OXYGEN POTENTIAL IN THE GAP OF DEFECTIVE CANDU FUEL RODS DURING SEVERE ACCIDENT CONDITIONS

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Abstract

A model has been developed to describe the multi-component transport of steam, hydrogen and stable fission-product gas in the fuel-to-clad gap of defective CANDU fuel rods during severe reactor accident conditions. The incoming steam must diffuse into a breached rod (i.e., with a defect located at the down stream end) against any counter-current flow of non-condensable fission gases and out-flowing hydrogen that is produced from the internal reaction of the steam with the Zircaloy cladding or urania. This treatment is used to predict the local molar distribution of hydrogen and steam so that the internal oxygen potential can be estimated along the gap as a function of time.

The present analysis demonstrates that fuel oxidation does not occur because of significant hydrogen production due to both external and internal Zircaloy oxidation. Moreover, even after clad oxidation is complete, the oxygen potential in the gap is significantly reduced from that in the bulk atmosphere of the reactor coolant due to reduced steam penetration into the gap and local internal hydrogen production from urania oxidation.

1. INTRODUCTION

In a fuel rod with a cladding defect, the volatile fission-product gases that are released from the fuel matrix will migrate along the fuel-to-clad gap toward the defect site, and eventually into the reactor coolant system (RCS). The transport of the short-lived volatile fission products in the gap has been studied extensively during normal reactor operation, where diffusion is shown to be the dominant process of transport in the gap.[1-5]

During a reactor transient, the presence of higher fuel temperatures and the possible occurrence of steam-oxidation of the uranium dioxide fuel following clad rupture may lead to enhanced stable gas release from the fuel matrix. In a high-temperature steam atmosphere, the cladding will remain in place as it is converted to zirconium dioxide. However, for fuel oxidation to take place, steam must diffuse into the breached element against any counter-current flow of non-condensable fission gases, and out-flowing hydrogen that is produced from internal reaction of the in-coming steam with the Zircaloy cladding or urania. The molar flux of a given gaseous component in the gap results from both a diffusive flux and a total molar bulk flow. Consequently, it is important to determine the molar concentration distribution along the gap for the multi-component (steam, hydrogen and fission gas) mixture since the oxygen potential in the gap will depend on the local constituent partial pressures.

In previous work, the effect of a reduced oxygen potential in the gap was modelled by simply reducing the given oxygen potential in the bulk coolant by an empirical factor; i.e., this factor was derived by matching the predicted fuel oxidation kinetics to the observed end-state weight gain for a mini-element in a specific annealing experiment.[6] In contrast, in the present analysis, a complete mathematical model is developed for multi-component transport in the fuel-to-clad gap of a breached fuel rod. A solution of the time-dependent steam, hydrogen and fission gas distributions in the fuel-to-clad gap is given for a specific temperature transient. With a knowledge of the molar distributions, the oxygen potential can be directly estimated. This model also accounts for the resultant hydrogen/steam distribution in the reactor coolant system (i.e., at the defect site) as a result of hydrogen production from external Zircaloy-clad oxidation, as well as the effect of steam reaction in the gap with the internal Zircaloy surface and urania fuel.

2. MODEL DEVELOPMENT

2.1 *Gap Transport Equations*

The transport equations for the one-dimensional multi-component flow of steam, hydrogen and stable fission gases in the thin, annular, fuel-to-sheath gap (see Fig. 1) follows from the standard conservation expression:[7]

$$\frac{\partial c_i}{\partial t} = -\frac{\partial N_i}{\partial z} + q_i - r_i \tag{1}$$

Here for a given component i, c_i (mol m^{-3}) is the molar concentration, N_i is the molar flux in the z-direction (mol m^{-2} s^{-1}) (resulting from diffusion and a total bulk molar flow), and q_i and r_i are the production and loss rates, respectively (in mol m^{-3} s^{-1}). The fluxes and concentration gradients in an ideal gas mixture of n components are related by the Stefan-Maxwell equations:[7]

$$\frac{\partial y_i}{\partial z} = \sum_{j=1, j\neq i}^{n} \frac{1}{cD_{ij}}\left[y_i N_j - y_j N_i\right] \tag{2}$$

where c is the total molar concentration

$$c = \sum_{j=1}^{n} c_j \tag{3}$$

and y_i (= c_i/c) is the mole fraction of species i. The diffusivity parameter cD_{ij} (mol m^{-1} s^{-1}) corresponds to the i-jth pair of the binary mixture (see Appendix A).

For the present transport problem, in addition to the components of the bulk atmosphere (steam and hydrogen), there is also a release of fission gas from the fuel into the gap, which can be represented by xenon. For this ternary system (i.e., H_2O-H_2-Xe mixture), only two equations are independent due to the constraint on the mole fractions which must sum to unity:

$$y_1 + y_2 + y_3 = 1 \tag{4}$$

Thus, Eq. (2) can be solved as a reduced system of two coupled equations for the molar fluxes N_1 and N_2, where employing Eq. (4):[8]

$$N_1 = -c\left(Đ_{11}\frac{\partial y_1}{\partial z} + Đ_{12}\frac{\partial y_2}{\partial z}\right) + y_1 N_T \tag{5a}$$

$$N_2 = -c\left(Đ_{21}\frac{\partial y_1}{\partial z} + Đ_{22}\frac{\partial y_2}{\partial z}\right) + y_2 N_T \tag{5b}$$

In the derivation of Eq. (5), the total molar flux N_T is given by

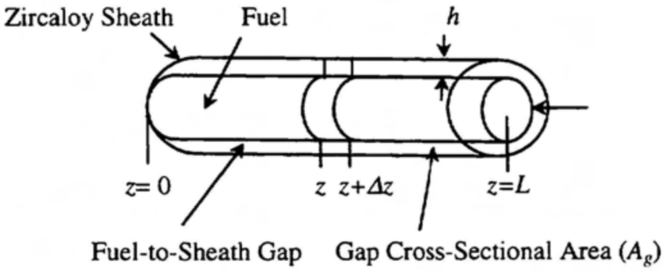

Figure 1. Schematic of a defective fuel rod.

$$N_T = N_1 + N_2 + N_3 \tag{6}$$

The multicomponent diffusion coefficients $Đ_{ij}$ are defined as:

$$Đ_{11} = \frac{Y_{12} + Y_{32} + Y_{23}}{\det}, \quad Đ_{12} = \frac{Y_{12} - Y_{13}}{\det}, \quad Đ_{21} = \frac{Y_{21} - Y_{23}}{\det}, \quad Đ_{22} = \frac{Y_{21} + Y_{31} + Y_{13}}{\det} \tag{7}$$

where

$$\det = \frac{y_1}{D_{12} D_{13}} + \frac{y_2}{D_{12} D_{23}} + \frac{y_3}{D_{13} D_{23}} \tag{8}$$

and

$$Y_{12} = \frac{y_1}{D_{12}}, \quad Y_{13} = \frac{y_1}{D_{13}}, \quad Y_{21} = \frac{y_2}{D_{12}}, \quad Y_{23} = \frac{y_2}{D_{23}}, \quad Y_{31} = \frac{y_3}{D_{13}}, \quad Y_{32} = \frac{y_3}{D_{23}} \tag{9}$$

Thus, in general, for the 2-components (i = 1 and 2),

$$N_i = -c\left(Đ_{i1} \frac{\partial y_1}{\partial z} + Đ_{i2} \frac{\partial y_2}{\partial z} \right) + y_i N_T \tag{10}$$

Finally, substituting Eq. (10) into Eq. (1) yields the one-dimensional transport equation (for species i = 1 and 2)

$$\frac{\partial (c y_i)}{\partial t} = \frac{\partial}{\partial z}\left[c\left(Đ_{i1} \frac{\partial y_1}{\partial z} + Đ_{i2} \frac{\partial y_2}{\partial z} \right) - y_i N_T \right] + q_i - r_i \tag{11}$$

The corresponding system of equations for the stable fission gas ($1 \equiv Xe$) and steam ($2 \equiv H_2O$) is therefore given by:

$$\frac{\partial (c y_1)}{\partial t} = \frac{\partial}{\partial z}\left[c\left(Đ_{11} \frac{\partial y_1}{\partial z} + Đ_{12} \frac{\partial y_2}{\partial z} \right) - y_1 N_T \right] + q_1(z,t) \tag{12a}$$

$$\frac{\partial (c y_2)}{\partial t} = \frac{\partial}{\partial z}\left[c\left(Đ_{21} \frac{\partial y_1}{\partial z} + Đ_{22} \frac{\partial y_2}{\partial z} \right) - y_2 N_T \right] - r_2^{\text{clad ox}}(z,t) - r_2^{\text{fuel ox}}(z,t) \tag{12b}$$

The hydrogen component ($3 \equiv H_2$) follows directly from Eq. (4). In the derivation of Eq. (12a) there is no loss rate term since the xenon is chemically inert and stable. In addition, the source term is zero in Eq. (12b) since there are no chemical reactions which produce H_2O.

The total molar concentration c and molar flux N_T in Eqs. (12a) and (12b) are related through the total gas balance in the gap. Hence, from the conservation statement of Eq. (1):

$$\frac{\partial c}{\partial t} = -\frac{\partial N_T}{\partial z} + q_1 \tag{13}$$

This result follows where the production rate of hydrogen and the loss rate of steam are equal for a given chemical process (see Section 2.4) so that fission gas release is the only net source in the gap. It is also implicitly assumed that hydrogen losses do not occur in the gap, i.e., hydrogen absorption into the clad is prevented due to the production of a protective oxide layer on the inner clad surface as a result of the clad oxidation reaction (see Section 4).

Using Eq. (13), and applying the chain rule in Eqs. (12a) and (12b), the transport equations can be written alternatively as

$$c\frac{\partial y_1}{\partial t} = \frac{\partial}{\partial z}\left[c\left(Đ_{11}\frac{\partial y_1}{\partial z} + Đ_{12}\frac{\partial y_2}{\partial z}\right)\right] - N_T\frac{\partial y_1}{\partial z} + (1 - y_1)q_1(z,t) \tag{14a}$$

$$c\frac{\partial y_2}{\partial t} = \frac{\partial}{\partial z}\left[c\left(Đ_{21}\frac{\partial y_1}{\partial z} + Đ_{22}\frac{\partial y_2}{\partial z}\right)\right] - N_T\frac{\partial y_2}{\partial z} - y_2 q_1(z,t) - r_2^{\text{clad ox}}(z,t) - r_2^{\text{fuel ox}}(z,t) \tag{14b}$$

The initial and boundary conditions for the transport equations are:

$$y_1 = y_1^o, \quad y_2 = y_2^o, \quad \text{for} \quad t = 0, \quad 0 < z < L \tag{15a}$$

$$\frac{\partial y_1}{\partial z} = \frac{\partial y_2}{\partial z} = 0, \quad \text{for} \quad x = 0, \quad t > 0 \tag{15b}$$

$$y_1 = 0, \quad y_2 = y_2^c(t), \quad \text{for} \quad x = L, \quad t > 0 \tag{15c}$$

The quantities y_1^o and y_2^o are the initial quantities specified for the given accident scenario at the start of the transient. The boundary conditions in Eq. (15b) simply indicate that there is no flow at the intact end of the fuel rod in Fig. 1 (i.e., a reflexive condition). The boundary condition in Eq. (15c) indicates that the fission gas concentration is zero at the defect end since the fission gas is continually being swept away by the bulk gas atmosphere flowing past the fuel rod. On the other hand, there is a constant supply of steam (with a mole fraction y_2^c) at this exposed end from the bulk atmosphere in the reactor coolant system (see Section 2.4.3).

For a solution of Eqs. (12a) and (12b), Eq. (13) must be solved for the total molar flux N_T and total molar concentration c (see Section 2.2). In addition, the source term due to fission gas release in the gap (q_1) in Eq. (12a) (see Section 2.3), as well as the loss terms for steam in Eq. (12b) (see Section 2.4), must be evaluated.

2.2 *Total Molar Flux N_T*

During a reactor transient, a temperature gradient may be present in the fuel rods, which should be known *a priori* based on reactor safety calculations. Thus, the temperature function $T(z,t)$ will be known for numerical solution of the gap transport equations. In addition, a pressure gradient may arise along the gap due to the continual release of stable fission gas into the gap.[5,9] The effect of the pressure gradient can be estimated as follows.

Assuming that the bulk velocity is the same as the mole average velocity, N_T can be estimated from the Hagen-Poiseuille flow law where, from a momentum balance, the bulk velocity (v) is calculated to be proportional to the pressure gradient (dP/dz), i.e.,[5]

$$N_T = vc = \left[-\frac{h^2}{12\mu}\frac{dP}{dz}\right]c \tag{16}$$

where h is the radial gap thickness and μ is the viscosity for a gas mixture (see Appendix B). Allowing for the possibility of a temperature gradient as well, the ideal gas law is given by:

$$c(z,t) = \frac{P(z,t)}{RT(z,t)} \tag{17}$$

where R is the ideal gas constant. Thus, Eqs. (13), (16) and (17) yield a partial differential equation for the pressure in the gap:

$$\frac{1}{R}\frac{\partial(P/T)}{\partial t} = \frac{1}{12R}\frac{\partial}{\partial z}\left[\left(\frac{h^2}{\mu}\right)\left(\frac{\partial P}{\partial z}\right)\frac{P}{T}\right] + q_1 \tag{18}$$

This equation is subject to an initial and two boundary conditions:

$$P = P^o_{sys} = \text{constant}, \quad t = 0, \quad 0 < z < L \tag{19a}$$

$$P = P_{sys}(t), \quad z = L, \quad t > 0 \tag{19b}$$

$$dP / dz = 0, \quad z = 0, \quad t > 0. \tag{19c}$$

where P^o_{sys} is the initial coolant pressure at $t = 0$ and $P_{sys}(t)$ is the bulk system pressure at the defect end of the rod (see Fig. 1). Equation (19c) follows from Eq. (16) where it is assumed that the velocity $v = 0$ at the intact end of the rod. Thus, Eq. (18) with the given conditions can be numerically solved to provide $P(z,t)$.

As an illustrative example, Eq. (18) can also be solved analytically if steady-state flow conditions are achieved in a relatively short period of time. Thus, in the steady state, Eq. (13) becomes:[5]

$$\frac{dN_T}{dz} = q_1 \tag{20}$$

Assuming a constant fission gas generation (q_l) along the gap, with no flow at the intact end of the rod (see Fig. 1), i.e., $N_T = 0$ at $z = 0$, the solution of Eq. (20) is:

$$N_T = q_1 z \tag{21}$$

Hence, from Eqs. (16), (17) and (21)

$$v(z) = -\frac{h^2}{12\mu}\frac{dP}{dz} = \frac{q_1 RTz}{P} \tag{22}$$

Furthermore, assuming isothermal conditions and a constant radial gap, Eq. (22) can be directly integrated as

$$q_1 RT \int_x^L z\, dz = -\frac{h^2}{12\mu} \int_{P(x)}^{P_{sys}} P\, dP \tag{23}$$

yielding

$$P^2(z) = \frac{12 q_1 RT\mu}{h^2}\left(L^2 - z^2\right) + P_{sys}^2 \tag{24}$$

If there is little gas release q_l, or a large radial gap h exists, $P(z) \approx P_{sys}$ = constant, and therefore pressure gradient effects can be neglected. For instance, under realistic conditions, the pressure gradient is not expected to be significant since ballooning of the Zircaloy tubes is likely to occur at temperatures below 1000°C. Hence, the radial gap should be large (~1 mm), where an increased value of h will reduce the pressure gradient in accordance with Eq. (24). For example, employing Eq. (24) as shown in Ref. 5, for a CANDU-size rod with a length of 0.48 m and a small gap size of $h = 10$ µm, a pressure gradient of only $\Delta P = 0.055$ MPa was estimated along the entire length of the rod for a temperature transient at 1600 K (for an atmospheric system pressure of $P_{sys} = 0.1$ MPa). For larger gap thicknesses, the pressure gradient clearly becomes negligible (as predicted by Eq. (24)).

In fact, analogous equations to Eqs. (14a) and (14b) have been previously proposed for multi-component transport modelling for severe accident analysis in light water reactor fuel rods.[8] In this analysis, however, it was implicitly assumed that there was no pressure or temperature gradient in the gap, where the molar concentration c and temperature T were independent of z.

Thus, for a given transient temperature history along the rod, $T(z,t)$, and knowing $P(z,t)$ from Eq. (18) (or setting $P(z,t) = P_{sys}(t)$ if pressure differential effects are negligible), the total molar concentration can be derived from Eq. (17). Given $c(z,t)$, Eq. (13) can then be solved for $N_T(z,t)$ employing the initial and boundary conditions

$$c = \frac{P^o_{sys}}{RT}, \quad t = 0, \quad 0 < z < L \tag{25a}$$

$$N_T = 0, \quad z = 0, \quad t > 0 \tag{25b}$$

where P^o_{sys} is the initial coolant pressure at $t = 0$. The boundary condition in Eq. (25b) arises since there is no flow at the intact end of the rod.

2.3 *Fission Gas Source Term q_l*

The parameter q_1 in Eq. (12a) is equal to the stable fission gas release from the fuel matrix[8]

$$q_1 = \left(\frac{V}{S}\right)_{fuel} \frac{c^o_{Xe}}{h} \frac{df_{rel}}{dt} \tag{26}$$

where $(V/S)_{fuel}$ is the volume-to-surface ratio of the fuel (= $a_f/2$ where a_f is the fuel pellet radius) and h is the radial gap thickness. The parameter c^o_{Xe} is the initial fission gas concentration in the fuel:

$$c^o_{Xe} = Y_{Xe+Kr} c_U \beta_f \tag{27}$$

where Y_{Xe+Kr} is the rare gas fission yield (= 0.25 atom fission^{-1}), c_U is the molar density of uranium in UO_2 (= 41×10^3 mol m^{-3}), and β_f is the burnup fraction (i.e., 1 at% burnup equals 0.95×10^4 MWd/tU). The fission gas release rate from the fuel (df_{rel}/dt) can be evaluated from the slope of the generalized Booth diffusion model:[10]

$$f_{rel} = \begin{cases} 6\sqrt{\dfrac{\tau}{\pi}} - 3\tau & \text{for } \tau \leq 0.155 \\ 1 - \dfrac{6}{\pi^2}\exp\left(-\pi^2 \tau\right) & \text{for } \tau > 0.155 \end{cases} \tag{28}$$

where $D'(t) = D/a^2$, and D is the time-dependent fission gas diffusivity in the fuel grain of radius a. The parameter τ is a dimensionless variable:

$$\tau = \int_0^t D'(t)\, dt \tag{29}$$

which accounts for a time-dependent diffusivity. A variable diffusivity results from changing temperature conditions $T(t)$ during the transient and from changing atmospheric conditions that leads to a variable stoichiometry deviation $x(t)$ in the UO_{2+x} fuel matrix (see Section 2.4). The start of the transient is assumed to occur at $\tau = 0$. The functional dependence of the fission gas diffusivity (in m^2 s^{-1}) is given by:[6,10]

$$D(x,T) = 7.6 \times 10^{-10} \exp\left\{-\frac{70000}{RT}\right\} + 2.22 \times 10^{-8} x^2 \exp\left\{-\frac{40200}{RT}\right\} \tag{30}$$

where R is the ideal gas constant (= 1.99 cal mol^{-1} K^{-1}) and T is in K.

The quantity of fission gas release q_l into the gap will implicitly depend on the distribution of the molar fractions (due to the effect of the oxygen potential on the fuel oxidation and fission gas solid-state diffusivity in the fuel matrix). Hence, an iteration will be required for the solution of Eqs. (12a), (12b) and (18) when feedback effects are considered.

2.4 *Fuel Rod Oxidation Processes*

The production rate of hydrogen and the loss rate of steam are equal to one another for a given chemical process. This result arises since the molar quantities of hydrogen and steam are balanced in each oxidation reaction for the Zircaloy and fuel:

$$Zr + 2H_2O \Leftrightarrow ZrO_2 + 2H_2 \tag{31}$$

$$xH_2O + UO_2 \Leftrightarrow UO_{2+x} + xH_2 \tag{32}$$

where x is the stoichiometry deviation in UO_{2+x}.

The kinetics for the fuel and Zircaloy oxidation processes are given in Sections 2.4.1 and 2.4.2, respectively. However, due to a reduced oxygen potential, as a result of hydrogen production from clad oxidation, the internal fuel oxidation reaction does not typically become important until after the cladding has been completely oxidized. Water will also react more rapidly with the cladding than with the fuel.[8] In particular, equilibrium thermodynamics indicate that the free energy of formation of the oxide is lower for ZrO_2 than for UO_{2+x}.[11] This result is demonstrated, for example, in annealing experiments with mini-elements containing loose-fitting end caps. Here, significant cesium release (indicating the occurrence of fuel oxidation) did not occur until after complete clad oxidation (see discussion in Section 4).[6]

2.4.1 Urania Oxidation

The fuel oxidation process has been extensively studied at atmospheric pressure where it has been shown that the kinetics are controlled by a reaction at the solid/gas interface. In this case, the fuel oxidation kinetics are described by:[6]

$$c_U \left(\frac{V}{S}\right)_{fuel} \frac{dx}{dt} = c_U \left(P_{H_2O}\right)^{1/2} \alpha \{x_e - x(t)\} \tag{33}$$

where c_U is the molar density of uranium (mol of uranium m^{-3}), P_{H_2O} is the steam pressure (atm), α is a surface exchange coefficient (= 0.365 exp{-23500/T(K) m s^{-1}}), x_e is the equilibrium stoichiometry deviation, and $(V/S)_{fuel}$ is the volume-to-surface area ratio of the fuel (m). Thus, using Eq. (33), the steam loss rate due to fuel oxidation is:

$$r_{H_2}^{Fuel\ ox} = c_U \left(\frac{V_{fuel}}{V_{gap}}\right) \frac{dx}{dt} = \frac{c_U \left(P_{H_2O}\right)^{1/2} \alpha}{h} \{x_e - x(t)\} \tag{34}$$

where V_{gap} is the gap volume (m^3) and h is the radial gap thickness (m).

The oxygen partial pressure in the fuel , i.e., $P_{O_2}(x_e)$ (in atm), is given by the Blackburn thermochemical model:[12]

$$\ln P_{O_2} = 2 \ln\left(\frac{x_e(2 + x_e)}{1 - x_e}\right) + 108 x_e^2 - \frac{32700}{T} + 9.92 \tag{35}$$

Thus, the value of x_e in Eq. (34) is obtained by equating the oxygen partial pressure in the fuel in Eq. (35) to that in the atmosphere (see Section 2.5).

2.4.2 Internal Clad Oxidation

The steam loss rate for the internal Zircaloy oxidation process can be described by:

$$r_{H_2O}^{clad\ ox} = \dot{w}_{tot}^{inside} \frac{A_{Zr}}{V_{gap}} = \frac{\dot{w}_{tot}^{inside}}{h} \tag{36}$$

where A_{Zr} is the internal surface area of the clad and V_{gap} is the gap volume. Here the metal water reaction is mass transfer limited by the amount of steam which can be transported inside the gap, where the overall steam reaction rate is defined as

$$\dot{w}_{tot}^{inside} = \min\left(\dot{w}_{corr}, \dot{w}_{MT}^{inside}\right) \tag{37}$$

The mass transfer rate is given by

$$\dot{w}_{MT}^{inside} = N_{H_2O} \frac{A_g}{A_{Zr}} \tag{38}$$

where N_{H_2O} is the molar flux of steam as given by Eq. (5b), and A_g is the gap cross sectional area (see Fig. 1).

The corrosion rate, $\dot{w}_{corr}$, follows from parabolic rate theory. In particular, if w is the mass of zirconium consumed per unit area (kg m^{-2}) by the steam reaction, the reaction rate is given by:[13]

$$\dot{w}_{corr} = \frac{2}{M_{Zr}}\left(\frac{dw}{dt}\right) \tag{39}$$

where M_{Zr} is the molecular weight of zirconium (= 0.091 kg mol^{-1}). The factor of two in Eq. (39) arises since one mole of Zr requires two moles of H_2O (see Eq. (31)). From the parabolic rate law for Zircaloy corrosion:

$$w^2 = k_w t \tag{40}$$

it follows that

$$\left(\frac{dw}{dt}\right) = \frac{1}{2}\sqrt{\frac{k_w}{t}} \tag{41}$$

The parameter k_w is the parabolic rate constant:

$$k_w = k_{wo} \exp\left\{-\frac{Q_o}{RT}\right\} \tag{42}$$

where k_{wo} and Q_o are constants determined by various investigators (see Table 1).[14-17] For the numerical implementation of Eq. (41), for a given time step Δt, this equation can be discretized as[18]

$$\frac{dw(t)}{dt} = \frac{\sqrt{w^2(t) + k_w \Delta t} - w(t)}{\Delta t} \tag{43}$$

The Zircaloy oxidation reaction will cease when the total clad thickness is consumed.

Table 1: Parametric Values For Parabolic Rate Constant For Zircaloy Oxidation In Steam

Investigators	Temperature range (K)	k_{wo} (kg^2 m^{-4} s^{-1})	Q_o (× 10^3 J mol^{-1})
Baker and Just[14]	1273 to melting point	3.33×10^3	190
Urbanic and Heidrick[15]	1323 to 1853	2.96×10^1	140
	1853 to melting point	8.79×10^1	138
Pawel et al.[16]	1273 to 1773	2.94×10^2	167
Prater and Courtright[17]	1783 to 2773	2.68×10^4	220

2.4.3 External Clad Oxidation

The mole fractions of the gas constituents in the bulk coolant at the defect site (e.g.,the steam mole fraction $y_2^c(t)$ in Eq. (15c)) are boundary conditions which must be known *a priori* for a solution of the gap transport equations. Although steam is initially the main component in the RCS at the start of the transient, hydrogen will be generated due to external clad oxidation under high-temperature conditions.

The mole fraction distributions in the RCS can be derived as follows. Consider a total molar gas flow rate Q (mol s^{-1}) into a control volume ($\Delta V_c = S_c\, \Delta z$) for the bulk coolant with a constant cross-sectional flow area S_c (m^2) (see Fig. 2). Applying the conservation statement of Eq. (1) to this volume element, the steam molar concentration in the bulk coolant $c^c_{H_2O}$ is given by:

$$\frac{\partial c^c_{H_2O}}{\partial t} = -\frac{\partial\left(\dfrac{Q}{S_c} y^c_{H_2O}\right)}{\partial z} - r^{\text{ext clad ox}}_{H_2O} \tag{44}$$

where the term $r^{\text{ext clad ox}}_{H_2O}$ (mol m^{-3} s^{-1}) accounts for steam losses due to external clad oxidation. From the corrosion reaction in Eq. (31), since one mole of H_2O is consumed as one mole of H_2 is produced, the number of moles of gas is unchanged by the corrosion reaction if hydrogen absorption by the metal does not occur. In this case, Q will be independent of z so that Eq. (44) becomes:

$$\frac{\partial\left(c^c y^c_{H_2O}\right)}{\partial t} = -\frac{Q}{S_c}\frac{\partial y^c_{H_2O}}{\partial z} - r^{\text{ext clad ox}}_{H_2O} \tag{45}$$

Here c^c is the total molar gas concentration in the RCS such that:

$$c^c = \frac{P_{sys}(t)}{RT_{sys}(t)} \tag{46}$$

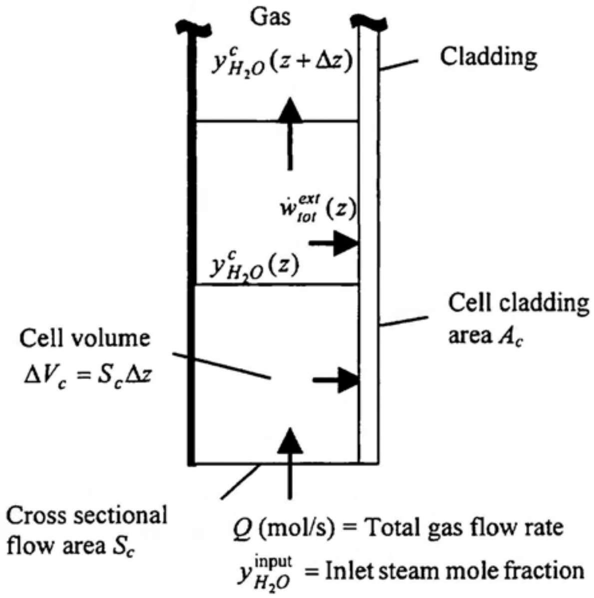

Figure 2. Schematic of the cell geometry for the bulk coolant and cladding for the external cladding oxidation model.

and $r_{H_2O}^{\text{ext clad ox}}$ is given by

$$r_{H_2O}^{\text{ext clad ox}} = \left(\frac{\pi d}{S_c}\right)\dot{w}_{tot}^{ext} \tag{47}$$

where d is the fuel rod diameter (m) and

$$\dot{w}_{tot}^{ext} = \min\left(\dot{w}_{corr}, \dot{w}_{MT}^{ext}\right) \tag{48}$$

In Eq. (48), $\dot{w}_{corr}$ is again evaluated from Eqs. (39) and (41). Similarly, Eq. (48) accounts for limitations in the oxidation process of the outside cladding surface due to mass transfer through the external boundary layer of the fuel rod where:[19,20]

$$\dot{w}_{MT}^{ext} = k_g y_{H_2O}^c \tag{49}$$

The mass transfer coefficient k_g (mol m^{-2} s^{-1}) can be obtained from a heat-mass transfer analogy:[7,10,11]

$$Nu_{ij} = \frac{k_g D_e}{cD_{ij}} \approx 4 \tag{50}$$

where Nu_{ij} is the Nusselt number for mass transfer (which equals 4 for laminar flow). D_e is the equivalent diameter (which equals the channel diameter minus the fuel rod diameter), and cD_{ij} is the diffusion coefficient parameter in Appendix A (which can be evaluated for the H_2O-H_2 binary mixture).

Thus, neglecting any inert gas in the bulk coolant, the hydrogen and steam molar distributions in the RCS follows from the numerical solution of Eqs. (45) to (50). Eq. (45) is subject to the following initial and boundary conditions:

$$y_{H_2O}^c = y_{H_2O}^o, \quad t = 0, \quad 0 < z < L \tag{51a}$$

$$y_{H_2O}^c = y_{H_2O}^{\text{input}}, \quad z = 0, \quad t > 0 \tag{51b}$$

where $y_{H_2O}^o$ is the initial mole fraction for steam in the bulk coolant and $y_{H_2O}^{\text{input}}$ is the input mole fraction of steam in the bulk coolant at $z = 0$. The corresponding distribution for hydrogen is determined from the mass balance relation $y_{H_2}^c = 1 - y_{H_2O}^c$.

At steady state, $\partial\left(c^c y_{H_2O}^c\right)/\partial t = 0$, and Eq. (45) can be directly integrated over the cell distance Δz. Thus, if $r_{H_2O}^{\text{ext clad ox}}$ is constant over Δz (see Fig. 2),

$$\frac{Q}{S_c}\int_z^{z+dz} d\left(y_{H_2O}^c\right) = -r_{H_2O}^{\text{ext clad ox}}\int_z^{z+dz} dz \tag{52a}$$

$$\Rightarrow y_{H_2O}^c(z+dz) = y_{H_2O}^c(z) - \left(\frac{\Delta V_c}{Q}\right) r_{H_2O}^{\text{ext clad ox}} = y_{H_2O}^c(z) - \left(\frac{A_c}{Q}\right)\dot{w}_{tot}^{ext} \tag{52b}$$

where A_c (= $\pi d\,\Delta z$) is the surface area of the clad in the given cell. The second relation in Eq. (52b) follows on use of Eq. (47). Equation (52b) has also been proposed previously, where it was argued that the storage capacity of gas in the cell is much less than the total quantity of steam fed to the cell for the normal time duration of a typical experiment or accident.[19] Thus, the steam distribution in the reactor coolant system can be given by the marching numerical solution of Eq. (52b).

2.5 *Oxygen Potential in the Gap*

Solving the given system of transport equations in Section 2.1, one is able to obtain the oxygen potential along the gap as a function of time from the mole fraction (i.e., partial pressure) distribution. It is important to realize, however, that there is a feedback effect where the source term (q_l) in Eq. (21) actually depends on the state of fuel oxidation which, in turn, is affected by the oxygen potential.[10]

The oxygen potential for an ideal gas mixture in the gap consisting of Xe, H_2O and H_2 can be evaluated as follows.[6] For the H_2O decomposition reaction

$$H_2O \overset{K_{H_2O}}{\Leftrightarrow} H_2 + \tfrac{1}{2}O_2 \tag{53}$$

the equilibrium constant is

$$K_{H_2O} = \frac{P_{H_2}\sqrt{P_{O_2}}}{P_{H_2O}} = \exp\left\{0.9794\ln T - 1.1125 - \frac{28820}{T}\right\} \tag{54}$$

The oxygen partial pressure, P_{O_2} (in atm), can therefore be evaluated at equilibrium on solving the following cubic equation, which results from mass balance considerations for the H and O in the gas mixture before and after steam dissociation:[6]

$$4(P_{O_2})^3 + 4\left[P^o_{H_2} - K^2_{H_2O}\right](P_{O_2})^2 + \left[\left(P^o_{H_2}\right)^2 + 4P^o_{H_2O}K^2_{H_2O}\right]P_{O_2} - \left[\left(P^o_{H_2O}\right)^2 K^2_{H_2O}\right] = 0 \tag{55}$$

Here the superscript "o" refers to the initial partial pressure quantities derived from the solution of the gap transport equations in Section 2.1. The resultant steam and hydrogen partial pressures after dissociation are also given by

$$P_{H_2O} = P^o_{H_2O} - 2P_{O_2}, \quad P_{H_2} = P^o_{H_2} + 2P_{O_2} \tag{56}$$

3. NUMERICAL RESULTS

The system of equations developed in Section 2 are solved using a finite difference technique based on a Crank-Nicholson numerical scheme. The details of the numerical solution are given in Ref. 21.

As an example, consider a calculation for an isothermal temperature of 1873 K and an input RCS steam mole fraction of $y^{\text{input}}_{H_2O} = 1$ (with an external gas flow rate of $Q = 2 \times 10^{-2}$ mol s^{-1}) at atmospheric pressure ($P_{sys} = 1$ atm). The fuel rod dimensions are taken for a CANDU-type rod with a length and diameter of 50 cm and 1.3 cm, respectively, and a clad thickness of 0.43 mm. A ballooned gap size of 100 µm is assumed in the analysis. For the mass transfer calculation, a channel diameter of 2.5 cm is assumed, where the intermolecular parameters for hydrogen and steam are obtained from Table A-1. The coefficients of Urbanic and Heidrick in Table 1 have been used for the parabolic rate constant for Zircaloy oxidation. This simulation is performed with a step length $\Delta z = 0.5$ cm and a time step $\Delta t = 1$ s for the external clad oxidation model, and 0.1 s for the gap-transport calculation. The initial mole fractions for the gap atmosphere are taken as $y^o_1 = 0$ (xenon), $y^o_2 = 1$ (steam) and $y^o_3 = 0$ (hydrogen). The pressure differential in the gap is determined in accordance with the steady-state relation of Eq. (24).

The numerical results for the mole fraction distributions in the gap are shown in Fig. 3(a) prior to complete clad oxidation. Steam is the dominant component in the RCS at the downstream (defect) end of the rod since there is an essentially unlimited supply of steam due to a relatively high mass flow rate. The downstream mole fractions in the RCS are the boundary conditions for the gap transport problem (i.e., at the defect end). As seen in Fig. 3(a), the boundary values for the mole fractions at the given time step are 0.95 and 0.5 for steam and hydrogen, respectively. However, these quantities are immediately reversed inside the gap due to the internal Zircaloy oxidation process where, as far as the gap is concerned, the defect end of the rod becomes essentially a source of hydrogen. A similar observation is seen in the analysis of Ref. 8. Once the clad oxidation process is complete (see

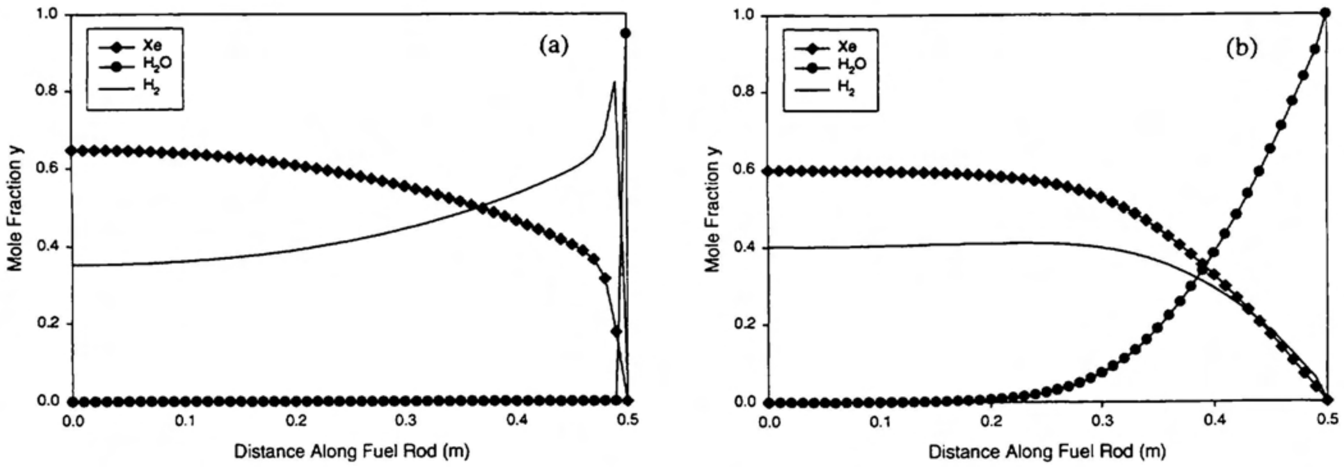

Figure 3. Mole fraction distribution of xenon, steam and hydrogen along the fuel-to-clad gap for a high-temperature transient at 1873 K in an initial steam atmosphere:
(a) at time $t = 9.5$ min from the start of the transient (just prior to complete clad oxidation);
(b) at time $t = 110$ min from the start of the transient.

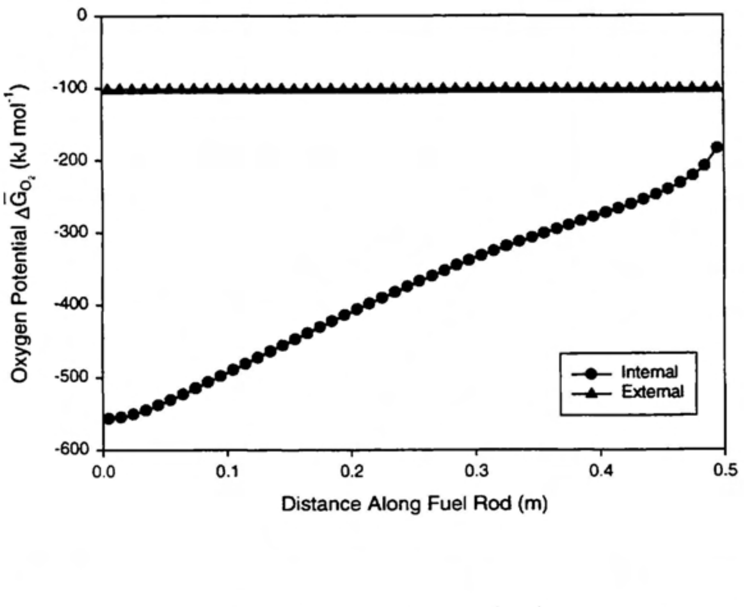

Figure 4. Comparison of the oxygen potential $\Delta\overline{G}_{O_2} = RT\ln(P_{O_2})$ along the length of the fuel rod in the RCS and in the fuel-to-clad gap at time $t = 110$ min from the start of the transient.

Fig. 3(b)), steam begins to diffuse into the fuel-to-clad gap, where the internal oxygen potential decreases towards the intact end of the rod (see Fig. 4). The oxygen potential in the gap, however, is significantly less than that in the RCS after clad oxidation. With time, as the fission gas inventory in the fuel is depleted, and the fuel reaches its equilibrium stoichiometry value, the oxygen potential in the gap increases with continued steam penetration and approaches that of the bulk coolant. Finally, for similar transient conditions, but with a reduced gas flow rate in the RCS (i.e., $Q = 2 \times 10^{-3}$ mol s^{-1}), mass transfer effects now become important, which results in steam-starved conditions that impede the external clad reaction and lead to a lower mole fraction of steam (i.e., boundary condition) at the defect end of the rod.

4. DISCUSSION

As shown in Section 3, the gap can offer an important feedback effect, where the outflowing fission gas can inhibit steam penetration into the gap which, in turn, will reduce the amount of fuel oxidation. The local oxygen potential in the gap will also be lower than that of the bulk coolant due to continued hydrogen production from fuel oxidation. A lower oxygen potential will directly affect the fuel oxidation state, and hence the rate of fission-product diffusion in the fuel matrix and the subsequent release into the gap.[6] Hence, a limiting effect on the release behaviour can be achieved compared to that for unclad fuel. In addition, the oxygen potential will dictate the amount of fuel volatilization, as well as the chemical form of the fission product.[10,11,22] The chemical speciation will determine the amount of vaporization of low-volatile products from the fuel surface.[10,11] In fact, a reduced fission product release has been observed in annealing experiments conducted in steam at the Chalk River Laboratories (CRL) with Zircaloy-clad specimens versus bare fuel fragments, even after the clad had been oxidized.[23,24]

Simulation of the oxidation process at the outer clad surface is required to provide boundary conditions in the reactor coolant system for the gap transport problem. A rate limitation may occur due to gas-phase mass transfer of steam from the bulk coolant to the outer surface of the Zircaloy cladding. With steam transport to the surface, the widely-used parabolic kinetic formulation provides a reasonable representation of the Zircaloy oxidation process under oxidizing conditions. However, if a strongly reducing atmosphere later becomes available, dissolution of the oxide scale into the remaining metal will occur which, in turn, can lead to absorption of hydrogen into the unprotected metal.[19,20] The parabolic scaling model cannot treat this behaviour and simply indicates that the oxide scale will remain in place. However, a more complex model, based on moving-boundary diffusion theory, is available to replace the parabolic treatment.[25] Moreover, parabolic kinetics is only specifically applicable for a semi-infinite medium. For isothermal conditions, parabolic kinetics will match the proper moving-boundary diffusion solution until a small thickness of the clad is left, after which the diffusion model indicates an accelerated behaviour.[25] This latter effect is not significant, however, since parabolic kinetics have been successfully applied in the analysis of hydrogen generation behaviour for steam experiments at the Oak Ridge National Laboratory and Chalk River Laboratories.[13,26]

5. CONCLUSIONS

A model, based on a general Stefan-Maxwell formalism, has been developed to describe the multi-component transport of steam, hydrogen and fission gas in the fuel-to-clad gap of defective fuel rods during reactor accident conditions.

The gap-transport model has been numerically solved using a finite difference method. With knowledge of the molar distributions, a methodology is given to calculate the oxygen potential along the gap as a function of time. This analysis indicates that the oxygen potential in the gap is significantly less than that in the bulk coolant, even after complete clad oxidation. The Zircaloy cladding acts as both a physical and chemical barrier, in which steam cannot penetrate against an outflowing fission gas release and the local oxygen potential is reduced from hydrogen production from both the internal Zircaloy and fuel oxidation processes.

The oxygen potential is an important parameter in severe accident analysis since it will dictate the low-volatile fission product and fuel vaporization behaviour, as well as the (volatile) fission gas release kinetics.

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APPENDIX A: BINARY DIFFUSION COEFFICIENT

The diffusivity parameter cD_{ij} (mol m^{-1} s^{-1}) (= cD_{ji}) for the *i-j*th pair of the binary mixture can be calculated from the standard kinetic theory of Chapman-Enskog:[7]

$$cD_{ij} = 2.2646 \times 10^{-3} \frac{\sqrt{T\left(\dfrac{1}{M_i}+\dfrac{1}{M_j}\right)}}{\sigma_{ij}^2 \Omega_{D_{ij}}} \tag{A-1}$$

where T is the gas-mixture temperature (K), M_i is the molecular weight of gas component i (g mol^{-1}) and σ_{ij} is the collision diameter (Å). The collision integral $\Omega_{D_{ij}}$ is a function of the Lennard-Jones force constant ε_{ij}/κ (in K):[10]

$$\Omega_{D_{ij}} = \frac{1}{0.7049 + 0.2910 \ln(T\kappa / \varepsilon_{ij})} \tag{A-2}$$

The combined quantities for the force constants can be evaluated as

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad \frac{\varepsilon_{ij}}{\kappa} = \sqrt{\frac{\varepsilon_i}{\kappa}\frac{\varepsilon_j}{\kappa}} \tag{A-3}$$

where the individual quantities for the gas components are given in Table A-1.

Table A-1: Intermolecular Parameters For Various Gas Constituents[(a)]

Gas Component	Molecular Weight, *M* (g mol^{-1})	Lennard-Jones Parameters	
		σ (Å)	ε/κ (K)
H_2	2.016	2.915	38.0
He	4.003	2.576	10.2
H_2O	18.015	2.65	380
Xe	131.3	4.055	229

(a) Taken from Refs. 7 and 11.

APPENDIX B: GAS VISCOSITY

For a gas mixture, the viscosity μ can be determined from[7]

$$\mu = \sum_{i=1}^{n} \frac{y_i \mu_i}{\sum_{j=1}^{n} y_j \phi_{ij}} \tag{B-1}$$

in which

$$\phi_{ij} = \frac{1}{\sqrt{8}}\left(1+\frac{M_i}{M_j}\right)^{-1/2}\left[1+\left(\frac{\mu_i}{\mu_j}\right)^{1/2}\left(\frac{M_j}{M_i}\right)^{1/4}\right]^2 \qquad \textbf{(B-2)}$$

The individual viscosity μ_i (in g cm^{-1} s^{-1}) for each component can be calculated from

$$\mu_i = 2.6693\times10^{-5}\,\frac{\sqrt{M_i T}}{\sigma_i^2\Omega_{\mu_i}} \qquad \textbf{(B-3)}$$

where T is in K, M_i is in g mol^{-1} and σ_i is in Å. The parameter $\Omega_{\mu i}$ can similarly be calculated from

$$\Omega_{\mu_i} = \frac{1}{0.6641+0.2581\ln(T\kappa/\varepsilon_i)} \qquad \textbf{(B-4)}$$

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