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TRITIUM PERMEABILITY OF STRUCTURAL MATERIALS
AND SURFACE EFFECTS ON PERMEATION RATES*

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Tritium management in any system always will include containment such that tritium release rates will be less than established limits and also will be as low as practical. The well known properties of hydrogen to permeate through most materials make the complete containment of tritium an impossible task. However, tritium release rates from a given system can be minimized by two primary efforts. First is the selection of a compatible containment material which frequently also will be the structural material. This effort should include films and barriers that would be compatible with the structural material. Second and sometimes more important, the material should have surface chemistry in the particular system that continuously impedes tritium permeation.

Containment

Construction materials generally are limited to the iron-chromium-nickel alloys and several publications each have reported hydrogen permeabilities of one or a few alloys [1-3]. More recently the permeabilities of three ferritic alloys were compared to three austenitic alloys and one high nickel alloy [4]. That work [4] was unusual, because it was able to show systematic differences in permeabilities between the f.c.c alloys and the b.c.c. alloys and also systematic differences within each of the two types of alloys. Those differences were observable because the permeabilities for the different materials were determined by identical techniques and with care to avoid surface oxidation.

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Tritium containment by the lamination of thin layers of low permeability materials onto or by painting surfaces of construction alloys is conceivable and frequently discussed. However, there is no experimental evidence of significant tritium containment at high temperatures by those techniques. Some permeation impedance factors that could be expected with laminated metals have been presented [5,6], and the current evaluation of lamination techniques is that they are not practical with current technology and materials. However, painting an alloy with a material that at high temperature forms a glass or an oxide coating may be a technique worthy of development.

A construction material that reacts with its environment to completely cover its surface with a thin layer of low permeability material, i.e., an oxidation product, may be the best technique to minimize tritium permeation. Several papers describe observations that oxide layers on construction metals reduce hydrogen permeation rates through those materials [7-13] sometimes by as much as three orders of magnitude. Such permeation barriers would be adequate for tritium containment in most systems. However, there has been no demonstration of such barriers under realistic operating conditions, namely high temperatures.

This paper will review primarily the recent tritium permeation studies at the Oak Ridge National Laboratory and will present some conclusions pertinent to tritium containment. The dependence of permeation rates through various materials as functions of hydrogen pressures will be discussed first. The permeabilities of austenitic and ferritic alloys will be compared and final consideration will be the in-situ measured permeation rates through alloys while they were oxidized by steam. The barrier properties of the identified oxides will be correlated to the chemical compositions of the oxides.

Pressure Dependence of Hydrogen Permeation from Mixed Isotope Sources

There are two mechanisms by which hydrogen can permeate through materials; atomic diffusion after surface dissociation and molecular diffusion. Permeability is the product of solubility and diffusivity, and the rate controlling step in either mechanism generally will be diffusion through the bulk. The permeation mechanism is thus the same as that for solubility and discussions can be simplified to those for solubility. Since tritium usually will be accompanied by protium, containment should consider mixtures of the isotopes, and should include systems with near equal and with very unequal quantities of the isotopes. The general equations for hydrogen concentration as atoms, S_a , and as molecules, S_m , into materials are, respectively,

$$S_a = K_o \exp(-\Delta H/RT) P^{\frac{1}{2}}, \quad (1)$$

and

$$S_m = K'_o \exp(-\Delta H'/RT) P, \quad (2)$$

where K_o , ΔH and P are respectively the solubility constants, the heats of solution and the pressures. The term $K_o \exp(-\Delta H/RT)$ is the solubility, K_s . Then for a pure tritium source;

$$S_T = K_s P_{T_2}^{\frac{1}{2}}, \quad (3)$$

and

$$S_{T_2} = K_{m,s} P_{T_2}. \quad (4)$$

Mixtures of protium and tritium in hot metal systems usually will be at equilibrium as

and the equilibrium constant is near 3.9 for temperatures above 300°C. Before considering the solution of isotope mixtures, it is of interest to consider a hypothetical system of HT in equilibrium with a solution of atoms and of molecules in materials as

and

The equilibrium solubility constants for equations 6 and 7 are respectively

$$K_{\text{eq}} = \frac{[\text{M} \cdot \text{H}][\text{M} \cdot \text{T}]}{P_{\text{HT}}} = \frac{[\text{M} \cdot \text{T}]^2}{P_{\text{HT}}} , \quad (8)$$

and

$$K'_{\text{eq}} = \frac{[\text{M}' \cdot \text{HT}]}{P_{\text{HT}}} . \quad (9)$$

Then from equations 8 and 9 the concentrations of tritium atoms and of HT molecules in the materials are respectively

$$S_{\text{T}} = K_{\text{eq}} P_{\text{HT}}^{\frac{1}{2}} , \quad (10)$$

and

$$S_{\text{HT}} = K'_{\text{eq}} P_{\text{HT}} . \quad (11)$$

It is interesting that the solubility of tritium atoms into a material from a hypothetical pure HT source is one-half power dependent on the HT pressure, similar to equation 3 for a pure T_2 source.

In an equilibrium mixture of protium and tritium the pressures of HT and T_2 are mutually dependent, equation 5. If the pressures were independent as sometimes considered, the solubility of tritium atoms would be

$$S_{\text{T}} = K P_{\text{T}_2}^{\frac{1}{2}} + K' P_{\text{HT}}^{\frac{1}{2}} ;$$

and when $P_{HT}^{\frac{1}{2}} \gg P_{T_2}^{\frac{1}{2}}$ the solubility is essentially

$$S_T = K' P_{HT}^{\frac{1}{2}} .$$

The experimental tritium permeation rates through metals with equilibrium mixtures of the isotopes where $P_{HT} \gg P_{T_2}$ and with a fixed H_2 pressure have always been first power dependent on P_{HT} ; the above equations for the mutually independent HT and T_2 systems are invalid. Therefore, only the mutually dependent system should be considered, and the concentration of tritium atoms dissolved from a T_2 -HT source is

$$S_T = K_s P_{T_2}^{\frac{1}{2}} = K_s \frac{P_{HT}}{K_e P_{H_2}^{\frac{1}{2}}} . \quad (12)$$

Observed permeation rates through metals mentioned above have always obeyed equation 12. Rates have not been observed from a source of near equal pressures of T_2 and HT, but such rates should also obey equation 12.

The concentration of HT and T_2 molecules in a material from any mixture of the isotopes would be

$$S_{HT} + S_{T_2} = K P_{HT} + K P_{T_2} , \quad (13)$$

and the total tritium permeating as molecules through a material would be based on equation 13. However, when $P_{HT} \gg P_{T_2}$ the tritium permeation flux would be dependent essentially only on P_{HT} which is dependent on the product $P_{T_2}^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}$. Then the amount of tritium permeating as molecules from a mixed source with essentially constant P_{H_2} would erroneously appear to be 0.5 power dependent on P_{T_2} .

Tritium permeation rates from an equilibrium source of protium and tritium with atomic diffusion through the material may be expressed as

$$J = DK P_{T_2}^{\frac{1}{2}} = DK \frac{P_{HT}}{K_e^{\frac{1}{2}} P_{H_2}^{\frac{1}{2}}}, \quad (14)$$

and rates from an equilibrium source of protium, deuterium and tritium may be expressed as

$$J = DK P_{T_2}^{\frac{1}{2}} = DK \frac{(P_{HT})^{\frac{1}{2}} (P_{HD})^{\frac{1}{2}} (P_{DT})^{\frac{1}{2}}}{K_e^{\frac{1}{2}} (P_{H_2})^{\frac{1}{2}} (P_{D_2})^{\frac{1}{2}}}. \quad (15)$$

Equation 14 and 15 were previously derived [14] and are here considered only to show new higher pressures of protium or deuterium in equilibrium with a given amount of tritium will reduce tritium permeation rates. This isotope dilution and equation 14 are diagrammed in Figure 1. The tritium permeation rate decreases from an initial rate for a pure T_2 source as the amount of H_2 and hence HT are increased and when the maximum HT pressure is approached the tritium permeation rate becomes inversely related to the square root of the H_2 pressure. A more complicated discussion for an equilibrium tri-isotope source would be necessary and should be considered when the three isotopes are present.

Tritium Permeabilities of Clean Metals

Experimental measured permeabilities of several austenitic and ferritic alloys have indicated that the inherent permeabilities of alloys are not important parameters in selecting construction materials for tritium containment. However, it is interesting to note the differences in the observed permeabilities of austenitic and ferritic materials. Accurate permeability rates through clean construction alloys at high temperatures are difficult to observe because the alloys contain metals that are extremely susceptible to oxidation. This difficulty as previously discussed [14] forces one to protect the alloy

surface with a metal that does not oxidize under the experimental conditions and that does not affect permeation. We have measured tritium permeabilities of nine clean construction alloys and avoided surface oxidation by first electroplating both sides of the tube samples with 7.6 μm of nickel. Diffusion through the thin layers of nickel was not significant, and the tritium permeabilities of the construction alloys, a tungsten alloy and nickel are shown in Figure 2 for the 550 to 1000 K range. Permeabilities of the seven structural alloys at 1000 K are all within a factor of 2.3 while at 500 K there is a factor of 30 between the highest and lowest. This division coincides with a separation of the ferritic alloys from the austenitic and high nickel base alloys. Similarities and differences in the permeabilities of the nine alloys divide these materials into two groups as can be seen in Figure 2. The fundamental difference in ferritic and austenitic alloys is the body-centered, b.c.c., versus respectively the face centered cubic, f.c.c., structures (the high nickel alloys also have the austenitic structure), and it appears that alloy permeability is related to crystal structure. The face-centered cubic structure is approximately 8% more dense than the body centered cubic structure of the ferritic alloys. In a phenomenological sense, the less dense structure could be expected to have the lower permeation activation energy, as well as the lower pre-exponential or permeability constant, which is related to entropy. The less dense structure likely would accommodate the tritium atoms with an overall smaller change in the entropy of the system.

Permeabilities of three sintered tungsten alloys also are shown in Figure 2. The nickel/iron ratios were about two. The permeability of these tungsten materials suggest that pure tungsten at 1000°K would have permeability of $\sim 3 \times 10^{-6} \text{ cc(STP) \cdot mm / (min \cdot cm}^2 \cdot \text{torr}^{\frac{1}{2}})$ which is about a factor of 30 greater

than hydrogen permeabilities for tungsten that are reported in the literature [15]. The difference at 500°K would be even greater. These differences suggest that permeabilities of tungsten should be reexamined or that small amounts of first row transition elements alloyed with tungsten greatly increase the permeability.

In Situ Formed Oxide Coatings Reduce Tritium Permeabilities

A few reports describe hydrogen permeation rates through alloys that were measured while the alloy oxidized, [7-11,15] and those works demonstrate that the in-situ surface oxidation of construction alloys can produce oxide barriers that reduce tritium permeation rates by significant factors. However, all such results have limitations when applied by extrapolation to operating systems with high temperature and corrosive conditions. Therefore, one must consider current conclusions of permeation barrier effects only as indications of effects under actual operating conditions.

The effects of 0.3, 0.7, and 0.94 atm H₂O to oxidize Incoloy 800 at 520, 660, and 725°C, to form oxide layers and to reduce tritium permeation rates, were described recently [16]. The largest effect was observed with 0.94 atm H₂O at 660°C; lower H₂O pressures gave smaller effects, Figure 3. A rapid decrease in permeability occurs during the first 30 hrs and is followed by a slower decrease such that the logarithm of permeability becomes linear with respect to the square root of time. Apparently the surface of the metal is effectively covered during the early times and thereafter the permeability decreases as the thickness or depth of the oxide increases. The depth of the oxide layer with respect to time is a measure of the oxidation rate, and is primarily a function of the rates at which the metal atoms and the water molecules encounter each other. Similar studies indicated

that the oxidation at 520°C was much slower than that at 600°C and the barrier effects were significantly lower. However, the material could be oxidized at a higher temperature, 660°C, and the temperature then reduced to 520°C and a barrier effect was observed at 520°C that was equivalent to that at 660°C. Even though the oxidation was faster at 725°C, the permeation barrier effect was lower than that at 660°C.

Permeation rates through Incoloy 800, stainless steels 316 and 406 at 660°C into 0.94 atmospheres steam were measured for long period of time. The relative decreasing permeabilities as the surface oxide grows are shown in Figure 4, and permeation barrier factors are given in Table 1. After about six days the permeability decreased approximately linearly with time. Austenitic stainless steel 316 did not produce an oxide permeation barrier of any significance. Another experiment with modified SS 316; i.e. with 1% titanium added, indicated that a titanium additive would not improve the barrier. Several experiments with a different batch of Incoloy 800 suggested that the cold-worked material produced oxide coatings that were less effective permeation barriers, and that preannealing those materials increased the barrier factors. Only one sample of the ferritic SS 406 has been investigated.

Analysis of the Barrier Oxides

Analysis of the oxides on Incoloy 800 produced by 0.94 atm H₂O oxidation at 520, 660, and 725°C was reported recently [17]. Depth-profile metal compositions through the oxide were determined by ion microprobe analysis

Table 1. Permeation barrier factors on three structural materials
materials at 660°C produced by 0.94 atm steam oxidation

	Initial DK_s	Factors by which permeabilities are reduced (days)				
		0.33	1	6	24	40
Austenitic SS 316	8.8×10^{-5}	—	1.6	2.8	3.8	4.3
Austenitic Incoloy 800	9.2×10^{-5}	7	11	55	91	129
Ferritic SS 406	16.2×10^{-5}	13	72	144	291	434

as functions of oxidation time, temperature, and of the pretreatment of the material surface. Those results indicated that the chemical composition of the oxides depended on all of those parameters as well as on the composition of the alloy and on the oxidation potential imposed on the alloy.

Oxides produced on Incoloy 800 were highly uniform and average thicknesses varied from 0.9 to 2.4 microns, thicker oxides being produced by higher steam pressures and higher temperatures. The ion microprobe profile for the sample exposed to 0.94 atm steam at 660°C for 3100 hours is shown in Figure 4. This is typical of oxides found on samples exposed at 520 or 660°C, in that high chromium and manganese and only minor amounts of iron and nickel were found. Such significant enrichment of manganese is surprising in that it comprised less than one atom percent of the bulk Incoloy 800. X-ray diffraction experiments showed this oxide to contain a hexagonal phase with lattice constants $a_o = 4.99$ and $c_o = 13.60 \text{ \AA}$, corresponding to Cr_2O_3 , and a cubic structure with lattice constant $a_o = 8.45 \text{ \AA}$, corresponding to a spinel phase of approximate stoichiometry MnCr_2O_4 . The oxide produced on the sample exposed at 725°C for 3000 hours was enriched in manganese to 80% at the steam-oxide interface. Diffraction experiments on this sample showed Cr_2O_3 , a small amount of MnCr_2O_4 , and a tetragonal phase of lattice constants $a_o = 5.78$ and $c_o = 9.35 \text{ \AA}$, which correspond well with $\gamma\text{Mn}_2\text{O}_3$. Generally, trends of higher manganese enrichment in oxides were seen with higher exposure temperatures and longer exposure times.

Oxides that were produced SS 316 were about 30 nm thick and essentially were all iron oxides. The oxide layer on SS 406 was thin, 1-5 nm, and the good barrier characteristics are believed to be related to the aluminum content in the alloy.

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Figure List

- Figure 1. The decrease in tritium permeation rate, Q_s from an initial rate, ${}^{0p}Q_s$ as protium is added to a given amount of tritium, ${}^{0p}T_2$.
- Figure 2. Tritium permeabilities of clean metals and alloys.
- Figure 3. Tritium permeabilities of Incoloy 800 at 660°C as the alloy is oxidized by water and forms an oxide surface layer.
- Figure 4. Tritium permeabilities of three construction alloys at 660°C as the alloys are oxidized by water at 0.94 atm (94 kPa).
- Figure 5. Relative composition of metals in an oxide formed on Incoloy 800 at 660°C and exposed to 0.94 atm (94 kPa) water for 3600 hrs.

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The Tritium Permeation Rate (Q) Decreases From an Initial Rate (0Q) as Hydrogen is Added.
 (Nickel at 10^3 °K, 1- cm² Area, 1-mm Thick)

— Lim. D₁₀ — $\frac{CC(200) T_{20} T_{2000}}{T_{2000} CC(200) T_{20} T_{2000}}$

Permeation of Tritium Through Incoloy 800 at 660 °C Exposed to Three Sub-atmosphere Steam Pressures.

STEAM CORROSION INCOLOY 800, STAINLESS STEEL
 TYPES 316, AND 406 AT 655°C WITH
 126 PS STEAM PRESSURE

Figure 5

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ELEMENTAL COMPOSITION OF STEAM OXIDIZED INCOLOY 800 ELECTROPOLISHED TUBE