



## Permeation Analysis of Tritium through the Titanium Hydride Storage Vessel

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### ABSTRACT

A preliminary design of a stainless steel vessel for the long-term storage of hydrogen isotopes has been proposed. The immobilized hydrogen as a titanium hydride could be used in a stainless steel vessel for this application. The vessel as a primary package is designed to form titanium hydride and to contain the hydrogen isotopes and helium-3 produced from the tritium decay. In order to predict against the possibility of a contamination and the deterioration of the mechanical properties, a numerical calculation was carried out for a diffusion analysis of the hydrogen isotopes and helium inside the stainless steel vessel. Numerical results showed that a negligible amount of tritium would be released by a permeation through the vessel wall of a 0.7cm thickness at normal conditions over the entire period of the storage. In the case that the vessel was heated up to a temperature of 600°C for the routine condition of an activation or exothermic hydriding, it would be of little concern regarding a tritium loss or a contamination. However, when the vessel was exposed to a fire condition with a temperature of 800°C, permeation of the hydrogen through the vessel wall resulted in a serious increase in the amount of tritium escaping, in a very short time.

### 1. INTRODUCTION

Tritium extracted from the heavy water of CANDU reactors can be immobilized in the form of a metal hydride [1]. The recovered tritium must be safely packaged for a long-term storage. Titanium has been recommended as the best immobilizing material due to its higher dissociation pressure [2,3]. A vessel of austenitic stainless steel could be used for the long-term storage of hydrogen isotopes [4-6]. These steels provide a good strength, weld-ability and resistance to hydrogen embrittlement. Low carbon grades of 316L stainless steel are preferred to avoid a weld sensitization and to reduce the number of inclusions of the impurity particles such as oxides and carbides. In addition, once tritium enters the steel, helium generated by the tritium decay can also cause a reduction in the ductility of the stainless steel [7,8].

Predictions of hydrogen and helium profiles are important to determine their amounts in the structure for a comparison with the values known to cause embrittlement or degradation during a period of storage [9-11]. Evaluation of the hydrogen isotope permeation and the helium formation through the stainless steel is one of the important factors to be considered in the designing of a storage vessel. Accordingly, it is desirable to estimate how the permeation of the hydrogen isotopes and the formation of helium through a vessel wall of the stainless steels might occur during periods of various storage conditions.

In this study, a numerical approach for a study using the finite difference method was applied to evaluate the safety concerns by estimating the behaviour of the hydrogen isotope and the helium through the vessel wall. From the numerical results of the permeation calculation for various storage conditions, quantitative predictions for the hydrogen isotope inventory in the storage vessel and the leakage of tritium from the vessel wall were carried out.

### 2. THEORETICALS

#### 2.1. Numerical model

When a diffusion process of hydrogen isotopes through a metal wall is the controlling step of a permeation, an ideal one-dimensional geometry could be considered to simulate the hydrogen isotopes diffusion and its leakage out through the vessel wall. Let  $C(x,t)$  denote the concentration of the hydrogen isotopes (mean H, D, or T) at a distance  $x$  from the inner surface of the vessel wall, at time  $t$ . Thus,  $C(x,t)$  is a solution of a diffusion equation with a decay term of a tritium balance:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} - \lambda C(x,t) \quad 0 \leq x \leq l, \quad t > 0 \quad (1)$$

in which  $\lambda$  is the tritium decay constant and  $D$  is the diffusivity of the hydrogen isotopes in the vessel wall. One must make sure that the decay term of Eq.(1) can be cancelled in the case of the stable hydrogen isotopes such as H and D.

Assuming that the concentration  $C(x,t)$  in position  $x$  at time  $t$  is expressed as  $C(x,t) = C(i\Delta x, n\Delta t) = C_i^n$ . The implicit scheme [12] for Eq.(1) is used to obtain the second-order analog for the parabolic partial differential equation:

$$\frac{C_i^{n+1} - C_i^n}{\Delta t} = D \frac{C_{i+1}^{n+1} - 2C_i^{n+1} + C_{i-1}^{n+1}}{(\Delta x)^2} - \lambda C_i^{n+1} \quad (2)$$

where the subscripts and superscripts refer to the distance and time, respectively.

Collecting all the terms, the difference equation becomes

$$C_{i+1}^{n+1} - \left[ 2 + \frac{(\Delta x)^2}{D\Delta t} + \frac{(\Delta x)^2}{D} \lambda \right] C_i^{n+1} + C_{i-1}^{n+1} = -\frac{(\Delta x)^2}{D\Delta t} C_i^n \quad (3)$$

Thus, we obtain a system of equations with unknown nodal concentrations  $C_i^{n+1}$  which may be solved by a simple substitution. The Thomas algorithm [13] is used for this purpose.

In all the cases considered it is initially assumed that there are no hydrogen isotopes in the wall, i.e.

$$C(x,0) = 0 \quad 0 < x < l, \quad (4)$$

At the boundaries  $x=0$  and  $x=l$ , i.e. at the inner and outer surface of the container wall, the concentration is governed by the immediate environment at these surfaces. We assume throughout that there is a negligible hydrogen pressure at the outer surface of the vessel for all the cases considered,

$$C(l,t) = 0 \quad \text{for all } t \quad (5)$$

With an ideally clean metal surface in contact with the gaseous hydrogen, the concentration in the surface layer of the metal,  $C_o$ , is related to the hydrogen pressure  $P$  and temperature  $T$  (isothermal condition assumed) through the Sieverts equation [6].

$$C(0,t) = C_o = SP^{1/2} = S \left[ \frac{1}{760} \exp\left(\frac{A}{RT} + B\right) \right]^{1/2} \quad (\text{cm}^3/\text{cm}^3 \text{ metal}) \quad \text{for all } t \quad (6)$$

where the solubility constant  $S$  is dependent on the temperature and is usually defined in the form of an Arrhenius equation [4]. Thus, these hydrogen isotopes will diffuse into the vessel wall at rates controlled by its diffusivity  $D$ . The Arrhenius type formula for the temperature dependency of the diffusivity has also been used for the tritium. In this analysis, it is assumed that the diffusivity depends on the mass of the isotope as given by the ratios [10]:

$$D_H : D_D : D_T = 1 : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{3}} \quad (7)$$

where the subscripts H, D, T denote the protium, deuterium and tritium, respectively. The values of the pre-exponential and activation energy for the austenitic stainless steel are shown in Table 1.

The hydrogen pressure term in Eq.(6) with a constant  $A$  and  $B$  can be calculated from the correlated equilibrium P-C-T data as given in Table 2. At temperatures up to about 300°C,  $\text{TiH}_{1.0}$  will exist as a mixture of the  $\alpha$  and  $\gamma$  phase, and above this temperature the  $\gamma$  phase co-exists with the solid solution of the  $\beta$  phase [4]. Because the pressure data correlated at below about 300°C does not exist, the extrapolated values were used with the assumptions that they should be bounded by the above equations.

Table 1. Arrhenius formulas on the temperature dependency of the solubility constant and the diffusivity for the tritium in austenitic stainless steel [4]

	Equation	Pre-exponential	Activation energy
Diffusivity, $\text{cm}^2/\text{s}$	$D = D_o \exp\left(-\frac{E_D}{RT}\right)$	$D_o$	$E_D$
		$8.17 \times 10^{-3}$	-55,990
Solubility constant, $\text{cm}^3/(\text{cm}^3 \cdot \text{Pa}^{1/2})$	$S = S_o \exp\left(-\frac{E_S}{RT}\right)$	$S_o$	$E_S$
		$3.36 \times 10^{-3}$	-7,213

Table 2. Correlated constants of the hydrogen pressure as function of the stoichiometry for the titanium hydride [3]

Stoichiometry	A	B
$\text{TiH}_{0.418} (\alpha+\beta)$	-24,350	15.45
$\text{TiH}_{0.604} (\beta)$	-30,400	19.86
$\text{TiH}_{0.803} (\beta)$	-30,600	21.55
$\text{TiH}_{1.009} (\beta+\gamma)$	-38,550	27.73

## 2.2. Helium-3 concentration through the vessel wall and the tritium inventory

Tritium decays to  $^3\text{He}$ , a monatomic gas, by emitting an electron and a neutrino from the nucleus. If the helium diffusivity is assumed to be negligible, helium concentrations during each time increment are calculated from the amount of tritium available for a decay at a given location in the wall:

$$C_{\text{He}}^{n+1} = C_{\text{He}}^n + 2C_i^{n+1} \{1 - \exp(\lambda \Delta t)\} \quad (8)$$

In the finite-difference program, calculations were performed for the tritium diffusion prior to any decaying of the species to helium. The amount of tritium in the structure was adjusted to be simultaneously decreased to maintain the mass balance.

For a given titanium metal storage, the tritium inventory during each time increment can be calculated from the mass balance in terms of the decay rate and release rate to the vessel wall.

$$M_T^{n+1} = M_T^0 - M_T^n \{1 - \exp(\lambda \Delta t)\} - \frac{A_{\text{IS}}}{22,400} \times J_{x=0}^{n+1} \Delta t \quad (9)$$

where  $M_T^0$  is the initial tritium content in the storage vessel (moles),

$M_T^n$  is the tritium content in the storage vessel (moles),

$A_{\text{IS}}$  is the inside surface area of the storage vessel ( $\text{cm}^2$ ),

$J_{x=0}$  is the flux of the hydrogen isotopes through the inner wall at time  $t$  (moles/ $\text{cm}^2 \cdot \text{sec}$ ).

For a solid storage, a helium retention phenomenon can be observed inside the hydrides. It is known that titanium retains the decay helium up to a concentration of a 0.3 He atom per Ti atom [2].

## 2.3. Tritium escape from the outer vessel wall

Knowing  $C(x,t)$ , the total tritium escape,  $Q(t)$ , through the vessel wall can be obtained from the flux of the tritium at the outer wall during the time increment as follows:

$$Q^{n+1} = Q^n + 58,250 \times \frac{A_{\text{OS}}}{22,400} \times J_{x=l}^{n+1} \Delta t \quad (10)$$

where  $Q$  is the total tritium escape from the storage vessel (Ci),

$A_{\text{OS}}$  is the outside surface area of the storage vessel ( $\text{cm}^2$ ),

$J_{x=l}$  is the flux of the hydrogen isotopes through the outer wall at time  $t$  (moles/ $\text{cm}^2 \cdot \text{sec}$ ).

## 2.4. Titanium hydride storage vessel for simulation

This vessel is designed to serve a dual purpose as a reactor in which the titanium hydride is formed and as a storage for the tritium and helium-3 produced from the tritium decay. Simulations are carried out based on the technical dimensions and specifications of the storage vessel as listed in Table 3. It is fabricated from a sort of type 316L stainless steel pipe closed with two standard end caps to give a volume of about 6.3L. Titanium sponge is loaded into the vessel prior to welding the second valve. Approximately 800g of titanium sponge would be required to package 0.5MCi of tritium as  $\text{TiH}_{1.0}$ .

## 3. RESULTS AND DISCUSSION

### 3.1. Long-term permeation behavior at a normal storage condition

Concentration distributions of the hydrogen isotopes and helium were calculated through a structure wall from the applied boundary condition at the temperature of the storage vessel. For a long-term storage at a temperature of  $40^\circ\text{C}$ , the concentration of the hydrogen isotopes and helium through the vessel wall were estimated to be very low for the entire storage life of 50 years as shown in Fig.1. In this figure, the unit of concentration on the axis of the ordinates was denoted as the atomic ratio(atomic ppm) to the stainless steel atoms (counting Fe, Cr, Ni, Mn, Mo and Si). At this temperature, the equilibrium hydrogen pressure of titanium is so low that it cannot be detected. Accordingly, a negligible amount of tritium would be released by a permeation through the stainless steel vessel wall under a normal storage condition. The calculated results suggest that a stainless steel vessel wall of 7mm thick is practically impervious to tritium.

Table 3. Technical dimensions and specifications of the storage vessel

	Dimensions & specifications		Remarks
Primary package	Inner diameter	16.78 cm	316L stainless steel 6 inch pipe (Sch.no.40) closed with two standard end caps
	Thickness	0.71 cm	
	Volume	6372.5 cm <sup>3</sup>	
	Height of storage section	~32 cm	
	Inner surface area	~2146 cm <sup>2</sup>	
Titanium sponge loaded in the vessel		850 g	Skeletal density = 4.76g/cm <sup>3</sup> (except open pore)
Initial inventory of hydrogen isotopes in titanium hydride	Deuterium	0.35 g	D/(D+T)=0.01
	Tritium	51.5 g	0.5MCi tritium as TiT <sub>1.0</sub>
Initial partial pressure of hydrogen isotopes and helium in the vessel	Deuterium	ND	
	Tritium	ND	
	Helium	1.4×10 <sup>-2</sup> atm	
Normal storage temperature		40°C	

Fig.2 shows the concentration profiles of the tritium with the passage of a long-term storage time at 40°C. In the case of a normal storage condition, the time required to reach the near steady state conditions could be very long even compared to the tritium half-life of 12.3years. As expected, a decay of tritium causes a decrease in the permeation rate and prolongs the approach to a steady state. Thus, it is expected that the steady state condition may never be established during a long-term period of a normal storage condition.

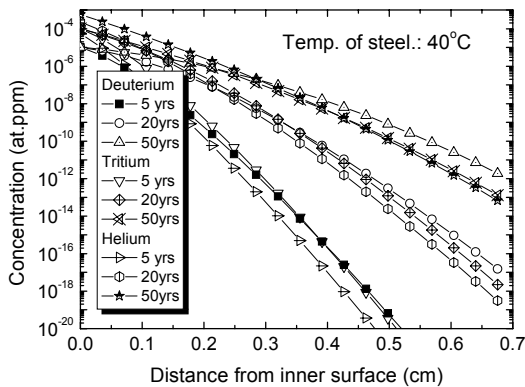


Fig. 1. Concentration profile of the hydrogen isotope and helium in the vessel wall of stainless steel at 40°C.

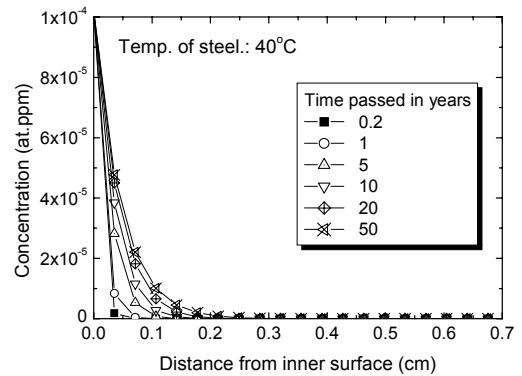


Fig. 2. Tritium concentration profiles during a permeation in the vessel wall of stainless steel at 40°C.

As time passed, the permeation process which began at the inner surface of the wall produced a gradual increment of the hydrogen isotope concentrations along the stainless steel vessel wall. Trends in the helium concentration follow those of the tritium calculation discussed above. Helium accumulation is a direct result of the tritium distribution because the helium diffusivity is assumed to be negligible. It is known that the level of helium concentration estimated here has no deleterious effect on the ductility of austenitic stainless steel [6].

As the tritium decays and the hydrogen isotope diffuses through the vessel wall, the equilibrium hydrogen pressure of the titanium hydride decreases and the partial pressure of the helium increases. Fig. 3 shows the rate of decay and the helium generation from the initial content of the hydrogen isotope under a normal storage condition over 50 years. The rate of the pressure change at a given helium content in the storage vessel over time is shown in this figure. Titanium retains up to a concentration of 0.3 helium atoms per titanium atom. The results show that titanium stored at this temperature condition could retain the decay helium for about 7 years.

Accordingly, a measurable partial pressure of the helium could be observed at first at about 7 years after storage had started. At the end of a long-term storage of 50 years, the estimated pressure of the helium released from the titanium sponge due to the tritium decay remains at a pressure of about 46 atm or over in the storage vessel.

### 3.2. Short-term permeation behavior at elevated temperature

The storage package could be faced with an elevated temperature for the activation and hydriding conditions. The storage vessel can be heated to about 600°C for an activation of titanium under a vacuum condition. The temperature during the hydriding reaction of the activated titanium can also reach the high temperature conditions, depending on the geometry of the vessel.

If a hypothetical fire accident condition could raise the steel temperature of the bare vessel up to 800°C, the concentrations of the hydrogen isotopes through the vessel wall were calculated to be significantly higher in a short time as illustrated in Fig.4. It is shown in Fig. 5 that the permeation rate increases during the approach to a steady state. Because a rapid permeation of tritium occurs at this temperature, a steady state permeation is achieved in approximately 5 hours. Once a steady state is achieved during a permeation, then the rate of the tritium escape becomes much higher. At this temperature, the vessel would be charged to about 20 atm of the hydrogen pressure based on the correlated equilibrium P-C-T data.

Fig.6 shows the leakage of the tritium expressed in curies(Ci) per total outer area of the storage vessel as a function of the elevated temperature. During the elevated temperature condition of 600°C for 5 hours, only a trace amount of tritium,  $\sim 10^{-17}$  Ci, would be released via the storage vessel wall. However, at 800°C significant amounts of tritium could escape from the vessel and about 0.1 Ci for 5 hours.

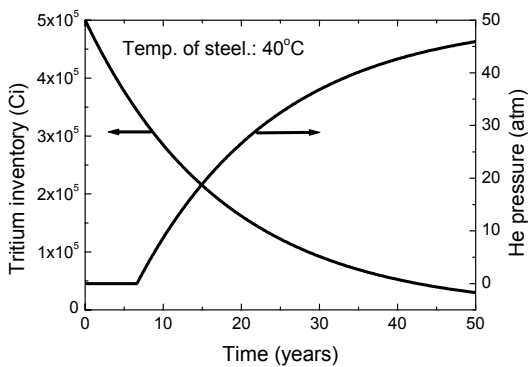


Fig. 3. Tritium inventory and helium pressure in the storage vessel at 40°C.

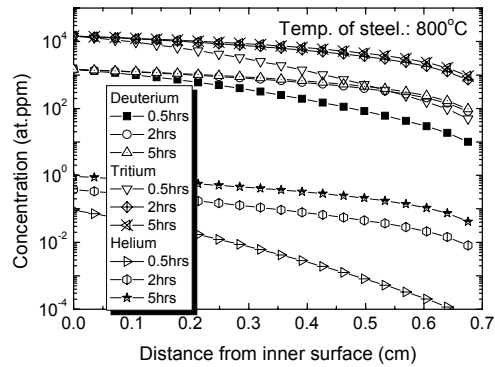


Fig. 4. Concentration profile of the hydrogen isotope and the helium in the vessel wall of stainless steel at 800°C.

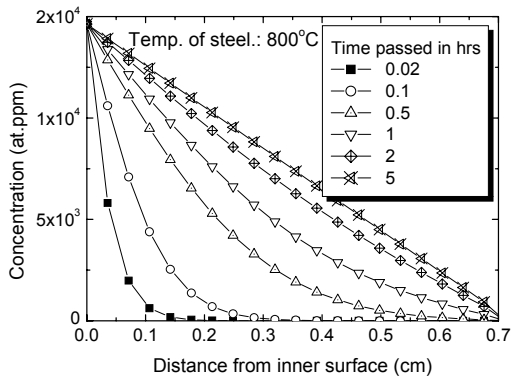


Fig. 5. Tritium concentration profiles during a permeation in the vessel wall of stainless steel at 800°C.

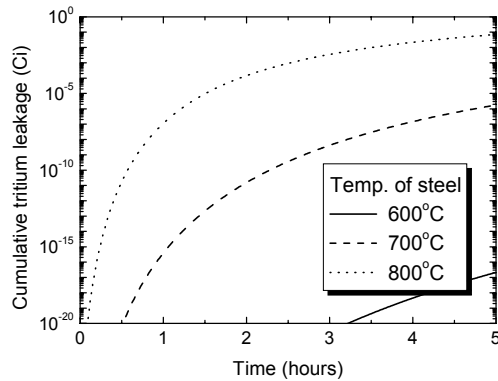


Fig. 6. Cumulative tritium leakage from an austenitic stainless vessel of a 0.7cm thickness for 5 hours at elevated temperatures.

#### 4. CONCLUSIONS

A numerical calculation was proposed for the evaluation of a safety concern resulting from the permeation of the hydrogen isotopes and helium behavior in a stainless steel storage vessel containing titanium hydride. This program based on the finite-difference method was able to calculate the hydrogen isotopes and helium concentration distributions through the vessel wall facing the titanium hydride in any storage condition. In addition, the numerical approach modeled in this study can be applied to predict the tritium inventory for the storage vessel of titanium hydride and the tritium escaping from the vessel wall associated with the permeation behavior of the hydrogen isotopes. Numerical results showed that a negligible amount of tritium would be released by a permeation through the stainless steel vessel wall of a 0.7cm thickness at a normal storage temperature. In the case that the vessel was heated up to a temperature of 600°C for the routine condition of an activation or exothermic hydriding, it would be of little concern regarding a tritium loss or a contamination. However, when the storage vessel was heated up to a temperature of 800°C, steady state permeation conditions are established in a number of hours and the permeation of the hydrogen isotopes through the vessel wall resulted in a significant increase in the amount of tritium escaping. This model was found to be useful in the design and safety analysis of the storage vessel for titanium hydride.

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