INL/CON-17-41968-Revision-0

Tritium permeability measurement in hydrogen-tritium system

M. Shimada, R.J. Pawelko

April 2018

INL/CON-17-41968-Revision-0

Tritium permeability measurement in hydrogen-tritium system

M. Shimada, R.J. Pawelko

April 2018

Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy

Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

FUSENGDES-D-17-00725 manuscript (Final version)

Tritium Permeability Measurement in Hydrogen-Tritium System

M. Shimada* and R. J. Pawelko

Fusion Safety Program, Idaho National Laboratory, Idaho Falls, ID, 83415, U.S.A

Understanding of thermodynamic equilibria of multi-components hydrogen isotopes is required to accurately measure tritium permeability at the expected low tritium partial pressure and non-negligible high hydrogen partial pressure in a fusion blanket system. A gas-driven tritium permeation system that is capable of independently controlling hydrogen and tritium partial pressures was developed at Idaho National Laboratory to accurately measure low partial pressure tritium permeability. The thermodynamic equilibria for hydrogen (H) - tritium (T) permeation through metal are discussed to accurately measure tritium permeability, and the experimental conditions required for evaluating tritium permeability in H-T system are presented.

Keywords: hydrogen, tritium, reduced activation ferritic/martensitic steel, permeation, blanket,

1. Introduction

Fusion power promises to provide electricity generation with outstanding safety and environmental performance. Safety plays a crucial role in fusion material selection since tritium behavior in materials determines two key safety evaluation source terms: in-vessel inventory source term (i.e. tritium retention) and ex-vessel release term (i.e. tritium permeation), which are used in reactor safety assessments for licensing fusion facilities [1,2]. Tritium permeation through materials at elevated temperature in test blanket system (TBS) is one of major tritium safety issues in ITER and an advanced understanding of tritium behavior in realistic TBS conditions is required to minimize tritium permeation to the port cell. Extensive work on hydrogen and deuterium behavior in fusion materials has been conducted, but only a very small database is available for tritium, the radioactive fuel for future reactors, due to the cost and difficulty associated with handling tritium [3-5]. Hydrogen isotope permeation in the fusion material is mostly investigated with high hydrogen partial pressure system with mono hydrogen isotope (p_{Q2}>1000 Pa where Q=H or D) in the primary side (high hydrogen isotope partial pressure side) and vacuum in the secondary side (low hydrogen isotope partial pressure side) [3-5]. Although these high partial pressure mono-component hydrogen permeation experiments provide variable fundamental databases of hydrogen isotope behavior in high partial pressure (diffusion-limited regime), the surface condition or/and impurities (especially background hydrogen gas) can have a profound impact on tritium behavior in material at low tritium partial pressure [6-7]. The physics of hydrogen (H) - tritium (T) permeation through metal are still poorly understood to confidently design environmentally benign and safe fusion systems at this moment.

Beta detection methods provide excellent detection sensitivities of tritium, enabling us to investigate permeation behavior at low tritium partial pressure, which cannot be achieved using either hydrogen or deuterium. In-line ionization chambers are one of most widely used diagnostics to measure tritium (HT or HTO) in gaseous environments from room air tritium monitoring to tritium detection in permeation experiments [8-13]. Ionization chambers provide superb detection sensitivity (e.g. ~ 1×10^{-6} Ci/m^3 for 1,000 cc chambers) and linear response in the wide range of tritium concentration from 0.386 parts per trillion (~1×10^{-6} Ci/m^3 at standard temperature and pressure, STP) to pure tritium (~ 2.589×10^{6} Ci/m^3 at STP). Special care, however, is needed when the ionization chambers are used for tritium permeation measurements at low partial pressure. When pure helium gas was used as a sweep gas in low tritium partial pressure, the equilibrium was not achieved after 30,000 seconds following the start of the tritium permeation test of Japanese reduced activation ferritic/martensitic steel (RAFM) F82H at 673K [11]. The tritium permeation should have been equilibrated after 100's of seconds, but the extra time was required for the tritium molecules to reach surface equilibrium with the dissolved tritium atoms along the inner surface of the tubing connecting the permeating surface to the detector system. Others also observed the effects of tritium dissolved on the wall of the tubing between the permeating surface and detector system, and it is common practice to add a trace amount of hydrogen gas (H_2) in a sweep gas to obtain a faster ionization chamber detection response [12,13]. Additional care is needed when a trace amount of H_2 is used in a sweep gas during a tritium permeation experiment since the existence of H_2 creates multi-hydrogen isotope system in both the primary and secondary sides. When the trace amount of H_2 is only added in the secondary side sweep gas, H permeates from the secondary side to the primary side, creating H-T counter-permeation system [14]. In order to accurately measure tritium permeability in the H-T system, one must measure both H_2 partial pressure (p_{H2}) and T_2 partial pressure (p_{T2}) in both the primary and secondary sides. The poor detection sensitivity of hydrogen (> 1 parts per million) often poses a critical

---

**Corresponding author address: 2525 N. Fremont Ave., Idaho Falls, ID, 83415, U.S.A.*
**Corresponding author E-mail: Masashi.Shimada@inl.gov*

challenge in measuring low H_2 partial pressure in the H-T system.

As an example of practical applications, a 1000-ppm (0.1 %) hydrogen-helium gas mixture is used as a purge gas at total pressure of 101,325 Pa in the Korean (KO) helium cooled ceramic reflector (HCCR) Test Blanket System (TBS) [15]. The estimated tritium partial pressure in the purge gas stream is less than 10 Pa, and the p_{H2} is higher than the produced HT partial pressure (p_{HT}, tritium is mostly as HT form due to $p_{H2} >> p_{HT} >> p_{T2}$) in the KO TBS purge gas. Improved understanding of tritium permeation behavior in RAFM steel under the H-T system is required to minimize the uncertainty associated with tritium release to the rooms that the TBS pipes pass through (e.g. TBS port cell, Tokamak cooling water systems vault annex) in the Tokamak building for ITER TBS safety. It is important to note that it is challenging to accurately estimate tritium permeability from the H-T system (typically low T_2 partial pressure and high H_2 partial pressure) to negligibly low hydrogen isotope partial pressure due to the decrease of H_2 partial pressure in the H-T co-permeation. Here, we intentionally maintained the identical H_2 partial pressures in both permeation sides, and developed an experimental setup and theory to accurately measure tritium permeability in the H-T system.

In this paper, we discuss the development of a tritium permeation system for low tritium partial pressure in Section 2, the theory of tritium permeability measurement in the H-T system in Section 3, and the required experimental condition for accurately measuring T permeability in Section 4.

2. Experiment

2.1 Experimental Apparatus

The Tritium Gas Absorption Permeation (TGAP) system is a vertically standing permeation system that was designed to study tritium absorption and permeation in both solid disc (such as RAFM and tungsten) and liquid materials (such as lead lithium eutectic) and is contained within a ventilated enclosure to minimize worker's tritium uptake [16, 18]. The permeation experiment test section consists of two solid gold (Au) wire-rings that are used to seal a disc sample between two custom-made 54.0 mm OD 316 stainless steel flanges as shown in Figure 1. The test section is installed inside quartz tubing to minimize tritium permeation to the ventilated enclosure. Gold has the second lowest tritium permeability in metal next to tungsten, and solid Au wire rings (e.g. wire diameter of 1 mm) minimize tritium permeation through the O-rings to the quartz tubing [3-5]. A series of COMSOL tritium modeling was performed to understand tritium permeation loss through the test section to the quartz tubing [17,18]. The COMSOL modeling confirmed that the tritium permeation loss to the quartz tubing was negligible for the typical experimental conditions [17,18]. Three test sections were fabricated for testing three different sample sizes (OD of 6.0, 10.0, and 20.0 mm). The sample thickness is typically between 0.5 and 2.0 mm.

Four thermocouples (TC) are inserted (two TC from top and two TC from bottom) to measure the sample temperature at four different locations. The four TCs (TC0, TC1, TC2, and TC3) readings typically agree within 5 K, and one TC, (TC0) is used to control the tube furnace power and the sample temperature by means of a National Instrument (NI) LabVIEW data acquisition and control system. The TC0 is typically maintains the desired sample temperature within ± 2K for the duration of the tritium permeation experiment. Maximum achievable temperature is 873K in the TGAP system. A detailed description of the TGAP system is provided elsewhere [16]. Two 1000 Torr range capacitance manometers (MKS Instruments) are used to measure the total pressure in the primary side (pP) and the secondary side (sP). Two mass flow controllers (Sierra Instruments) are used to control and monitor the mass flow rates in the primary side (pF) and the secondary side (sF). A 10 cm^3 ion chamber (Tyne Engineering) is used to measure the tritium concentration in the primary side (pIC), and a 1,000 cm^3 ion chamber (Tyne Engineering) is used to measure the tritium concentration in the secondary side (sIC). Two additional TCs are located at the ionization chamber locations and are used to measure the gas temperatures in the primary side (pTC) and the secondary side (sTC).

A Tritium Source System (TSS) was constructed to independently control H_2 and T_2 partial pressures in the balance helium (He) gas stream to the primary side. The TSS consists of a pressure vessel (maximum operating pressure at $2.3x10^6$ Pa) with several mass flow controllers (Sierra Instrument). Prior to mixing, the pressure vessel was baked at 573 K for 24-48 hr to remove moisture and outgas residual gas. Pure tritium gas was initially filled into a tritium transfer cylinder (volume 11.35 cm^3) using INL's Tritium Storage and Assay System. The tritium-filled cylinder was transferred to the TSS and the tritium gas was expanded into the TSS volume of 3770.24 cm^3. Maximum allowable inventory in TSS is 25 Ci. A commercially available 1000-ppm H_2-He gas cylinder was used to pressurize the TSS volume to approximately $2.0x10^6$ Pa. The majority of tritium is converted to HT form in the TSS due to high (1000-ppm) hydrogen concentration. It is important to note that we intended to keep the hydrogen partial pressure always higher than tritium partial pressure to satisfy the $p_{H2} >> p_{HT} >> p_{T2}$ condition and keep majority of tritium in the form of HT. The 1000-ppm H_2-He mixture was also used as a sweep gas in the secondary side to keep the H_2 partial pressure identical in both primary and secondary side. At a total pressure of 100,000 Pa, the 1000-ppm H_2-He mixture provides approximately 100 Pa of H_2 partial pressure.

During a permeation experiment, a 50 standard cubic centimeter per minute (sccm) of H_2-HT-He gas mixture flows from the TSS to the primary side through a molecular sieve trap (pMST) to remove the moisture in the primary gas. Similarly, a 200 sccm of H_2-He sweep gas flows through a molecular sieve trap (sMST) to remove the moisture in the secondary gas. Two moisture sensors (General Electrics) measure the moisture level in the primary (pMOS) and the secondary (sMOS). Tritium containing process gas from the primary and secondary sides is routed to the tritium exhaust processing (TEP) system prior to being exhausted to the stack. The TEP is equipped with 4 catalyst-bubbler sets (3 for secondary, 1 for primary). Each catalyst-bubbler set consists of a catalyst bed (e.g. platinum coated alumina and/or copper oxide) with a resistive heater, and two sets of 30 cm^3 bubblers (e.g. ethylene glycol or water) to convert elemental tritium (HT) to tritiated water (HTO) in a catalyst and to collect the HTO in bubblers with up to 99.99 % efficiency. Two different sets of catalyst beds and bubblers are used to measure the integrated amount of tritium radioactivity for the primary and secondary. The tritium concentrations in the bubblers are measured with a liquid scintillation counter (Beckman).

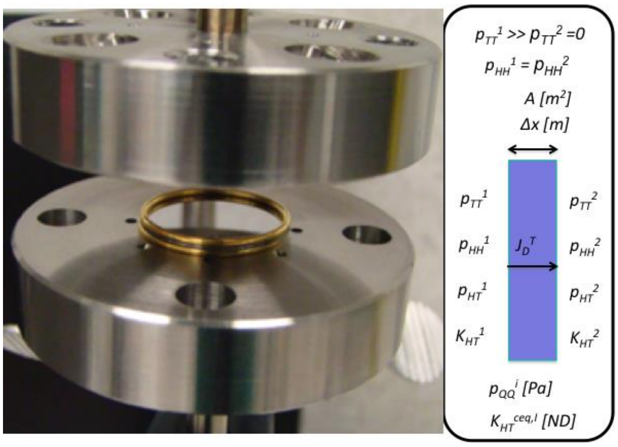

Figure 1: (Left) Photo of TGAP test section. Two solid gold (Au) wire-rings to seal disc a sample between two custom-made 2 1/8" OD stainless steel flanges. (Right) Schematic of tritium permeation in H-T system.

2.2 Comparison of tritium measurements by ion chamber and liquid scintillation counter

The ionization chambers and the liquid scintillation counter are the two key instruments for tritium concentration measurement in the tritium permeation experiment. We utilize ionization chambers for moderate to high HT partial pressure measurement, and use bubbler (liquid scintillation) counting for low HT partial pressure measurement. Comparisons of measured HT partial pressures between ion chambers (p_{HT}^{IC}) and liquid scintillation counter (p_{HT}^{BL}) were carried out at the wide HT partial range from 10^{-7} Pa to 1 Pa as shown in Figure 2. It is important to note that the radioactivity (e.g. Ci/m^3 and dpm/ml) measured was converted into HT partial pressure for this calibration. Various HT partial pressures of the HT- (100Pa) H_2-He gas mixture were flowed through the ion chambers. When the ion chamber reached an equilibrated HT concentration, the gas mixture was then flowed through the catalysis beds and bubbler systems for 150 minutes. The flow rates through the pIC and sIC were of 50 and 200 sccm respectively. The HT partial pressures calculated by the time-averaged ion chamber response were compared against the HT partial pressures calculated using integrated HT bubbler concentrations. The 10 cm^3 ion chamber (shown in solid circle in Figure 2) was used for higher HT partial pressure measurement, and the 1000 cm^3 ion chamber (shown in solid square in Figure 2) was used for lower HT partial pressure measurement. The high HT partial pressure measurements manifest good agreement between the 10 cc ionization chamber and the bubbler measurement. The possible reason for some discrepancy (the lowest HT partial pressure in 10 cc ionization chamber) is the memory effects of the ionization chamber. Excellent agreements were obtained for low HT partial pressure measurements between the 1000 cc ion chamber and the bubbler measurement. The ion chamber responses (typically calibrated with air at STP) were corrected for the (100Pa) H_2-He mixture [9].

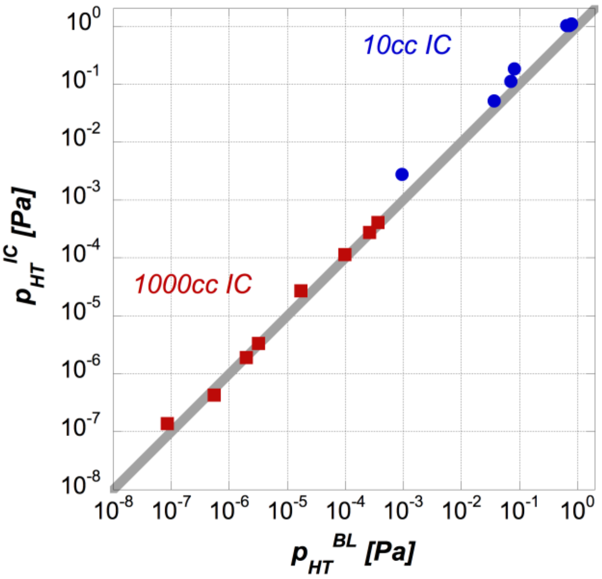

Figure 2: Comparisons of measured HT partial pressures between ion chambers (p_{HT}^{IC}) and liquid scintillation counter (p_{HT}^{BL}) at the wide HT partial range from 10^{-7} Pa to 1 Pa

2.3 Experimental Procedure

The tritium permeation experiment was carried out with HT–(100 Pa) H_2-He gas mixtures in the primary side at four different temperatures of 573(± 5), 673(± 5), 723(± 5), and 773(± 5) K. A (100 Pa) H_2-He sweep gas was used in the secondary side, and the total pressures were kept at 100,000 (± 500) Pa in both primary and secondary sides. The total mass flow rates were 50(± 1) sccm and 200(± 2) sccm for the primary and secondary sides, respectively. HT partial pressure was varied by several orders of magnitude while keeping H_2-He partial pressure constant. The detection limit of the primary ionization chamber (pIC) is approximately 10^{-3} Pa, and liquid scintillation countering of TEP bubbler samples were used to measure tritium concentration lower than the pIC detection limit. The detection limit of secondary ionization chamber (sIC) is approximately 10^{-8} Pa, and liquid scintillation countering of bubbler samples collected in TEP were used to measure tritium concentration lower than the sIC detection limit.

Between tritium permeation tests, both the primary and secondary lines (including the sample, the test section, the ion chambers and the catalysis beds) were purged with pure He gas for 2-4 hr and then with dry air for about 1 week (168 hr) to decontaminate the system and to minimize the tritium memory effects in the detection systems. Prior to each tritium permeation test, both the primary and secondary lines (including the sample, the test section, the ion chambers and the catalysis beds) were baked at desired temperature with (100 Pa) H_2-He mixture for 2 hr to remove natural surface oxide in reducing condition. After each tritium permeation test, both primary and secondary lines (including the sample, the test section, the ionization chambers and the catalysis beds) were again baked at desired temperature with (100 Pa) H_2-He mixture for at least 1 hr to desorb T atoms in the sample and to minimize the tritium contamination in the lines and the tritium memory effects in the detection systems.

It is important to note that keeping identical H_2 partial pressures and keeping tritium as the form of HT in the both primary and secondary sides are crucial for accurately measuring tritium permeability in H-T system. We discuss the theory in the following section.

3. Theory

Understanding tritium permeation behavior in multi-components hydrogen isotopes requires applications of classical thermodynamics in the gas phase and at the surface. Here we consider three hydrogen components (H_2, T_2, and HT) in H-T system and examine the following three thermodynamics equilibriums, one between H_2, T_2 and HT, one at surface between H_2 and dissolved H, and one at surface between T_2 and dissolved T as shown in Equations 1-3.

$$H_2 + T_2 \leftrightarrow 2HT \qquad (1)$$

$$\tfrac{1}{2} H_2 \leftrightarrow H \qquad (2)$$

$$\tfrac{1}{2} T_2 \leftrightarrow T \qquad (3)$$

Inclusion of the gas phase equilibrium (Equation 1) is important to accurately treat solubility of hydrogen isotopes in metal from mixed gases [19]. Additional equilibrium between the HT gas molecule and atoms of H and T dissolved in the metal can be expressed as a linear combination of Equations 1–3. [19]. This inclusion of the surface equilibrium of HT molecules and dissolved H and T atom is evidenced by the fact that the reaction (1) requires a catalyst (e.g. metal wall) to occur. Here we follow thermodynamics equilibriums for three components (H_2, D_2 and HD) system by *San Marchi et al.* and adapt it for H_2, T_2 and HT system [19]. We use a single subscript letter to represent the atomic state dissolved in a metal lattice, and a pair of letters to represent the diatomic gas, following the notation used by *San Marchi et al.*

The gas phase equilibrium constant (K_{HT}) can be obtained from the gas phase thermodynamics equilibrium (Equation 1) as Equation 4:

$$K_{HT} = \frac{p_{HT}{}^2}{p_{HH}\, p_{TT}} = \frac{x_{HT}{}^2}{x_{HH}\, x_{TT}} \qquad (4)$$

where $p_i = x_i \, p_{total}$, x_i is the mole fraction of i in the gas phase. The surface equilibrium constant (K_H) for H can be obtained from the surface equilibrium (Equation 2) as Equation 5:

$$c_H = K_H \sqrt{p_{HH}} = \sqrt{x_{HH}}\, K_H \sqrt{p_{total}} \qquad (5)$$

where c_H is the dissolved H atom concentration in metal. In a similar manner, the surface equilibrium constant (K_T) for T can be obtained from the surface equilibrium (Equation 3) as Equation 6:

$$c_T = K_T \sqrt{p_{TT}} = \sqrt{x_{TT}}\, K_T \sqrt{p_{total}} \qquad (6)$$

where c_T is the dissolved T atom concentration in metal. It is important to note that the formation of HT molecules (Equation 4) reduces the partial pressures of hydrogen (p_{HH}) and tritium (p_{TT}), and the surface equilibrium between HT molecules and dissolved H and T atoms in the metal was included/implied by the gas phase equilibrium (Equation 4) [19]. The surface equilibrium constants (K_H and K_T) are often called the solubility or Sievert's constant.

A simple schematic of tritium permeation conditions in three components (H_2, T_2 and HT) system was shown in Figure 1. The superscript 1 denotes for primary (high tritium concentration) side, and the superscript 2 denotes for secondary (low tritium concentration) side. In the TGAP experiment, we intentionally keep hydrogen partial pressure identical ($p_{HH}{}^1 = p_{HH}{}^2$) in the primary and secondary sides; therefore, hydrogen diffusion in metal can be neglected in this condition ($p_{HH}{}^1 = p_{HH}{}^2$).

In this study, one-dimensional (1D) diffusion equation of tritium through a metal was considered with the condition of negligible tritium partial pressure ($p_{TT}{}^2 = 0$) in secondary side as Equation 7:

$$J_D^T = \frac{D_T\, K_T\, A}{\Delta x}\left(\sqrt{p_{TT}{}^1} - \sqrt{p_{TT}{}^2}\right) \approx \frac{D_T\, K_T\, A}{\Delta x}\left(\sqrt{p_{TT}{}^1}\right) \qquad (7)$$

where J_D^T is tritium (T) permeation rate [mol/s], D_T is tritium diffusivity, A is permeation surface area, and Δx is sample thickness. The tritium partial pressure (p_{TT}) was re-written using Equation 4 as Equation 8:

$$p_{TT}{}^1 = \frac{(p_{HT}{}^1)^2}{K_{HT}{}^1 p_{HH}{}^1} \qquad (8)$$

Introducing Equation 8 into Equation 7 gives the final form of 1D diffusion equation of tritium as Equation 9:

$$J_D^T \approx \frac{D_T\, K_T\, A}{\Delta x \sqrt{K_{HT}{}^1}} \frac{p_{HT}{}^1}{\sqrt{p_{HH}{}^1}} \propto \frac{p_{HT}{}^1}{\sqrt{p_{HH}{}^1}} \qquad (9)$$

This is a similar diffusion equation that *Bell et al.*

derived for their three components (H_2, T_2 and HT) permeation in nickel [10]. It is important to note that the tritium permeation rate is now a linear dependence on partial pressure of HT and inversely proportional to square root of partial pressure of H_2. Tritium permeability (product of D_T and K_T) can be derived from Equation 9 as Equation 10:

$$P_T = D_T\, K_T \approx \frac{J_D^T\, \Delta x \sqrt{K_{HT}{}^1}}{A} \frac{\sqrt{p_{HH}{}^1}}{p_{HT}{}^1} \qquad (10)$$

The gas phase equilibrium constant (K_{HT}) for the reaction H_2+T_2=2HT was measured by *Jones et al.* [20] and an empirical equation was obtained by fitting the Jones's data with the following formula. $log_{10}K_{eq} = A + Blog_{10}T + CT^{-1}$, where A, B, and C are fitting parameters and T is gas temperature in Kelvin. Figure 3 shows the equilibrium constant for the reaction H_2+T_2=2HT and the best fit to the experimental data. Non-linear least square fitting was performed between the experimental data and the fitting to provide the following empirical equation: $log_{10}K_{eq} = (0.922275) + (-0.083398)log_{10}T + (-91.47218)T^{-1}$.

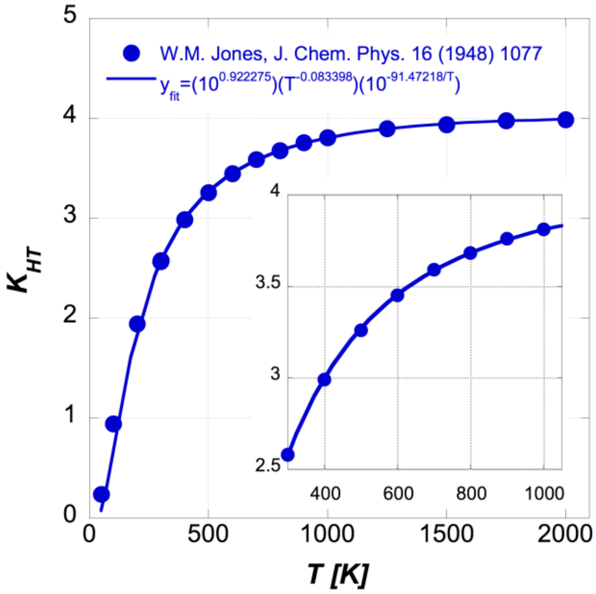

Figure 3: Gas phase equilibrium constant (K_{HT}) for the reaction H_2+T_2=2HT as measured by Jones et al. [19], and best fit empirical equation of the data.

With this empirical equation and the HT partial pressure, we can calculate the T_2 partial pressure as follows: $p_{TT} = \frac{p_{HT}{}^2}{K_{HT}p_{HH}}$, where p_{TT}, p_{HH}, and p_{HT} are partial pressure of T_2, H_2, and HT. Now we keep the hydrogen partial pressure (p_{HH}) constant in the both primary and secondary sides, and also we can assume the tritium is in the form of HT in the both primary and secondary in the condition of $p_{HH} >> p_{HT} >> p_{TT}$. It is important to note that ionization chamber cannot distinguish HT and T_2 if the form of tritium (HT or T_2) is unknown. This hydrogen isotope condition ($p_{HH} >> p_{HT} >> p_{TT}$) eliminates the uncertainty associated with the form of the tritium producing the ionization chamber response. Here, the primary ion chamber (pIC) provides HT partial pressure ($p_{HT}{}^1$), and HT permeation rate (J_D^T) can be calculated from the secondary ion chamber (sIC) and secondary flow rate (sF). Assuming H_2, T_2 and HT molecules are at thermodynamics equilibrium in experiment, the gas phase equilibrium constant K_{HT} can be calculated from the empirical equation above. Now tritium permeability can be obtained from Equation 10 since all the parameters are either known (K_{HT}, A, Δx) or can be measured ($p_{HH}{}^1$, $p_{HT}{}^1$, J_D^T).

4. Required condition to measure tritium permeability in H-T system

As described in Section 4, it is critical to keep the following three conditions to accurately measure tritium permeability in H-T system:

1) $p_{HH}{}^1 = p_{HH}{}^2$ to keep H_2 partial pressure constant and to neglect hydrogen diffusion in metal.
2) $p_{HH} >> p_{HT} >> p_{TT}$ to keep the majority of tritium in the form of HT ($p_{HT} >> p_{TT}$) in the both primary and secondary.
3) $p_{HH} \gg \left(\frac{P_T}{K_{diss}\Delta x}\right)^2$ to remain in diffusion limited permeation regime.

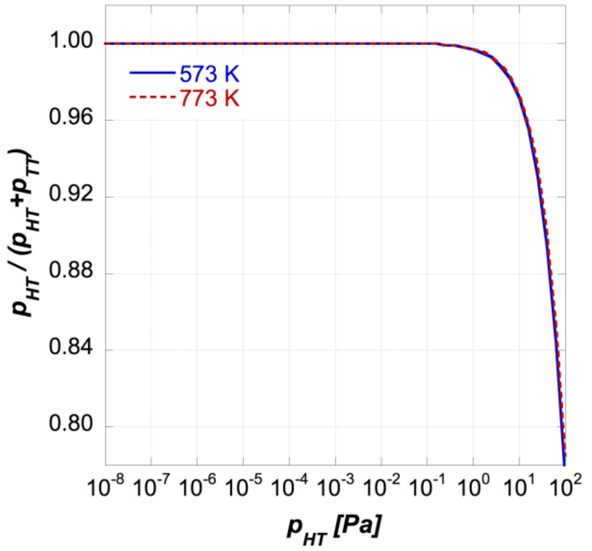

Figure 4: HT partial pressure dependence of ratio of HT partial pressure to sum of HT and T_2 partial pressures for the HT-(100 Pa) H_2-He mixture in the case of 573K and 773K.

The condition 1) is easy to achieve. T_2 partial pressure decreases as the square of HT partial pressure as shown in Equation 8, and the condition 2) of $p_{HT} >> p_{TT}$ is satisfied when HT partial pressure is less than 1 Pa for the HT-(100 Pa) H_2-He mixture. Figure 4 shows HT partial pressure dependence of ratio of HT partial pressure (p_{HT}) to sum of HT and T_2 partial pressures ($p_{HT} + p_{TT}$) for the HT-(100 Pa) H_2-He mixture in the case of 573K and 773K. It shows that more than 96% of tritium is in the form of HT when HT partial pressure is less than 10 Pa. The condition 3) has material and temperature dependence since the permeability (P_T) and dissociation coefficient (K_{diss}) are dependent on temperature and material [4,6]. For RAFM steel case, hydrogen isotope permeability (P_T) are $5.0\text{x}10^{-12}$ and $5.0\text{x}10^{-11}$ mol $\text{m}^{-1}\text{s}^{-1}\text{Pa}^{-0.5}$ at 573K and 773K, respectively [21-26]. Hydrogen isotope dissociation coefficient (K_{diss}) for MANET, similar RAFM steel, are $2.0\text{x}10^{-8}$ and $4.0\text{x}10^{-8}$ mol^{-1} $\text{m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ at 573K and 773K, respectively [3]. The condition 3) can be written as $p_{\text{HH}} >> 0.06$ Pa for 573K and $p_{\text{HH}} >> 1.50$ Pa for 773K in case of Δx of 1 mm. The experimental condition of $p_{HH}^1 = p_{HH}^2 = 100$ Pa satisfies the condition 3) from 573K to 773K. Therefore, we can apply Equation 10 to calculate the tritium permeability in RAFM steel from 573K to 773K when HT partial pressure is less than 10 Pa in the HT-(100 Pa) H_2-He mixture system.

5. Discussion

We discussed the three conditions required for measuring tritium permeability in the H-T system in Section 5, and the setting $p_{HH}^1 = p_{HH}^2 = 100$ Pa in both primary and secondary sides allows us to measure tritium permeability in RAFM steel from 573K to 773K when HT partial pressure is less than 10 Pa in the HT-(100 Pa) H_2-He mixture system.

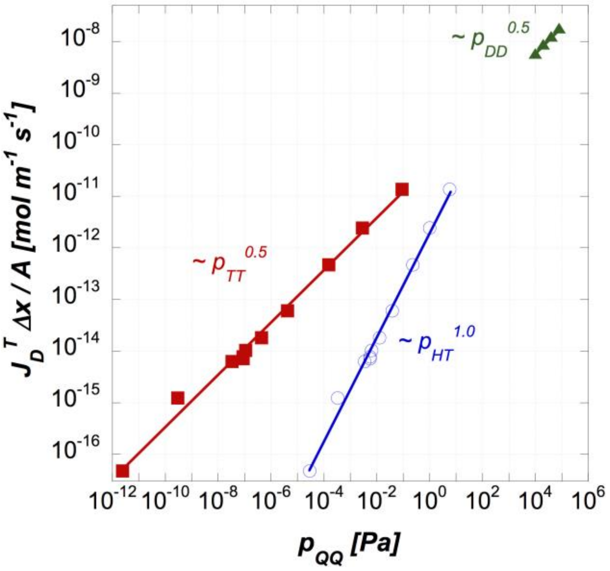

Figure 5: Deuterium and tritium permeation behavior in RAFM for the temperature of 773K. Tritium permeation rate appears to follow the linear dependence with HT partial pressure (open circle). When the same tritium permeation rate was plotted against T_2 partial pressures, it follows the square root dependence with T_2 partial pressures (solid square) [26]. Deuterium partial pressure dependence of deuterium permeation rate was also plotted for the temperature of 773K as a comparison [28].

Figure 5 shows tritium permeation behavior in KO RAFM steel at the temperature of 773K [27] along with deuterium permeation behavior in JA RAFM steel at the temperature of 773K [28]. Tritium permeation rates were measured for HT partial pressures ranging from 10^{-5} to 10^{1} Pa at 773K [27]. When the tritium permeation rate was plotted against HT partial pressure (open circle), tritium permeation behavior appeared to follow the linear dependence with HT partial pressure ($\sim p_{\text{HT}}$). When the tritium permeation rate, however, was plotted against T_2 partial pressure (solid square), tritium permeation behavior becomes the square root dependence with T_2 partial pressure ($\sim p_{\text{TT}}^{0.5}$). As a comparison, deuterium permeation behavior in JA RAFM steel at the temperature of 773K is shown in Figure 5 [28]. The deuterium permeation behavior follows the square root dependence with D_2 partial pressure ($\sim p_{\text{DD}}^{0.5}$) in the high D_2 partial pressure range from 10^4 to 10^5 Pa. When high H_2 partial pressure ($p_{HH}^1 = p_{HH}^2 = 100$ Pa) exists, tritium permeation still follows diffusion-limited behavior even at extremely low T_2 partial pressure range from 10^{-12} to 10^{-1} Pa. This experimental observation confirmed that we can measure tritium permeability in RAFM steel for HT partial pressure less than 10 Pa in the HT-(100 Pa) H_2-He mixture system.

6. Concluding remarks

Understanding the thermodynamic equilibria of multi-components hydrogen isotopes is the key for measuring tritium permeability in H-T system. A gas-driven tritium permeation system that is capable of independently controlling hydrogen and tritium partial pressures was developed at Idaho National Laboratory to accurately measure low partial pressure tritium permeability. Thermodynamic equilibria for the H-T system permeation through metal are discussed to accurately measure tritium permeability, and the experimental conditions required for evaluating tritium permeability in the H-T system are presented. When the conditions are satisfied and high H_2 partial pressure ($p_{HH}^1 = p_{HH}^2 = 100$ Pa) exists, tritium permeation still follows diffusion-limited behavior in metal even in the low T_2 partial pressure range from 10^{-12} to 10^{-1} Pa. We demonstrated experimentally and theoretically tritium permeability measurement in low partial pressure when the required conditions are satisfied.

Acknowledgments

This work was prepared for the U.S. Department of Energy, Office of Fusion Energy Sciences, under the DOE Idaho Field Office contract number DE-AC07-05ID14517.

References

[1] N. Taylor, C. Alejaldre, and P. Cortes, Progress in the safety and licensing of ITER, *Fusion Sci. Technol.* **64** (2013) 111-117.

[2] N. Taylor, B. Merrill, L. Cadwallader, L. di Pace, L. El-Guebaly, P. Humrickhouse, D. Pnayotov, T. Pinna, M.T. Porfiri, S. Reyes, M. Shimada, and S.R. Willms, Materials-related issues in the safety and licensing of nuclear fusion facilities, *Nuclear Fusion* **57** (2017) 092003.

[3] F. Reither, K.S. Forcey and G. Gervasini, A Compilation of Tritium-Material Interaction Parameters in Fusion

Reactor Materials (1993), Joint Research Centre, EUR 15217 EN.

[4] E. Serra, Hydrogen and Tritium Kinetics in Fusion Reactor Materials (1996), Joint Research Centre, EUR 16471 EN.

[5] R.A. Causey, R.A. Karnesky, and C. San Marchi, “4.16 Tritium Barriers and Tritium Diffusion in Fusion Reactors”, *Comprehensive Nuclear Materials* (2012) *Chapter 4.16.*

[6] I. Ali-Khan, K.J. Dietz, F.G. Waelbroeck, and P. Wienhold, The rate of hydrogen release out of clean metallic surfaces, *J. Nucl. Mater.* **76-77** (1978) 337-343

[7] A.S. Zarchy and R.C. Axtmann, Tritium permeation through 304 stainless steel as ultra-low pressures, *J. Nucl. Mater.* **79** (1979) 110-117.

[8] G.F. Knoll *“Radiation Detection and Measurement”* (John Wiley and Sons, Inc. 1979)

[9] N.P. Kherani and W.T. Shmayda, In-line processing tritium monitors, *Fus. Technol.* **21** (1992) 340-345.

[10] J.T. Bell and J.D. Redman, Permeation of hydrogen isotopes in nickel, *J. Phys. Chem.* **82** (1978) 2834.

[11] T. Chikada, M. Shimada, R.J. Pawelko, T. Terai, and T. Muroga, Tritium permeation experiments using reduced activation ferritic/martensitic steel tube and erbium oxide coating, *Fus. Eng. Des.* **89** (2014) 1402-1405.

[12] S. Tanaka, T. Terai, H. Mohri, and Y. Takahashi, In-situ tritium release experiments from solid breeding materials (TTTEx) – Effect of sweep gas composition, *J. Nucl. Mater.* **155-157** (1988) 533-537.

[13] R.G. Clemmer, P.A. Finn, B. Misra, M.C. Billone, A.K. Fischer, S.W. Tam, and C.E. Johnson, The TRIO experiment, *J. Nucl. Mater.* **133-134** (1985) 171–175.

[14] P. Humrickhouse, R.J. Pawelko, M. Shimada, and P. Winston, Tritium Permeability of Incoloy 800H and Inconel 617, INL/EXT-11-23265 Rev.1 (2011).

[15] M.-Y. Ahn, S. Cho, D.W. Lee, C.W. Lee, K.I. Shin, D.Y. Ku, Y.-H. Park, C.-S. Kim, I.-K. Yu, Y.O. Lee, E.H. Lee, H.G. Jin, S.-K. Kim, Design change of Korean HCCR TBM to vertical configuration, *J. Nucl. Mater.* **88** (2013) 2284–2288.

[16] R.J. Pawelko, M. Shimada, K. Katayama, S. Fukada, P.W. Humrickhouse, and T. Terai, Low tritium partial pressure permeation system for mass transport measurement in lead lithium eutectic, *Fus. Eng. Des.* **102** (2016) 8-13.

[17] COMSOL Multiphysics User’s Guide, v.5, COMSOL, Inc., Burlington, Massachusetts (2014).

[18] H. Zhang, A. Ying, M. Abdou, M. Shimada, R.J. Pawelko, and S. Cho, Characterization of tritium isotopic permeation through ARAA in diffusion limited and surface limited regimes, *Fus. Sci. Technol.* (in press). https://doi.org/10.1080/15361055.2017.1333826

[19] C. San Marchi, B.P. Somerday, R.S. Larson, and S.F. Rice, Solubility of hydrogen and its isotopes in metals from mixed gases, *J. Nucl. Mater.* **372** (2008) 421.

[20] W.M. Jones, Thermodynamic function for tritium and tritium hydride. The equilibrium of tritium and hydrogen with tritium hydride. The dissociation of tritium and tritium hydride, *J. Chem. Phys.* **16** (1948) 1077.

[21] S.J. Noh, S.K. Lee, W.J. Byeon, Y.B. Chun, and Y.H. Jeong, Transport of hydrogen and deuterium in the reduced activation martensitic steel ARAA, *Fus. Eng. Des.* **89** (2014) 2726.

[22] G.A. Esteban, A. Peña, I. Urra, F. Legarda, and B. Riccardi, Hydrogen transport and trapping in EUROFER97, *J. Nucl. Mater.* **367-370** (2007) 473.

[23] A. Aiello, I. Ricapito, G. Benamati, and R. Valentini, Hydrogen isotope permeability in EUROFER97 martensitic steel, *Fus. Sci. Technol.***41** (2002) 872.

[24] E. Serra, Influence of traps on the deuterium behavior in the low activation martensitic F82H and Batman, *J. Nucl. Mater.* **245** (1997) 108-114.

[25] A. Pisarev, V. Shestakov, S. Kulsartov, and A. Vaitonene, Surface effects in diffusion measurements: deuterium permeation through martensitic steel, *Phys. Scr.* **T94** (2001) 121.

[26] T. Chikada, A. Suzuki, C. Adelhelm, T. Terai, and T. Muroga, Surface behavior in deuterium permeation through erbium oxide coatings, *Nucl. Fusion* **51** (2011) 063023

[27] M. Shimada, M.-Y. Ahn, R.J. Pawelko, A. Ying, and S. Cho, Tritium permeation behavior in reduced activation ferritic/martensitic steel, in preparation

[28] T. Chikada, A. Suzuki, Z. Yao, D. Levchuk, H. Maier, T. Terai, and T. Muroga, Deuterium permeation behavior of erbium oxide coating on austenitic, ferritic, and ferritic/martensitic steels, *Fus. Eng. Des.* **84** (2009) 590.