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## **COUPLED PROTIUM AND DEUTERIUM DIFFUSION MODEL FOR PREDICTION OF HYDROGEN ISOTOPE DISTRIBUTIONS IN Zr-Nb PRESSURE TUBES**

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### **ABSTRACT**

Evaluating the effect of hydrogen isotopes on DHC and fracture toughness in Candu reactor pressure tubes requires determination of the concentration distribution along the pressure tube. The concentration distribution depends on the spatial distribution of the sources for hydrogen isotopes, as well as the redistribution of the isotopes by diffusion. Since Candu reactors are heavy water reactors, the sources are expected to involve only deuterium, while protium is present from the initial manufacturing process for the pressure tube material. Typically, the approach to model and predict the concentration distribution considers the net effect of all isotopes in terms of an equivalent concentration of a single isotope. Measurements from pressure tubes can distinguish separate distributions of protium and deuterium, and some of the data indicates changes in the protium concentration from the initial as-manufactured values. The cause of changes in protium concentration may affect the validity of models if an additional source term is required, or if some other phenomenon needs to be included. A diffusion model is extended to include both the protium and deuterium isotopes and, applications are solved with a finite volume method. Results of the new model are presented and compared with the simplified equivalent concentration approach.

### **INTRODUCTION**

Evaluating the effect of hydrogen isotopes on DHC and fracture toughness in CANDU reactor pressure tubes requires determination of the concentration distribution along the pressure tube. Initial concentration is nominally uniformly distributed protium acquired during manufacture of the pressure tubes. During reactor operation, deuterium is continuously picked up due to corrosion in the heavy water system. The pickup rate of deuterium varies with time and position in the pressure tube with significantly higher pickup rate where the ends of the pressure tube are connected to end fittings of a dissimilar material with a roller expanded joint. Figure 1 shows the portion of the fuel channel where the pressure tube is connected to the end fitting, and Figure 2 depicts the main sources of deuterium ingress into the pressure tube material. The concern is that the high concentration of deuterium picked up in the compressive region of the rolled joint can diffuse inboard to affect the pressure tube properties where it is no longer supported by the end fitting.

The approach to model and predict the concentration distribution considers the net effect of all isotopes in terms of an equivalent concentration of a single isotope,  $[H_{eq}] = P + \frac{1}{2}D$  or  $[D_{eq}] = 2P + D$ . This equivalent measure has long been accepted in applicable models and codes, and is applied in the CSA standard (CSA N285.8-15). It is clearly an approximation, but it has been shown to be adequate for the purpose of determining the conditions to form hydrides when assessing the pressure tube integrity.

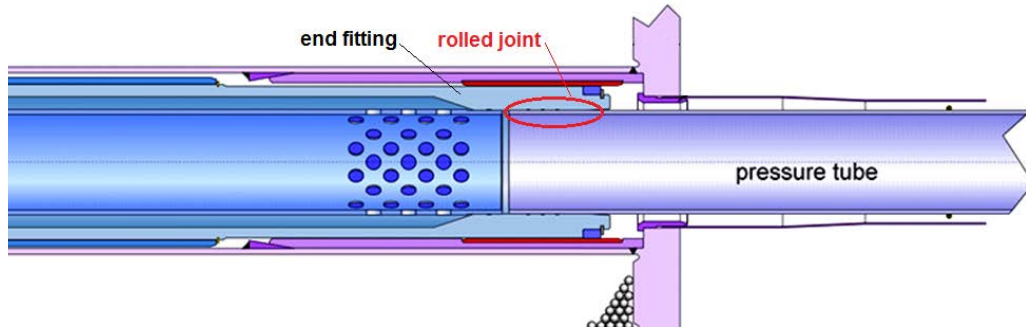


Figure 1 – Fuel channel detail showing pressure tube rolled joint

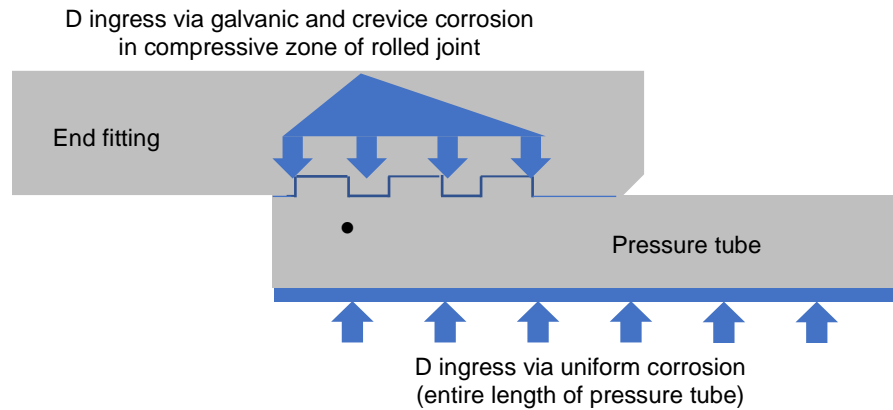


Figure 2 – Sources of deuterium ingress to the pressure tube

Measurements from surveillance channels can distinguish separate distributions of protium and deuterium, and some of the data indicates changes in the protium concentration from the initial off-cut values. The cause of changes in protium concentration may affect the validity of models if an additional protium source term is required, or if some other phenomenon needs to be included. In principle, different isotopes should be treated as distinct species in the diffusion model, and the possibility of isotope interaction (or separation) effects by a diffusion mechanism has not been previously considered. Previous diffusion modelling of hydride blister growth considered protium and deuterium as separate quantities, but these were decoupled with respect to Fick's law of diffusion.

Although the model predictions have largely consistent with the axial distributions of protium and deuterium observed from surveillance pressure tubes, the more recent observations regarding protium motivated the updating of the model. For proper modelling of both of the measured distributions, the model needs to be extended to include both protium and deuterium concentrations.

## DIFFUSION MODEL DEVELOPMENT

### Multi-Element Diffusion

In the absence of temperature and stress gradients, the diffusion of multiple species can be described by a generalized Fick's law

$$J_i = - \sum_{j=1}^{n-1} D_{ij} \nabla c_j \quad (1)$$

where  $J_i$  is the flux of component  $i$ , the  $D_{ij}$  are terms in the multicomponent diffusivity matrix,  $c_j$  is the concentration of component  $j$ , and  $\nabla$  is the gradient operator. In Equation (1),  $n$  is the total number of

elements, but conservation of mass allows for  $n-1$  fluxes to effectively define the diffusion. For hydrogen diffusion in the predominantly Zr alloy, the eliminated element is logically taken to be the immobile Zr.

Equation (1) does not consider that the elements may involve different isotopes, which diffuse at different rates in relation to their mass, but otherwise are chemically similar. Thus, treating each isotope as if it were a distinct element may not account for the role of isotopic interaction.

The determination of the diffusion coefficients in equation (1) typically follows a rigorous application of non-equilibrium thermodynamics. References on the subject matter (De Groot, 1952), (Jost, 1960), show examples for multiple elements, but do not provide guidance on isotope-specific interaction phenomena.

### Multi-isotope Diffusion

A review of the literature concerning the diffusion of hydrogen isotopes in metals did not reveal any relevant prior consideration for the concurrent modelling of multiple isotope diffusion. The studies either focus on a single isotope, or consider the net flux of all isotopes in terms of an equivalent quantity.

A broader literature search for diffusion involving isotopes other than hydrogen isotopes found examples of practical use for developing a two-isotope model. The most relevant information is found in the study of isotope separation in molten silicates in (Richter, Liang and Davis, 1999), (Watkins, DePaolo, Ryerson, Peterson, 2011) and (Watkins, Liang, Richter, Ryerson and DePaolo, 2014). These references make use of incorporating the self-diffusion phenomenon into the diffusion model, and attribute the first introduction of this approach for isotopes to the Ph.D. dissertation of (Liang, 1994). The concept in essence defines the isotopic interaction effect in terms of isotopic exchange (or self-diffusion) superimposed on the chemical diffusion.

For the details of developing the two-isotope model, the notation of and (Watkins, Liang, Richter, Ryerson and DePaolo, 2014) is adopted to distinguish multiple elements which can also have different isotopes. Equation (3.2) from (Watkins, Liang, Richter, Ryerson and DePaolo, 2014) states the extension of equation (1) as:

$$J_i^k = \underbrace{-D_i^k \nabla c_i^k + \sum_{m=1}^{m_i} f_i^k D_i^m \nabla c_i^m}_{\text{Self-diffusion}} - \underbrace{\sum_{j=1}^{n-1} f_i^k D_{ij}^k \nabla c_j}_{\text{Chemical diffusion}} \quad (2)$$

where subscripts  $i$  and  $j$  denote the diffusing elements, the superscript  $k$  denotes the isotope of element  $i$ ,  $m_i$  is the number of isotopes of element  $i$ , and  $f_i^k$  is the mole fraction of isotope  $k$  in element  $i$ .

The first two terms on the RHS of equation (2) represent the self-diffusion effect which is dependent on the self-diffusion coefficient,  $D_i^k$ , while the last term represents the chemical diffusion as per the diffusion coefficient  $D_{ij}^k$ . Chemical diffusion only causes flux if there is a gradient in the total concentration of all isotopes, while self-diffusion can cause flux of individual isotopes even if there is no gradient in the total concentration. Note that in our case the subscript ( $i$  or  $j$ ) has a range of one since only a single element (hydrogen) is mobile, but the range of the superscript  $k$  is two in accordance with the two isotopes.

The total flux for all isotopes of element  $i$  is found by summing equation (2) over the number of isotopes. In this sum, by virtue of the  $f_i^k$  summing to unity the self-diffusion terms cancel out, leaving

$$\sum_{k=1}^{n_k} J_i^k = J_i \equiv - \sum_{k=1}^{m_i} \left( \sum_{j=1}^{n-1} f_i^k D_{ij}^k \nabla c_j \right) \quad (3)$$

Equation (3) can be rearranged by multiplying the right hand side by  $\nabla c_i / \nabla c_i$  to give

$$\begin{aligned}
 J_i &\equiv -\sum_{k=1}^{m_k} f_i^k \left( \sum_{j=1}^{n-1} D_{ij}^k \frac{\nabla c_j}{\nabla c_i} \right) \nabla c_i \\
 &= -\sum_{k=1}^{m_i} \left( f_i^k D_i^{E,k} \right) \nabla c_i
 \end{aligned} \tag{4}$$

The term inside the brackets in the first line of equation (4) defines an effective (superscript  $E$ ) binary diffusion coefficient

$$D_i^{E,k} = \sum_{j=1}^{n-1} D_{ij}^k \frac{\nabla c_j}{\nabla c_i} \tag{5}$$

which is a function of the diffusion coefficients of each isotope as well as the portion of each isotope in the mixture. The use of effective binary diffusion coefficients allows for the diffusion model of equation (2) to be completed in terms of fewer physical quantities in multi-element systems.

### Diffusion for Protium and Deuterium

For the specific case of diffusion of the P and D isotopes in zirconium, the system is nominally the binary H-Zr system with one mobile element ( $n-1=1$ ), but with two isotopes ( $m_k=2$ ). Equation (2) accordingly simplifies to

$$\begin{aligned}
 J_1^k &= -D_1^k \nabla c_1^k + \sum_{m=1}^2 f_1^k D_1^m \nabla c_1^m - f_1^k D_{11}^k \nabla c_1 \\
 &= -D_1^k \nabla c_1^k + f_1^k \left( D_1^1 \nabla c_1^1 + D_1^2 \nabla c_1^2 \right) - f_1^k D_{11}^k \nabla \left( c_1^1 + c_1^2 \right)
 \end{aligned} \tag{6}$$

Subsequently, the superscript denoting the isotope is explicitly denoted as either P ( $k=1$ ) or D ( $k=2$ ). Then, equation (6) becomes

$$\begin{aligned}
 J_1^P &= -D_1^P \nabla c_1^P + f_1^P \left( D_1^P \nabla c_1^P + D_1^D \nabla c_1^D \right) - f_1^P D_{11}^P \nabla \left( c_1^P + c_1^D \right) \\
 J_1^D &= -D_1^D \nabla c_1^D + f_1^D \left( D_1^P \nabla c_1^P + D_1^D \nabla c_1^D \right) - f_1^D D_{11}^D \nabla \left( c_1^P + c_1^D \right)
 \end{aligned} \tag{7}$$

In equation (7), there are two diffusion coefficients for each isotope that require numerical values.

### Diffusion Coefficients

The chemical diffusion coefficient for protium,  $D_{11}^P$ , is the most prevalently measured value, and is traditionally fit to an Arrhenius models. The chemical diffusion coefficient for deuterium is scaled based on the mass dependent relationship

$$\frac{D_{11}^D}{D_{11}^P} = \left( \frac{m_P}{m_D} \right)^\beta \tag{8}$$

In equation (8), the exponent  $\beta$  is theoretically equal to  $1/2$  for ideal systems.

Equation (7) also requires numerical values of the self-diffusion coefficients which in the absence of direct measured values are determined by theoretical relationships. The quantitative relationship between the chemical diffusion and self-diffusion coefficients generally requires consideration of two other definitions of diffusion coefficients. These are the intrinsic diffusion coefficient and the tracer

diffusion coefficient. Typically, self-diffusion is measured by tracking a radioactive isotope. The so-measured diffusion coefficient is the self-diffusion coefficient for the radioactive isotope, and is hence related to the self-diffusion coefficient of the other isotopes as per equation (8).

The intrinsic diffusion coefficient concerns the effect of counter-flow of the other element in a binary system. Since the hydrogen diffusion mechanism is by movement between interstitial sites, the Zr is effectively fixed in position and the chemical diffusion coefficient is equal to the intrinsic diffusion coefficient. Thus, the chemical diffusion coefficient is directly related to the self-diffusion coefficient by a thermodynamic factor (Kizilyalli, Corish and Metselaar, 1999) as per

$$D_{chem} = D_{self} \left( 1 + \frac{\partial \ln \gamma}{\partial \ln c} \right) \quad (9)$$

where  $\gamma$  is the activity of the mobile element in the system. For dilute mixtures,  $\gamma$  is practically constant, so the second term in the parentheses can be neglected. Thus, the chemical diffusion coefficient is approximately the same as the self-diffusion coefficient such that the chemical diffusion coefficients  $D_{11}^P$  is related to the self-diffusion coefficient  $D_1^P$  as per

$$D_{11}^P = D_1^P \text{ and } D_{11}^D = D_1^D \quad (10)$$

### Diffusivity Matrix

Equations (10) are applied in equation (7) to provide

$$\begin{aligned} J^P &= -D^P \nabla c^P - f^P (D^P - D^D) \nabla c^D \\ J^D &= -D^D \nabla c^D - f^D (D^D - D^P) \nabla c^P \end{aligned} \quad (11)$$

The subscripts appearing up to equation (10) are redundant and hence are omitted in the following developments. The fractions of each isotope appearing in equation (11) are expressed explicitly in terms of the concentrations as

$$f^P = \frac{c^P}{c^P + c^D}, \quad f^D = \frac{c^D}{c^P + c^D} \quad (12)$$

The isotopic diffusivities depend on the atomic mass, such that the protium diffusivity is nominally  $\sqrt{2}$  higher than for deuterium. This is as per equation (8) with  $\beta=1/2$ , so equation (11) can be expressed as the diffusivity matrix

$$\begin{Bmatrix} J^D \\ J^P \end{Bmatrix} = -D^D \begin{bmatrix} 1 & -f^D(\sqrt{2}-1) \\ f^P(\sqrt{2}-1) & \sqrt{2} \end{bmatrix} \begin{Bmatrix} \nabla c^D \\ \nabla c^P \end{Bmatrix} \quad (13)$$

which involves only the deuterium diffusivity, along with the fractions of each isotope that is determined internally during the simulation. Hence, no additional input data is required for diffusivity properties.

### Two-isotope Diffusion Model with Hydrides Present

When the hydrogen concentration exceeds the Terminal Solid Solubility (TSS), a portion of the concentration may be in form of hydride, so the driving force for diffusion depends on the gradients in solute concentrations. Then equation (13) must be restated as

$$\begin{Bmatrix} J^D \\ J^P \end{Bmatrix} = -D^D \begin{bmatrix} 1 & -f_s^D(\sqrt{2}-1) \\ f_s^P(\sqrt{2}-1) & \sqrt{2} \end{bmatrix} \begin{Bmatrix} \nabla c_s^D \\ \nabla c_s^P \end{Bmatrix} \quad (14)$$

where the subscript “s” denotes the driving force depending on the solute portions of D and P. In equation (14), the fraction parameters now relate to the fraction of solute portions only, since any concentration in hydride phase is regarded as being immobile and its presence does not contribute to the diffusion. This corresponds to the fractions being defined as

$$f_s^P = \frac{c_s^P}{c_s^P + c_s^D}, \quad f_s^D = \frac{c_s^D}{c_s^P + c_s^D} \quad (15)$$

The relationship between total and solute concentrations requires the TSS model developed below.

## TSS MODEL DEVELOPMENT

### Basis for Two-isotope TSS Model

Prior unpublished work to develop a two-isotope diffusion model complete with TSS interaction applied two key assumptions:

- 1) When two isotopes are present (protium & deuterium), the TSS logic is used on the total combined concentrations.
- 2) When hydrides are present, the ratio of protium to deuterium in solution is assumed to be the same as the ratio of protium to deuterium in the local hydride.

The first point (1) above can be stated quantitatively as

$$c_s = c_s^P + c_s^D = \min(c^P + c^D, TSS) \quad (16)$$

to provide one equation to be applied in the TSS model. However, this does not uniquely define the concentrations of each isotope and an additional equation required to complete the model. The statement in item (2) of the above list translates to

$$\frac{c_s^P}{c_s^D} = \frac{c_h^P}{c_h^D} \quad (17)$$

where the subscript “h” denotes concentration in hydride phase. Equation (17) provides the additional equation to combine with equation (16) to provide two equations required to uniquely determine the two values of concentrations in solution (or hydride).

In order to practically apply equations (16) and (17), some algebraic manipulation is done to obtain an alternate but equivalent pair of equations.

$$c_s^P = f^P \min(c^P + c^D, TSS) \quad (18a)$$

$$c_s^D = f^D \min(c^P + c^D, TSS) \quad (18b)$$

These equations show how simple factors corresponding to the isotope fractions extend the TSS model based on  $[D_{eq}]$  to two isotopes.

### Physical Implications of Ratio-based TSS Model

The ratio assumption of equation (17) corresponds to some physical conditions which are listed here:

- a) The protium and deuterium in solution precipitate at the same rate relative to the quantity of each isotope present in solution. This ignores rate effects in the precipitation process that may be affected by the different isotope mass.
- b) The protium and deuterium in the hydride phase dissolve at the same rate relative to the quantity of each isotope present in the hydride. This ignores rate effects in the dissolution process that may be affected by the different isotope mass.
- c) When hydrides are present during operation, the concentration in solution becomes supersaturated due to pickup of deuterium. The pickup of deuterium will effectively increase the fraction of deuterium in solution above that of the fraction in the hydride at the beginning of the operating cycle. In order for the isotope fraction assumption to hold, the isotopic fraction in the hydride must be allowed to change instantaneously even though there is no precipitation. Physically, this is achieved by a mechanism of isotopic exchange in the existing hydride. The hydride ratio model of equation (17) corresponds to the condition where this exchange rate is fast in comparison with pickup and diffusion.

In the context of the pressure tube applications, the virtually complete precipitation of all isotopes at shutdown temperature will make the response insensitive to assumption (a). However, the validity of assumptions (b) and/or (c) should be checked by comparison with measurements.

## APPLICATION OF THE MODEL

The flux components as determined in equation (14) lead to the rate of change of concentration determined from the divergence of the flux

$$\dot{c} = -\nabla \cdot J = \nabla(D\nabla c_s) \quad (19)$$

This is basically Fick's law except with the subscript "s" denoting the solute concentration relating to the driving force for diffusion; this does not apply on the left side of the equation which accumulates the total concentration.

Equation (19) is solved numerically with a finite volume spatial discretization of the pressure tube from the rolled joint end and extending for 1.5 m inboard. The numerical solution is necessary due to the temporal and spatial variation in deuterium pickup rate, and due to the interaction of TSS during temperature transients corresponding to shutdown and start-up events. In the following verification cases, equation (19) is first solved using the approximate  $[D_{eq}]$  approach in which the initial protium is applied as if it were deuterium. Then, the same input conditions are applied to the two-isotope version of the diffusion model.

Since diffusion rate and TSS is strongly dependent on temperature, two cases are presented relating to the the hotter outlet end and colder inlet end of the pressure tube. The rolled joint galvanic and crevice corrosion ingress profile depicted in Figure 2 is simplified to be uniform and only applies to a small length of pressure tube at the rolled joint end. The magnitude of this source term decreases with time in accordance with build-up of barriers due to corrosion products. Over the entire length of the model is applied a lower constant rate of corrosion with a uniform spatial distribution.

### Outlet Conditions

The case corresponding to outlet conditions is simulated for demonstration purposes with the two-isotope model with initial protium of 15 ppm and all pickup during operation is deuterium. For comparison purposes, the same input conditions are applied to the single isotope approximation in which the initial concentration is taken to be an equivalent amount of deuterium. Both models have the same net equivalent quantity of hydrogen, but the redistribution is different due to the higher mobility of protium.

The simulations are run for a nominal reactor lifetime, and Figure 3 shows the profiles of the total equivalent  $[D_{eq}]$  concentration at different numbers of Hot Days (HD) of operation. The two-isotope model (labelled D+P in the legend of Figure 3) results in slightly enhanced diffusion inboard such that the

the peak concentration in the rolled joint compressive region is lower than the single isotope model (labelled D only in the legend). This is as expected because the two-isotope model accounts for the protium portion of the hydrogen concentration having a higher diffusion coefficient. Inboard of the compressive region the total concentration is higher for the two-isotope model, but only slightly so. Inboard of the compressive region of the rolled joint, the difference between the two models is not significant with respect to assessment of hydrogen related degradation.

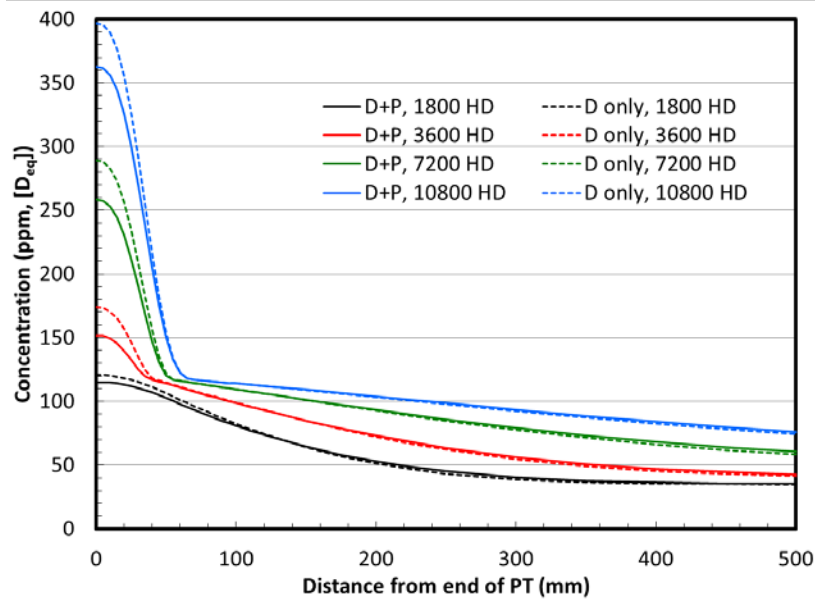


Figure 3– Comparison of equivalent concentration profiles for outlet conditions

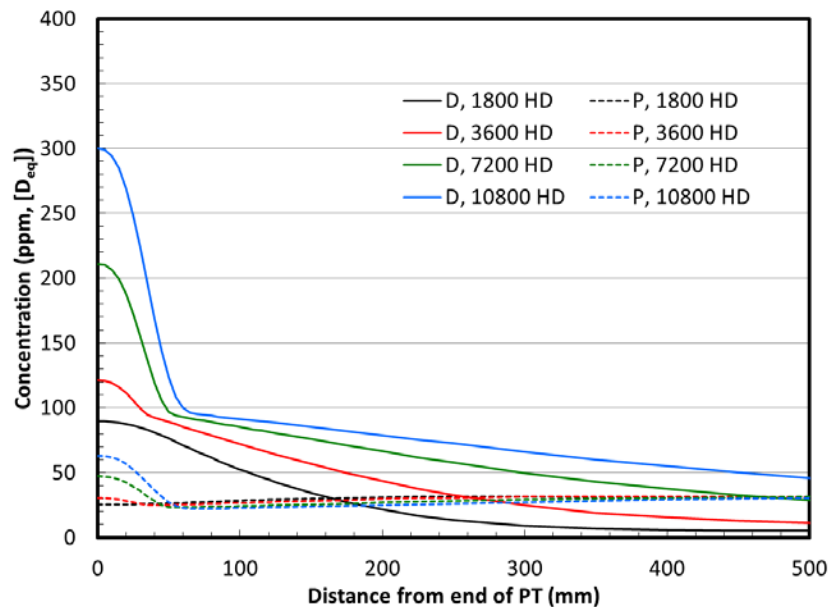


Figure 4– Evolution of deuterium and protium profiles for outlet conditions

The details of diffusion of the protium and deuterium isotopes are plotted in Figure 4 and show that the uniform initial concentration of protium redistributes over time. When the total concentration is below the Terminal Solid Solubility Dissolution (TSSD), diffusion depletes the concentration of protium



slightly in the compressive region. When the total concentration exceeds TSSD, the protium concentration is increased in the compressive region. This effect is due to the interaction of the diffusion and TSS processes. Since the only source of protium is the initial concentration, this result demonstrates that the protium concentration can increase without any additional source of pickup during operation.

### Inlet Conditions

The inlet case example is similar to the outlet case but with lower pickup rates due to the lower operating temperature at the inlet. Also, a lower value of initial protium is assumed to be 10 ppm. Figure 5 shows the total  $[D_{eq}]$  concentration profiles for the two-isotope and single isotope models at various times during the simulation. In both the single and two-isotope cases, TSSD is exceeded before 1800 hot days leading to a concentration peak in the rolled joint. Aside from the expected difference in peak concentration in the rolled joint region, the  $[D_{eq}]$  profiles are in very close agreement, and the influence of protium does not significantly affect the equivalent concentration that would be applied in assessment of the pressure tube inboard of the compressive zone.

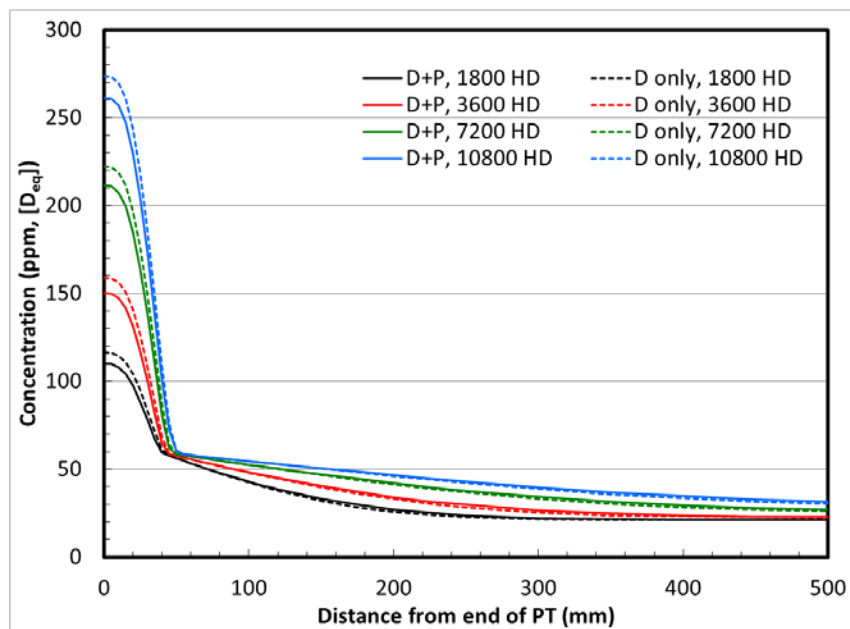


Figure 5– Comparison of equivalent concentration profiles for inlet case

The protium and deuterium concentration profiles for the inlet case plotted in Figure 6 show the same general trend as the outlet case results in Figure 4. Quantitative differences are due mainly to the lower diffusion coefficient and lower TSS at the lower inlet temperature.

### CONCLUSIONS

A two-isotope model for the diffusion of protium and deuterium has been developed and implemented into a numerical model. The model incorporates interaction between the protium and deuterium isotopes on the basis of physical process of chemical diffusion and self-diffusion. The revised model has been tested, and the results demonstrate that the derived model is properly implemented.

Preliminary results indicate that the diffusion with isotopic interaction will cause a uniform initial protium distribution to become non-uniform. Diffusion alone will tend to deplete initial protium from the rolled joint region, but interaction with TSS leads to an increase in protium in the compressive zone of the rolled joint region. This result suggests that redistribution of initial protium can explain observations of higher protium in the rolled region.

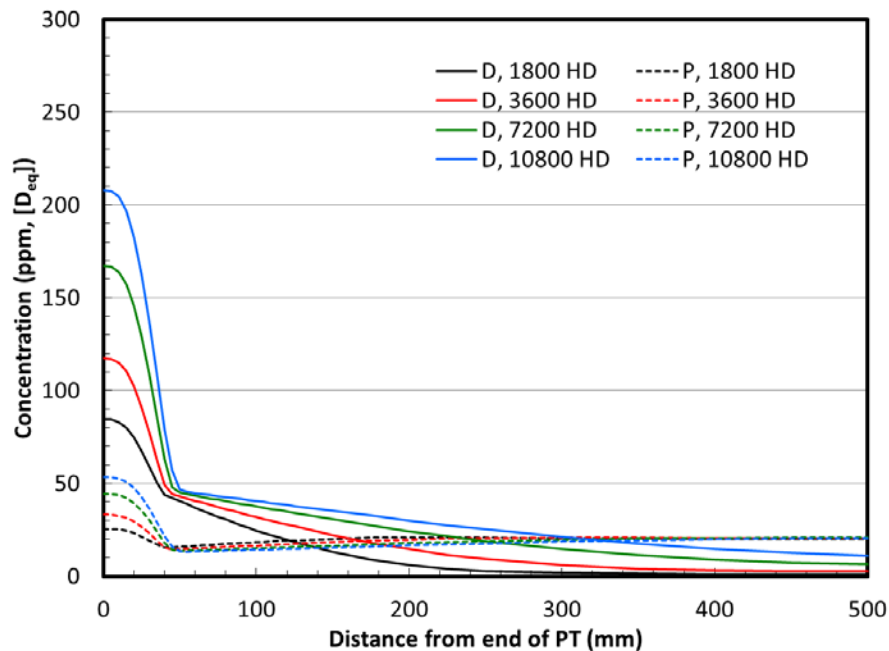


Figure 6– Evolution of deuterium and protium profiles for inlet case

## ACKNOWLEDGMENTS

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## REFERENCES

- CSA N285.8-15, *Technical requirements for in-service evaluation of zirconium alloy pressure tubes in CANDU reactors*, Canadian Standard Association, July 2015.
- De Groot, S.R., *Thermodynamics of Irreversible Processes*, North-Holland Publishing Company, Amsterdam, Interscience Publishers, Inc. New York, 1952.
- Jost, W., *Diffusion in Solids, Liquids, Gases*, 3rd printing, Academic Press Inc. Publishers New York, 1960.
- Richter, F.M., Liang, Y., and Davis, A. M., *Isotope fractionation by diffusion in molten oxides*, *Geochimica et Cosmochimica Acta*, Vol. 63, No. 18, 2853–2861, 1999.
- Watkins, J.M., DePaolo, D.J., Ryerson, F.J., Peterson, B.T., *Influence of liquid structure on diffusive isotope separation in molten silicates and aqueous solutions*, Lawrence Berkeley National Laboratory series, LBNL-5133E, Permalink:<https://escholarship.org/uc/item/54t7x95x>, 2011.
- Watkins, J.M., Liang, Y., Richter, F., Ryerson, F.J., DePaolo, D.J., *Diffusion of multi-isotopic chemical species in molten silicates*, *Geochimica et Cosmochimica Acta*, Vol. 139, No. 18, 313-326, 2014.
- Liang, Y., *Models and experiments for multicomponent chemical diffusion in molten silicates*. Ph.D. thesis, Univ. Chicago, 1994.
- Kizilyalli, M., Corish, J., Metselaar, R., *Definitions of Terms for Diffusion in the Solid State*, *Pure and Applied Chemistry*, Vol. 71, No. 7, 1307-1325, 1999.