hr. The apparent linear relation between $\ln DK_s$ and $t^{1/2}$ for the 36 to 2016 hr interval has no particular significance. However, a linear fit of DK_s versus $t^{1/2}$ over the same time interval is statistically a better correlation and indicates that the permeability over this time interval is linearly dependent on the thickness of the oxide film. This interpretation is based on generalizations that the rates of oxidation for many metals are dependent on $t^{1/2}$. The linear dependence of DK_s on $t^{1/2}$ also indicates that the physical character of the oxide layer did not change during the 36 to 2016 hr time, and also suggests that the chemical composition of the oxide film did not change during the experiment.

The most important conclusion from the data in Fig. 3 is that the formation of the oxide layer on I800 at these conditions for a period of 84 days decreased the permeability of the sample by a factor of 160. An impedance of this magnitude will be significant in reducing the amount of tritium that escapes from a reactor coolant into the steam system. Furthermore, extrapolation of these data indicates that the tritium permeability of this sample under these conditions would be reduced by a factor of 10^3 after 7 months.

There are three important questions that follow these results which will need to be answered in future experiments: (1) After the oxide layer is formed, what is the relation between the permeability and the tritium pressure, (2) How will temperature cycling affect the physical integrity of the oxide coating, and (3) How do these data relate to systems with high steam pressures on the downstream side. The goal of continuing experiments is to answer these questions and others that may arise.

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7. The experiment is continuing and the permeability continues to diminish. At a later time, the temperature will be cycled to determine such effects on the physical integrity of the sample.

LIST OF FIGURES