THE PREDICTION OF DEUTERIUM INGRESS IN ZIRCONIUM ALLOY PRESSURE TUBES

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ABSTRACT

In the CANDU pressurized heavy water reactor (PHWR), the nuclear fuel is contained in hundreds of Zr-2.5 Nb alloy pressure tubes. The corrosion of zirconium alloy produces deuterium that is absorbed by the body of the pressure tube. The presence of this deuterium causes hydrogen embrittlement of zirconium alloy with an adverse effect on the integrity of the pressure tube. An accurate prediction of deuterium accumulation over time is an important step for ensuring the fitness-for-service of pressure tubes.

Deuterium ingress data collected from in-service inspection of pressure tubes exhibit heteroscedasticity, i.e., the variance of deuterium concentration is dependent on operating time (or exposure) and temperature. The currently used model by the nuclear industry involves a logarithmic regression of deuterium content over time and temperature. Since this approach does not deal with heteroscedasticity precisely, it results in a conservative prediction of the deuterium ingress.

The paper presents a new approach for predicting deuterium ingress based on a weighted least-squares (WLS) regression that overcomes the limitations of the existing model, and it provides realistic prediction bounds of deuterium ingress.

1. INTRODUCTION

1.1 Background

In the CANDU[3] pressurized heavy water reactor (PHWR), the nuclear fuel is contained in hundreds of Zr-2.5 Nb alloy pressure tubes. The heavy water (deuterium oxide) used as the primary coolant reacts with the zirconium on the inside surface of pressure tubes, forming a corrosion film of zirconium oxide with concomitant release of deuterium:

$$Zr + 2\,D_2O = ZrO_2 + 2\,D_2$$

The deuterium generated by this reaction diffuses into the body of the pressure tube in spite of the physical barrier of the oxide film [1]. The deuterium hydrogen tends to accumulate in the regions of high stress concentration, such as crack tips of flaws in the zirconium alloy pressure tube. This presence of excessive deuterium in the causes hydrogen embrittlement, which is detrimental to integrity of the pressure tube, as explained in Section 1.2. For this reason, the CSA Standard N285.8 [2] specifies the upper limit of deuterium concentration above which the integrity of the pressure tube is considered to be compromised.

Therefore, an accurate fitness-for-service assessment of pressure tubes requires an accurate prediction of their deuterium concentration throughout the service life of the reactor.

The corrosion and subsequent deuterium ingress are affected by the fast neutron flux, operating time (or exposure), fluence i.e., flux×operating time), temperature, water chemistry, oxide film thickness, and microstructure of the zirconium alloy. Because of a complex effect all these factors, the amount of deuterium ingress in zirconium alloy samples taken from the population of in-service pressure tubes show large variability.

The prediction of the ingress of the deuterium over time is as an important step in the life cycle management of pressure tubes in the reactor. If at a certain time in the future the deuterium concentration is predicted to exceed the code specified limit, extra measures will need to be taken to ensure the structural integrity of the pressure tube. Thus, an overly conservative predictive model would lead to premature inspections and

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[3] CANada Deuterium Uranium is a trademark of the Atomic Energy Canada Ltd.

replacement of pressure tubes resulting in loss of operational efficiency. On the other hand, a non-conservative predictive model would result in an increased risk of delayed hydride cracking and pressure tube rupture with serious consequences.

Several studies [3-5] have attempted to correlate the deuterium ingress with the microstructure of zirconium alloy by means of mechanistic models, but the practical application of such models to the fitness-for-service assessment of in service pressure tubes remains unclear. The reason is that input parameters required for mechanistic models cannot be obtained from in-service inspections of pressure tubes.

A more practical approach is to use a statistical regression model to correlate deuterium ingress with the temperature and exposure measured in terms of the reactor hot hours. In general, an increase in the temperature accelerates the corrosion rate, and longer exposure permits greater accumulation of deuterium released from the corrosion reaction.

A logarithmic regression model is typically used by the nuclear industry, in which log of deuterium concentration is correlated with exposure (in hot hours) and temperature. The regression model is then used to predict an upper bound of deuterium concentration at a future time. The time at which the upper bound is expected to exceed the code specified limit is considered as the remaining life of the pressure tube.

The paper shows that the current typically used logarithmic regression model is not precise in modelling the statistical features of the deuterium ingress data collected from in-service pressure tubes. The choice of logarithmic model is heuristic and it appears to predict conservative upper bound of deuterium concentration. Therefore, the paper presents an improved model that incorporates all the statistical features in an explicit manner and provides more realistic upper bound of deuterium concentration.

1.2 Deuterium Ingress and Fitness for Service Requirements

Hydrogen equivalent concentration at time t, $H_{eq}(t)$, is defined as the concentration of hydrogen by weight that would be present in the material if all the deuterium atoms, $D(t)$, were replaced by hydrogen atoms. Thus

$$H_{eq}(t) = H_i + \frac{D(t)}{2}$$

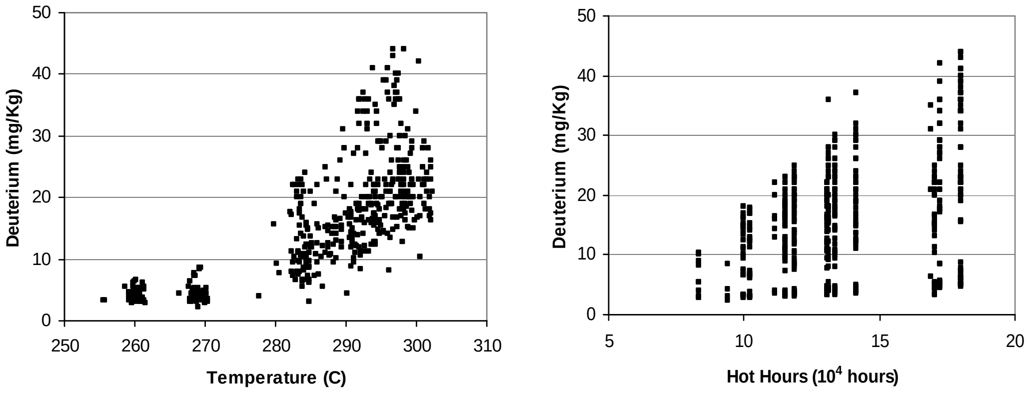
where H_i is the initial hydrogen concentration present in the material. Note that H_{eq} is variable along the length of pressure tube, because the temperature increases from inlet to outlet of a pressure tube.

Section 8.2(a) of CSA N285.8 specifies that H_{eq} shall be less than the limit specified in Table 5 of the Standard [2]. For example, H_{eq} should not exceed 70 ppm at the inlet and 100 ppm at the outlet of the pressure tube. Furthermore, Clause 12.3.5.2 of CSA N285.4 [6] specifies additional limits on the rate of change in H_{eq}. For example, the maximum allowable rate of change is specified as 3 ppm per 10,000 hot hours for a pressure tube with maximum outlet temperature less than 315° C.

The code specified upper limits on the deuterium concentration represent the terminal solid solubility for hydrogen dissolution (TSSD). If H_{eq} exceeds the TSSD limit, flaw tip hydride ratcheting is expected to occur with each reactor heat-up/cool-down cycle. Accumulation of hydrides over time then can make the pressure tube vulnerable to delayed hydride cracking (DHC).

1.3 Data

Deuterium concentration data used in this study come from a CANDU nuclear station in Canada. The sample consists of 488 observations taken between 80,000 and 180,000 hot hours of operation. The deuterium concentration measured in the unit of mg/kg or *ppm* by weight is determined from the chemical analysis of scrape samples taken from the body of in-service pressure tubes. Typically four scrape samples are taken from each pressure tube. In the present dataset, the sampling sections are approximately located at 1.5, 4, 5 and 5.8 meter from the inlet of the pressure tube. Since the temperature along the pressure tube increases from inlet to outlet, these sections correspond to temperatures ranging from 255 to 303°C.



(a) Deuterium ingress vs. Temperature (b) Deuterium ingres vs. Hot hours

Fig.1: Deuterium ingress data

The deuterium ingress data against temperature (*T* °C) are plotted in Figure 1(a) and against operating time measured in the unit of ten thousand (10^4) hot-hours in Figure 1(b). The fanning-out of data with increase in time and temperature indicates that the variability of deuterium concentration is also an increasing function of these two variables. In statistical terms, this observation is referred to as heteroscedasticity of the data, which must be duly accounted in a statistical prediction model.

1.4 Currently Used Model

The Arrhenius equation describes the dependence of the rate constant of a chemical reaction on the absolute temperature. With the thinking that the deuterium ingress follows a diffusion type process influenced by temperature, the nuclear industry adopted the Arrhenius equation and modified it to account for deuterium accumulation during the operating life of the reactor. The following modified version of the Arrhenius equation has been currently used by the industry:

$$\log D_i = \beta_0 + \beta_1\left(\frac{1}{T_i+273}\right) + \beta_2\left[\log H_i\right] + \beta_3\left[\left(\frac{1}{T_i+273}\right)\log H_i\right] + E_i \qquad (i = 1,2,\ldots,n) \tag{1}$$

where D_i denotes deuterium concentration; T_i denotes temperature; H_i denotes time and E_i denotes residual/random error. Parameters $\beta_0 - \beta_3$ are regression coefficients. Note that the residual, E_i, is an *iid* normal random variable with zero mean and a standard deviation. It means that the D_i follows the log-normal distribution. Note that many variations of Eq.(1) have been utilized by the industry to model data coming from different stations, but logarithmic regression is common feature of all of them.

1.5 Research Objectives

This paper focuses on the problem of accurate statistical prediction of deuterium concentration in the future. The prediction of time at which the deuterium concentration exceeds the code specified upper limit is important, because after this time the initiation of delayed hydride cracking (DHC) of potential flaws becomes a possibility. In a risk-informed assessment of the evaluation of integrity of the reactor core requires the computation of probability of DHC initiation. The probability of deuterium concentration exceeding the code specified upper limit is an important input to this computation.

Therefore, a key objective of this paper is to develop an accurate regression model to predict the probability distribution and probabilistic upper bound of deuterium concentration in the pressure tubes. A new deuterium ingress model is derived using the theory of weighted least-squares (WLS) regression, which is shown to overcome the limitations of the currently used model.

2. PROPOSED WEIGHTED LEAST-SQUARES (WLS) MODEL

2.1 Model

A Weighted Least-Squares (WLS) regression with a variance function is a more systematic approach to account for heteroscedasticity of data. The basic idea is to model the variance of the data as a parametric function and use it to assign different weights to observations in the sample [7]. The WLS model is commonly used in data analysis and calibration curve estimation in chemical engineering [8].

The following model is proposed to predict the deuterium content, D_i,

$$D_i = \beta_0 + \beta_1 T_i + \beta_2 H_i + \beta_3 T_i H_i + \beta_4 T_i^2 + \beta_5 H_i^2 + E_i \qquad (i = 1,2,\ldots,n) \tag{2}$$

The residual, E_i, has zero mean, but its variance is modelled as a function of time and temperature as

$$(\sigma_i)^2 = \theta_0^2 (T_i - 240)^{\theta_1} H_i^{\theta_2} \text{ or } \log\sigma_i = \log\theta_0 + \tfrac{1}{2}\theta_1 \log(T_i - 240) + \tfrac{1}{2}\theta_2 \log H_i \tag{3}$$

Note that θ_0, θ_1 and θ_2. are three additional unknown parameters that need to be estimated from the data. In the analysis, 240°C is taken as the origin of temperature axis, which allows to rescale the range of temperature in the data. The results of statistical analysis are not sensitive to the choice of the origin. This model implies that the logarithm of variance is linearly related with time and temperature.

The weight $w_i = w(H_i, T_i)$ is taken as an inverse of the variance to ensure that parameters estimates will have the minimum variance (i.e., best estimates). Thus,

$$\frac{1}{w_i} = (\sigma_i)^2 \tag{4}$$

In order to predict Deuterium content at the time H_0 and a temperature T_0, the corresponding vector of predictors, $\mathbf{x_0}$, is given as

$$\mathbf{x_0} = (1, T_0, H_0, H_0 T_0, T_0^2, H_0^2) \tag{5}$$

The average and variance of deuterium content are given as

$$\mu(\hat{D}_o) = \mathbf{x_0}\hat{\boldsymbol{\beta}} \text{ and } \left[\sigma(\hat{D}_o)\right]^2 = \left[\mathbf{x}_o(\mathbf{X}^T\mathbf{W}^{-1}\mathbf{X})^{-1}\mathbf{x}_o^T + 1/w_0\right] \tag{6}$$

where the weight matrix $\mathbf{W}$ is a diagonal matrix, $\mathbf{W}_{n\times n} = diag[w_1, w_2, ..., w_n]$. Note that w_0 is the weight corresponding to T_0 and H_0, calculated from Eq. (3) and (4). The p^{th} percentile of the deuterium content can be derived as

$$d_p = \mu(\hat{D}_o) + \sigma(\hat{D}_o) \times t_{p,(n-6)} \tag{7}$$

Due to large sample size (n), in place of the *t*-variate, a standard normal variate, u_p, can be used without introducing any appreciable error, because the degrees of freedom are quite large. Thus,

$$d_p \approx \mu(\hat{D}_o) + \sigma(\hat{D}_o) u_p \tag{8}$$

2.2 Statistical Estimation

Conceptually, the regression model is fitted by minimizing the weighted sum of squares of residuals given as

$$RSS(\boldsymbol{\beta}, \boldsymbol{\theta}) = (\mathbf{D} - \mathbf{X}\boldsymbol{\beta})^T [\mathbf{W}] (\mathbf{D} - \mathbf{X}\boldsymbol{\beta}) \tag{9}$$

where $\boldsymbol{\beta} = \{\beta_o, \beta_1, \ldots, \beta_5\}$ is a vector of regression coefficient, $\boldsymbol{\theta} = \{\theta_0, \theta_1, \theta_2.\}$ is a vector of parameters of the variance function and $\mathbf{X}_{n\times 6}$ is the matrix of covarariates.

For estimating the model parameters, the maximum likelihood estimation (MLE) method is used [9]. Since the regression Eq. (2) implies that the deuterium content D_i is normally distributed with mean, $\mu_i = \mathbf{x}_i\boldsymbol{\beta}$, and variance, σ_i^2, given by Eq.(3), the probability density function (PDF) of D_i is written as

$$f(D_i) = \frac{1}{\sqrt{2\pi\sigma_i^2}} \exp[-\frac{(D_i - \mu_i)^2}{2\sigma_i^2}] \tag{10}$$

Since $\{D_i, i = 1, 2, 3, \ldots, n\}$ are independent, the likelihood function for the data is written in a product form as:

$$L(D_1, \ldots, D_n) = \prod_{i=1}^{n} f(D_i) \tag{11}$$

By maximizing the likelihood function with respect to parameters $\boldsymbol{\beta}$ and $\boldsymbol{\theta}$**,** their point estimates were calculated using an iterative maximization algorithm [9,10].

Table 1: Parameters of the WLS model

$\hat{\beta}_0$	$\hat{\beta}_1$	$\hat{\beta}_2$	$\hat{\beta}_3$	$\hat{\beta}_4$	$\hat{\beta}_5$	$\hat{\theta}_0$	$\hat{\theta}_1$	$\hat{\theta}_2$	R^2
1175	-8.164	-16.21	0.05998	0.01412	0.02917	1.139×10^{-4}	3.678	3.875	0.94

The parameters of the WLS model are presented in Table 1. Hypothesis tests confirmed that all model parameters are statistically significant. The goodness of fit of this model indicated by $R^2 = 0.94$ is quite high.

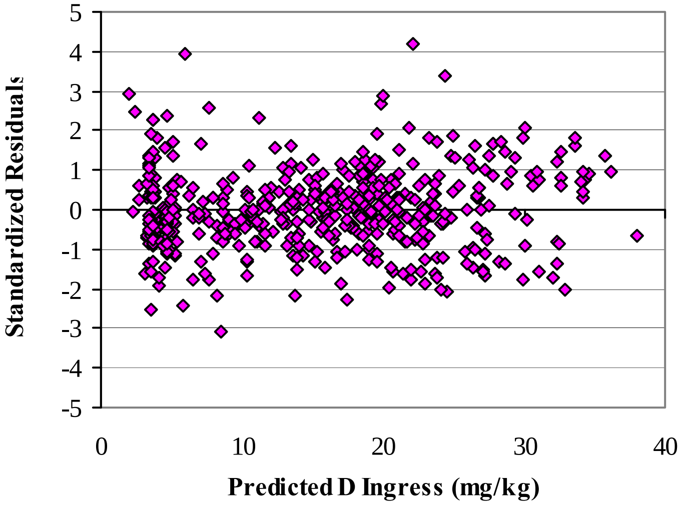


Fig. 2: Standardized weighted residuals of WLS model

The weighted residuals, calculated as $E_i\sqrt{w_i}$, of the WLS model are standardized and plotted in Figure 2. A uniform scatter of the residuals confirms that the WLS model has taken care of heteroscedasticity of data.

3. RESULTS

In Figure 3, 97.5% percentile ($D_{0.975}$) upper bounds of the deuterium concentration are plotted as a function of hot hours the for the outlet region of the pressure tube that is at 303°C.

The MAM upper prediction limit rises quite rapidly as the operating time increases and it appears to be fairly conservative upper bound of the data. In contrast, the upper limit of WLS model envelopes the data in less conservative but realistic manner. For example, at H = 200,000 hot hours, WLS model predicts 70 mg/kg deuterium, which is about 25% less than the prediction of the Arrhenius model (90 mg/kg).

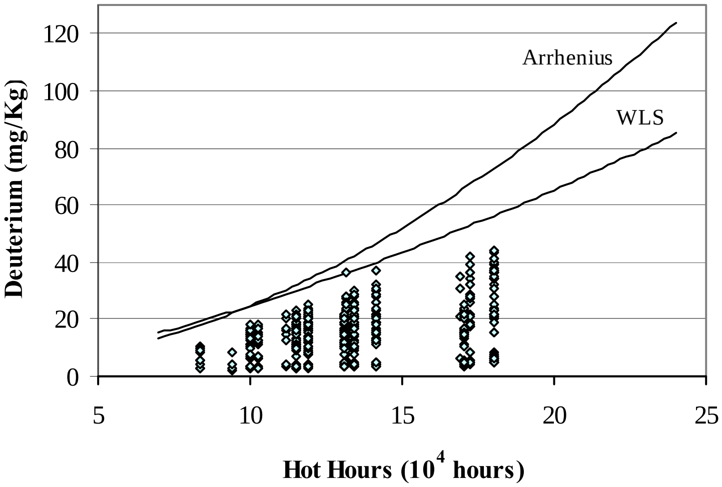


Fig. 3: Upper prediction limit (97.5% percentile) of deuterium ingress as a function of operating time (T=303°C)

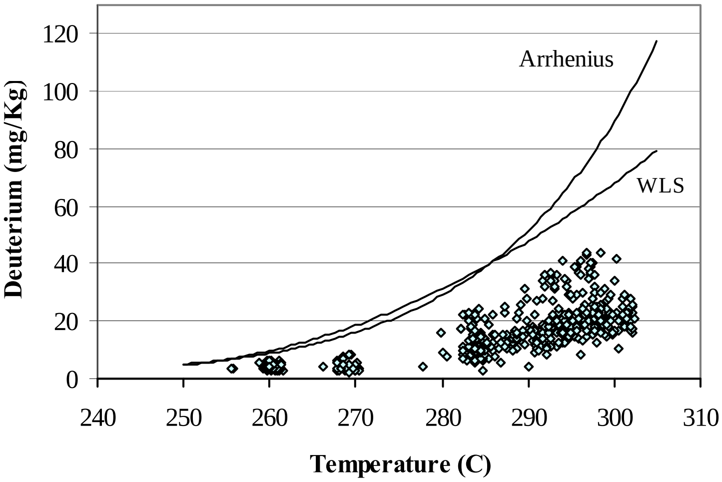


Fig. 4: Upper prediction limit (97.5% percentile) of deuterium ingress as a function of Temperature (operating time=220,000 hot hours)

Figure 4 compares the upper bounds of deuterium content as a function of temperature, while the operating time is fixed at 220,000 hot hours. At temperatures above 290°C, the Arrhenius upper limit appears to be fairly conservative. For example, for T = 300°C, the deuterium content predicted by the WLS model (60 mg/kg) is significantly less than the prediction of the Arrhenius model (82 mg/kg). At temperatures below 280°C, the WLS upper bound is slightly higher than that of MAM.

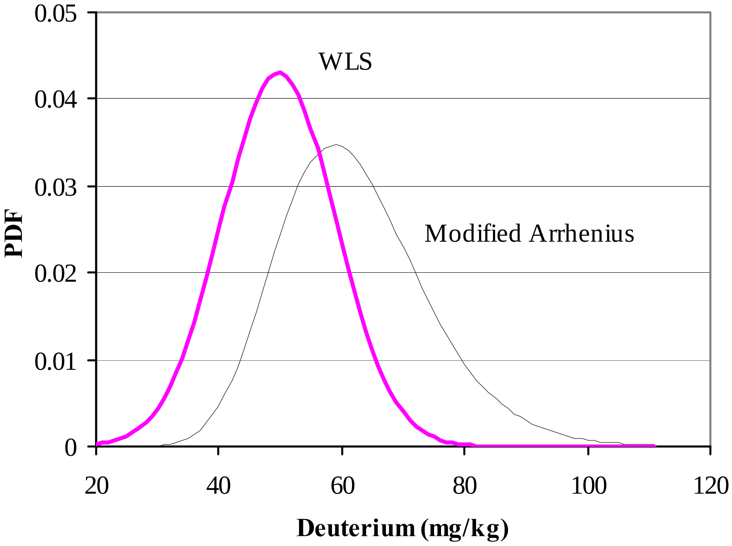


Fig. 5: Comparison of probability distributions of deuterium concentration at the outlet section (Temperature 300°C and operating time=220,000 hot hours)

The distribution of deuterium content is an input to the probabilistic assessment of delayed hydride cracking (DHC) of pressure tubes. The impact of the differences in the distribution predicted by WLS and MAM can be further understood by an example. Consider deuterium distribution at 220,000 hot hours and T = 300°C. According to MAM, the deuterium content follows a lognormal distribution with density function:

$$f(d_1) = \frac{1}{d_1 \sigma_1 \sqrt{2\pi}} \exp[-\frac{(\ln d_1 - \mu_1)^2}{2\sigma_1^2}] \quad (12)$$

where parameters, μ_1 = 4.11 and σ_1 = 0.192, are obtained from the regression equation (Eq. 5). The mean and standard deviation of deuterium concentration predicted by the MAM model are 62 mg/kg and 12 mg/kg. For the this case, the WLS predicts the deuterium distribution as normally distributed with mean, μ_w = 49.7 mg/kg, obtained from Eq.(21) and standard deviation, σ_w = 9.3 mg/kg, computed from Eq.(13). Its density function is given as:

$$f(d_w) = \frac{1}{\sigma_w \sqrt{2\pi}} \exp[-\frac{(d_w - \mu_w)^2}{2\sigma_w^2}] \quad (13)$$

The two distributions are compared in Figure 5. The lognormal distribution predicted by MAM is shifted towards higher values and it has higher variance than the normal distribution predicted by the WLS. The lognormal distribution is known for long and heavy tail, which will inflate the estimates of probability of DHC initiation in pressure tubes. In short, biased predictions of lognormal model can result in premature maintenance or removal of pressure tubes from the reactor.

4. CONCLUSIONS

The paper shows that a heuristic model currently used by the industry is not able to model accurately the statistical features of the deuterium ingress data collected from in-service pressure tubes.

The proposed WLS method is a consistent way of modelling the heteroscedasticity of data and predicting a realistic upper bound of deuterium ingress in pressure tubes. In contrast, the upper bound predicted by the currently used modified Arrhenius model is conservative, which is an artefact of the model.

The proposed approach is expected to improve the overall efficiency of management of the aging reactor components. This method is versatile and applicable to other time-dependent data sets collected from surveillance of the nuclear reactor.

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