

USED FUEL DISPOSITION CAMPAIGN

Radiolysis Model Formulation for Integration with the Mixed Potential Model

Fuel Cycle Research & Development

*Prepared for
U.S. Department of Energy
Used Fuel Disposition
Campaign*

*Edgar Buck
Rick Wittman*

July 10, 2014

FCRD-UFD-2014-000484

PNNL- 23459



Disclaimer

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

Submitted by:

Signature on file

Edgar C. Buck
PNNL

EXECUTIVE SUMMARY

This report fulfills the M4 milestone (M4FT-14PN0804061) to report on the model integration of the PNNL Radiolysis Model and the ANL Mixed Potential Model. The approach taken is to formulate a simplified analytical model that retains the main feature and predictions of the full Radiolysis Model applicable to the prediction of UO_2 degradation.

The main approach detailed in this report is as follows.

- Identify the significant reactions that govern the radiolytic generation of hydrogen peroxide in water with known hydrogen and oxygen concentrations.
- Define a solvable reduced analytical model of hydrogen peroxide generation that retains the main physical features of the full model.
- Demonstrate that the analytical model replicates the applicable predictions of the full radiolysis model.
- Present two analytical alternatives: 1) an explicit solution of significant reactions with minimal simplification and; 2) a simplified model with empirical aspects that is easily evaluated.

Details of the approach are intended to be sufficient for developing a module for calculating radiolytic generation of hydrogen peroxide. Listings of the programs used in this report are given in Appendices.

ACKNOWLEDGMENTS

We thank Jim Jerden and Bill Ebert for helpful discussions on the operation of the ANL Mixed Potential Model and proposing the definition of a conditional G -value. We thank Carlos Jové-Colón, and David Sassani for support and helpful discussions on model interface alternatives.

CONTENTS

EXECUTIVE SUMMARY	v
ACKNOWLEDGMENTS	vii
CONTENTS.....	ix
ACRONYMS.....	xi
1. INTRODUCTION.....	1
2. RADIOLYSIS MODEL FOR USE IN USED FUEL OXIDATION	3
2.1 Model Coupling Definition.....	3
2.2 Model Simplification	4
2.3 Future Work.....	11
3. REFERENCES.....	13
APPENDIX A: FORTRAN Listing for Analytical RM	15
APPENDIX B: FORTRAN Listing for Empirical RM.....	19

FIGURES

Figure 2-1. Comparison of Full RM and Analytical Steady-state [H ₂ O ₂] (solution 1).....	6
Figure 2-2. Comparison of Full RM and Analytical Steady-state [H ₂ O ₂] (solution 2).....	7
Figure 2-3. Both Analytical Steady-state [H ₂ O ₂] solutions for $k_{36} \rightarrow k_{36}/10$	8
Figure 2-4. Comparison of Full RM and Analytical RM Steady-state conditional <i>G</i> -values.	9
Figure 2-5. Comparison of Full RM and Empirical RM Steady-state conditional <i>G</i> -values.	10

TABLES

Table 2-1. Subset of reactions sufficient to represent full RM predictions.	4
Table 2-2. Diffusion constants (Christensen, et al. 1996).....	4
Table 2-3. <i>G</i> -values for α -radiolysis (Pastina, et al. 2001).....	5

ACRONYMS

ANL	Argonne National Laboratory
DOE	U.S. Department of Energy
DOE-NE	U.S. Department of Energy Office of Nuclear Energy
MPM	Mixed Potential Model
ODE	ordinary differential equation
PNNL	Pacific Northwest National Laboratory
RM	Radiolysis Model
SNF	spent nuclear fuel
UFDC	Used Fuel Disposition Campaign
UNF	used nuclear fuel

USED FUEL DISPOSITION CAMPAIGN

Radiolysis Model Formulation for Integration with the Mixed Potential Model

1. INTRODUCTION

The U.S. Department of Energy Office of Nuclear Energy (DOE-NE), Office of Fuel Cycle Technology has established the Used Fuel Disposition Campaign (UFDC) to conduct the research and development activities related to storage, transportation, and disposal of used nuclear fuel (UNF) and high-level radioactive waste. Within the UFDC, the components for a general system model of the degradation and subsequent transport of UNF is being developed to analyze the performance of disposal options [Sassani et al., 2012]. Two model components of the near-field part of the problem are the ANL Mixed Potential Model and the PNNL Radiolysis Model.

This report is in response to the desire to integrate the two models as outlined in [Buck, E.C, J.L. Jerden, W.L. Ebert, R.S. Wittman, (2013) “Coupling the Mixed Potential and Radiolysis Models for Used Fuel Degradation,” FCRD-UFD-2013-000290, M3FT-PN0806058]

The Appendixes provide the FORTRAN listing of the computer programs written to evaluate two analytical approximations to the Radiolysis Model.

2. RADIOLYSIS MODEL FOR USE IN USED FUEL OXIDATION

Previous work that reports the results of a radiolysis model sensitivity study [Wittman RS and EC Buck, 2012] showed that of the approximately 100 reactions [Pastina, B. and LaVerne, J. A., 2001] describing water radiolysis, only about 37 are required to accurately predict H_2O_2 to one part in 10^5 . The intended application of that radiolysis model (RM) was to calculate H_2O_2 production for an electrochemical based mixed potential model (MPM) [Jerden, J., Frey, K., Cruse, T., and Ebert, W., 2013] developed to calculate the oxidation/dissolution rate of used nuclear fuel [Shoosmith, D.W., Kolar, M., and King, F., 2003] under disposal conditions where O_2 is expected to be at low concentrations and H_2 is generated from oxidation of steel containers. As an initial approximation, that model (MPM) was developed under the assumption that H_2O_2 is generated at a rate determined only by its radiolytic G -value. Ideally, for a full RM-MPM integration, the MPM would use a reaction kinetics based model to predict H_2O_2 for various water chemistries. As a step in that direction, this report describes the steady-state behavior of a full RM under conditions relevant for the MPM and formulates an analytical expression that closely approximates the full RM.

2.1 Model Coupling Definition

The RM coupled kinetics/diffusion rate equations for H_2O_2 on discrete special zones (n) can be expressed in terms concentrations $[\text{H}_2\text{O}_2]_n$, fluxes J_n and dose rate \dot{d} according to

$$\frac{d[\text{H}_2\text{O}_2]_n}{dt} + \frac{J_n^{(\text{H}_2\text{O}_2)} - J_{n-1}^{(\text{H}_2\text{O}_2)}}{x_n - x_{n-1}} = G_{\text{H}_2\text{O}_2} \dot{d}_n + (\text{reaction kinetics})_n \quad (1)$$

Assuming nonzero reaction kinetics and dose-rate only in the radiation zone (x_R) with diffusion out to the boundary (x_B), the steady-state solution to Eq. (1) after inserting Fick's Law fluxes containing diffusion constant D and boundary concentration $[\text{H}_2\text{O}_2]_B$ can be written:

$$\frac{D_{\text{H}_2\text{O}_2}}{x_R x_B} [\text{H}_2\text{O}_2] = G_{\text{H}_2\text{O}_2} \dot{d} + (\text{reaction kinetics}) + \frac{D_{\text{H}_2\text{O}_2}}{x_R x_B} [\text{H}_2\text{O}_2]_B \equiv G_{\text{H}_2\text{O}_2}^C \dot{d} \quad (2)$$

Equation 2 serves as the working definition of "conditional" G -value [Buck, et al., (2013)] ($[\text{H}_2\text{O}_2]_B = 0$ is assumed). Here "conditional" refers to an effective H_2O_2 generation that is conditional on the local water chemistry. Additionally, because for each time-step of the MPM the radiolysis model would have effectively reached steady-state, Eq. (2) is assumed to define the interface between the RM and MPM – i.e. the MPM evaluates a new conditional G -value for its H_2O_2 production calculation for each time-step.

The next section describes an analytical simplification of the full RM to approximate $[\text{H}_2\text{O}_2]$ and Eq. (2) for use in the MPM.

2.2 Model Simplification

This section describes simple analytical functions for a conditional H_2O_2 G -value that could operate as an interface between the Radiolysis Model (RM) [Wittman and Buck, 2012] and the Mixed Potential Model (MPM). Two approaches are given here. The first attempts to retain the effect of both O_2 and H_2 on the reaction kinetics. The second (currently in use) keeps the of O_2 dependence, but treats the H_2 dependence empirically through adjusting the G -values for $\cdot H$ and $\cdot OH$ radicals. Both seem to give reasonable approximations to the full RM for the pure water system.

The physical justification for these approximations is shown by comparing the full RM results with an analytical solution to a simplified model (Table 2-1 reactions) for both the no-diffusion and diffusion cases. Notice that Table 2-1 retains the key reactions for H_2 to convert the $\cdot OH$ radical to the $\cdot H$ radical (33) to accelerate H_2O_2 destruction and for O_2 to effectively compete for $\cdot H$ radicals to disable H_2O_2 destruction (27) (reaction numbers are those of the full RM and rate constants are from [Elliot, A.J.; McCracken, D.R. 1990]).

Table 2-1. Subset of reactions sufficient to represent full RM predictions.

	Reaction	k_r
3	$H_2O_2 \rightarrow H^+ + \cdot HO_2^-$	1.1×10^{-1}
4	$H^+ + \cdot HO_2^- \rightarrow H_2O_2$	5.0×10^{10}
15	$\cdot HO_2 \rightarrow O_2^- + H^+$	1.3×10^6
16	$O_2^- + H^+ \rightarrow \cdot HO_2$	5.0×10^{10}
23	$\cdot H + H_2O \rightarrow H_2 + \cdot OH$	1.1×10^1
26	$\cdot H + H_2O_2 \rightarrow \cdot OH + H_2O$	9.0×10^7
27	$\cdot H + O_2 \rightarrow \cdot HO_2$	2.1×10^{10}
33	$\cdot OH + H_2 \rightarrow \cdot H + H_2O$	4.3×10^7
34	$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O$	2.7×10^7
35	$\cdot HO_2 + O_2^- \rightarrow \cdot HO_2^- + O_2$	8.0×10^7
36	$H_2O_2 \rightarrow \cdot OH + \cdot OH$	2.5×10^{-7}

Assuming that the primary reactions for H_2O_2 are given in Table 2-1 at a fixed pH and with fixed concentrations of O_2 and H_2 , 6 rate equations can be combined to eliminate all unknown species other than $\cdot H$, $\cdot OH$ and H_2O_2 (diffusion is considered only for species of Table 2-2).

Table 2-2. Diffusion constants (Christensen, et al. 1996)

Species	D_i ($10^{-5} \text{ cm}^2\text{-s}^{-1}$)
$\cdot OH$	2.3
$\cdot H$	1.5
H_2O_2	1.9
O_2	2.5

Additionally, if reactions are considered operate only in the radiation zone with diffusion occurring to the system boundary across discrete zones on the scale of the radiation zone x_R [as in Eq. (1)], the remaining steady-state rate equations in the radiation zone can be expressed as:

$$\begin{aligned} & \left(k_{26}[\text{H}_2\text{O}_2] + \frac{1}{2}\tilde{D}_{\cdot\text{H}} \right) [\cdot\text{H}] + \left(k_{34}[\text{H}_2\text{O}_2] + \frac{1}{2}\tilde{D}_{\cdot\text{OH}} \right) [\cdot\text{OH}] \\ & = \tilde{G}_{\text{H}_2\text{O}_2} + \frac{1}{2} \left(\tilde{G}_{\cdot\text{OH}} + \tilde{G}_{\cdot\text{HO}_2} + \tilde{G}_{\cdot\text{H}} \right) - \tilde{D}_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] \end{aligned} \quad (3)$$

$$\left(k_{27}[\text{O}_2] + k_{26}[\text{H}_2\text{O}_2] + k_{23}[\text{H}_2\text{O}] + \tilde{D}_{\cdot\text{H}} \right) [\cdot\text{H}] - k_{33}[\text{H}_2][\cdot\text{OH}] = \tilde{G}_{\cdot\text{H}} \quad (4)$$

$$\begin{aligned} -k_{34}[\text{H}_2\text{O}_2][\cdot\text{OH}] - k_{33}[\text{H}_2][\cdot\text{OH}] + k_{26}[\cdot\text{H}][\text{H}_2\text{O}_2] + 2k_{36}[\text{H}_2\text{O}_2] \\ + k_{23}[\cdot\text{H}][\text{H}_2\text{O}] + \tilde{G}_{\cdot\text{OH}} - \tilde{D}_{\cdot\text{OH}}[\cdot\text{OH}] = 0 \end{aligned} \quad (5)$$

where $\tilde{D} \equiv D/(x_R x_B)$, with x_R the range of the radiation zone (35 μm) and x_B is the distance to the system boundary. Also, for convenience $\tilde{G} \equiv G\dot{d}$, where the G -values for α -radiolysis are given in Table 2-3.

Table 2-3. G-values for α -radiolysis (Pastina, et al. 2001)

Species	G -value at 5 MeV (molecules/100-eV)
H_2O_2	1.00
$\cdot\text{H}$	0.10
$\cdot\text{OH}$	0.35
$\cdot\text{HO}_2$	0.10

The solution of the three equations [Eqs. (3-5)] for the three unknown concentrations give a cubic equation in $[\text{H}_2\text{O}_2]$

$$A_0 + A_1[\text{H}_2\text{O}_2] + A_2[\text{H}_2\text{O}_2]^2 + A_3[\text{H}_2\text{O}_2]^3 = 0 \quad (6)$$

where typically only one of the solutions yields physically positive concentrations. The coefficients are explicitly given in Eqs. (7-10):

$$\begin{aligned} A_0 = & \left(k_{27}k_{33}[\text{H}_2][\text{O}_2] + k_{27}\tilde{D}_{\cdot\text{OH}}[\text{O}_2] + k_{23}\tilde{D}_{\cdot\text{OH}}[\text{H}_2\text{O}] + k_{33}\tilde{D}_{\cdot\text{H}}[\text{H}_2] + \tilde{D}_{\cdot\text{H}}\tilde{D}_{\cdot\text{OH}} \right) \left(\tilde{G}_{\text{H}_2\text{O}_2} + \frac{1}{2}\tilde{G}_{\cdot\text{HO}_2} \right) \\ & + \frac{1}{2}k_{27} \left(k_{33}[\text{H}_2] + \tilde{D}_{\cdot\text{OH}} \right) [\text{O}_2]\tilde{G}_{\cdot\text{H}} + \frac{1}{2}k_{27}k_{33}[\text{H}_2][\text{O}_2]\tilde{G}_{\cdot\text{OH}} \end{aligned} \quad (7)$$

$$\begin{aligned}
 A_1 = & - \left(k_{27}k_{33}\tilde{D}_{\text{H}_2\text{O}_2}[\text{H}_2][\text{O}_2] + k_{27}\tilde{D}_{\text{H}_2\text{O}_2}\tilde{D}_{\cdot\text{OH}}[\text{O}_2] + k_{27}k_{36}\tilde{D}_{\cdot\text{OH}}[\text{O}_2] + k_{23}\tilde{D}_{\text{H}_2\text{O}_2}\tilde{D}_{\cdot\text{OH}}[\text{H}_2\text{O}] \right. \\
 & + k_{23}k_{36}\tilde{D}_{\cdot\text{OH}}[\text{H}_2\text{O}] + k_{33}\tilde{D}_{\cdot\text{H}}\tilde{D}_{\text{H}_2\text{O}_2}[\text{H}_2] + k_{33}k_{36}\tilde{D}_{\cdot\text{H}}[\text{H}_2] + \tilde{D}_{\cdot\text{H}}\tilde{D}_{\text{H}_2\text{O}_2}\tilde{D}_{\cdot\text{OH}} + k_{36}\tilde{D}_{\cdot\text{H}}\tilde{D}_{\cdot\text{OH}} \left. \right) \\
 & + \left(k_{27}k_{34}[\text{O}_2] + k_{23}k_{34}[\text{H}_2\text{O}] + k_{26}\tilde{D}_{\cdot\text{OH}} + k_{34}\tilde{D}_{\cdot\text{H}} \right) \left(\tilde{G}_{\text{H}_2\text{O}_2} + \frac{1}{2}\tilde{G}_{\text{H}_2\text{O}_2} \right) \\
 & + \frac{1}{2} \left(k_{27}k_{34}[\text{O}_2] - k_{23}k_{34}[\text{H}_2\text{O}] - 2k_{26}k_{33}[\text{H}_2] - 2k_{26}\tilde{D}_{\cdot\text{OH}} \right) \tilde{G}_{\text{H}} \\
 & - \frac{1}{2} \left(k_{27}k_{34}[\text{O}_2] + k_{23}k_{34}[\text{H}_2\text{O}] + 2k_{26}k_{33}[\text{H}_2] + k_{34}\tilde{D}_{\cdot\text{H}} \right) \tilde{G}_{\cdot\text{OH}}
 \end{aligned} \tag{8}$$

$$\begin{aligned}
 A_2 = & - \left(k_{27}k_{34}\tilde{D}_{\text{H}_2\text{O}_2}[\text{O}_2] + 2k_{27}k_{34}k_{36}[\text{O}_2] + k_{23}k_{34}\tilde{D}_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}] + 2k_{23}k_{34}k_{36}[\text{H}_2\text{O}] \right. \\
 & + 2k_{26}k_{33}k_{36}[\text{H}_2] + k_{26}\tilde{D}_{\text{H}_2\text{O}_2}\tilde{D}_{\cdot\text{OH}} + k_{34}\tilde{D}_{\cdot\text{H}}\tilde{D}_{\text{H}_2\text{O}_2} + 2k_{34}k_{36}\tilde{D}_{\cdot\text{H}} + k_{26}k_{36}\tilde{D}_{\cdot\text{OH}} \left. \right) \\
 & + k_{26}k_{34} \left(\tilde{G}_{\text{H}_2\text{O}_2} + \frac{1}{2}\tilde{G}_{\text{H}_2\text{O}_2} - \frac{3}{2}\tilde{G}_{\text{H}} - \frac{1}{2}\tilde{G}_{\cdot\text{OH}} \right)
 \end{aligned} \tag{9}$$

$$A_3 = -k_{26}k_{34}\tilde{D}_{\text{H}_2\text{O}_2} - 2k_{26}k_{34}k_{36} \tag{10}$$

For the no-diffusion case, Figures 2-1 and 2-2 show comparisons of the full RM and the solution of Eq. (6) for a dose rate of 160 rad/s. The full RM was run out to 10^8 seconds with the LBNL ODE solvers of references [Brown, et al. 1989 and Hindmarsh 1983], while the analytical RM simply involved finding the zeros of Eq. (6) with the FORTRAN code of Appendix A. It was determined that two acceptable steady-state solutions for $[\text{H}_2\text{O}_2]$ exist in the low $[\text{O}_2]$ region for both the full RM and simplified solution.

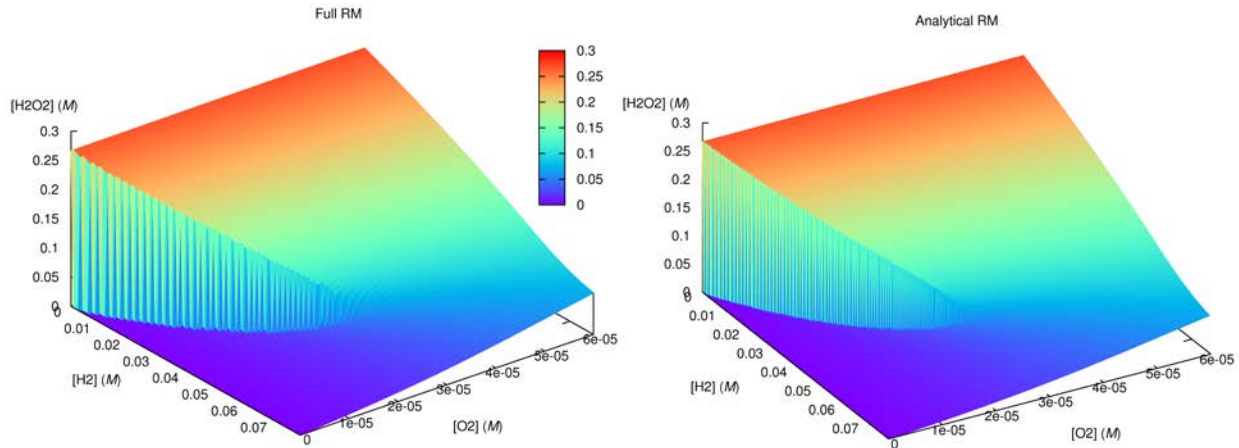


Figure 2-1. Comparison of Full RM and Analytical Steady-state $[\text{H}_2\text{O}_2]$ (solution 1).

Both the full and simplified RM agree within 5-10% over a wide range of dose-rates. Additionally, the fact that they both give two acceptable steady-state solutions for $[\text{H}_2\text{O}_2]$ indicates that nontrivial features are retained in the simplified analytical solution. It is interesting that the non-uniqueness of solution occurs in the region for which there has been some

discrepancy comparing α -radiolysis model predictions with $[\text{H}_2\text{O}_2]$ measurements – especially for large H_2 concentrations [Pastina, B. and LaVerne, J. A., 2001]. Another interesting feature

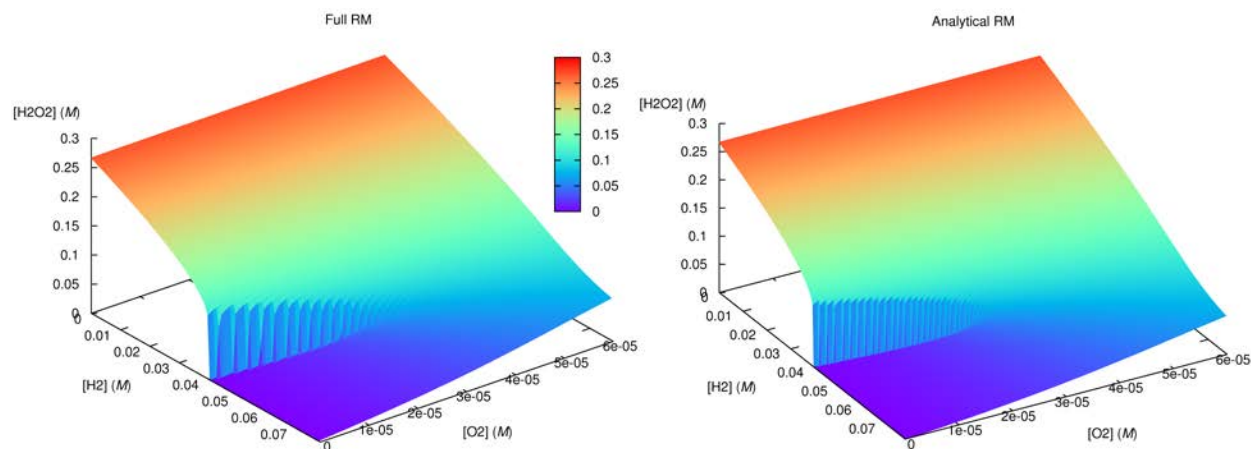


Figure 2-2. Comparison of Full RM and Analytical Steady-state $[\text{H}_2\text{O}_2]$ (solution 2).

of the solution is the apparent “cliff-edge” in concentration roughly along a linear boundary in $[\text{O}_2]$ and $[\text{H}_2]$. That boundary becomes increasingly well defined as the rate (k_{36}) of H_2O_2 thermal decomposition goes to zero. Figure 2-3 shows both solutions for k_{36} reduced by 10X – the lower $[\text{H}_2\text{O}_2]$ solution is defined in a narrow region of low $[\text{O}_2]$, the higher $[\text{H}_2\text{O}_2]$ solution is defined everywhere, but continues to increase as k_{36} goes to zero. In the latter case A_3 goes to zero and an analytical solution for the boundary can be determined where there is no steady-state solution for $[\text{H}_2\text{O}_2]$ in the region defined by:

$$S_-[\text{H}_2] \leq [\text{O}_2] \leq S_+[\text{H}_2] \quad (11)$$

where

$$S_{\pm} = \frac{2k_{26}k_{33}}{k_{27}k_{34}(G_{\cdot\text{OH}} - 2G_{\text{H}_2\text{O}_2} - G_{\cdot\text{H}})^2} \left\{ 2 [G_{\text{H}_2\text{O}_2}G_{\cdot\text{OH}} - G_{\cdot\text{OH}}^2 - 2G_{\cdot\text{H}}G_{\cdot\text{OH}} + 2G_{\text{H}_2\text{O}_2}^2 - G_{\cdot\text{H}}G_{\text{H}_2\text{O}_2} - G_{\cdot\text{H}}^2] \pm \left[(4G_{\text{H}_2\text{O}_2}^2 - (G_{\cdot\text{H}} + G_{\cdot\text{OH}})^2) (2G_{\text{H}_2\text{O}_2} - G_{\cdot\text{OH}} - 3G_{\cdot\text{H}}) (2G_{\text{H}_2\text{O}_2} + 3G_{\cdot\text{OH}} + G_{\cdot\text{H}}) \right]^{\frac{1}{2}} \right\} \quad (12)$$

For α -radiolysis, $S_- = 0.000341$ and $S_+ = 0.0362$, with $[\text{O}_2] = S_- [\text{H}_2]$ closely matching the “cliff-edge” boundary of Figure 2-1 and 2-3. It should be mentioned that for γ -radiolysis G -values there is no physical region that satisfies Eq. (11) meaning that the concentrations of radiolytically generated radicals are always sufficient to destroy H_2O_2 allowing a steady-state to exist even in the absence of thermal decomposition.

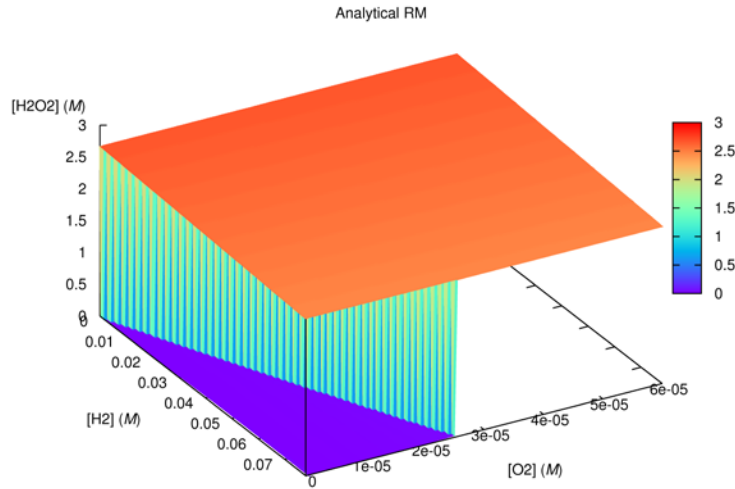


Figure 2-3. Both Analytical Steady-state $[H_2O_2]$ solutions for $k_{36} \rightarrow k_{36}/10$.

In the case where diffusion can operate it appears that only a single hybrid solution of Figure 2-1 and 2-2 persists. The role of thermal decomposition on the steady-state is relatively small compared to diffusion away from the radiation zone [Eq. (10)]. Also, in this case, given $[H_2O_2]$ as in Eq. (2), a “conditional” G -value for $[H_2O_2]$ can be defined according to:

$$G_{H_2O_2}^C \equiv \tilde{D}_{H_2O_2} [H_2O_2] / \dot{d} \quad (13)$$

The external O_2 concentration $[O_2]_B$ can be approximately mapped to the local O_2 concentration with:

$$\tilde{D}_{O_2} [O_2] = -k_{27} [\cdot H] [O_2] + \tilde{D}_{O_2} [O_2]_B \quad (14)$$

where given $[H_2O_2]$, $[\cdot H]$ can be solved for from Eqs. (3 & 4). Figure 2-4 shows the conditional G -value as a function of $[H_2]$ and $[O_2]_B$. In the region of small conditional G -value the full RM and Eq. (14) indicates that the spatial variation of $[O_2]$ is huge, while it was observed that the spatial variation of $[H_2]$ was very small over many conditions. That small variation could be handled empirically in this case by reducing k_{33} by a factor of 5X and assuming here that $[H_2] \approx [H_2]_B$.

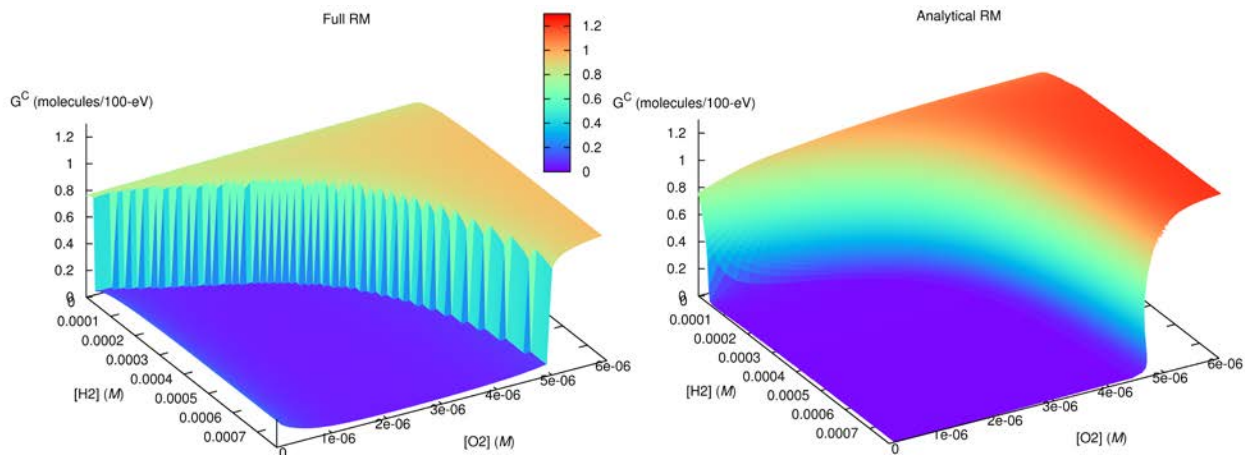


Figure 2-4. Comparison of Full RM and Analytical RM Steady-state conditional G -values.

It was determined that an even greater simplification to a conditional G -value could be made by accounting for O_2 competing for the same radicals that destroy H_2O_2 , but treating the strength of the H_2 effect empirically. This approach is based on four “simplified” rate equations that dominate when hydrogen concentration is large. In the radiation zone assuming diffusion only for H_2O_2 and O_2 the four equations are:

$$\tilde{D}_{H_2O_2}[H_2O_2] = \tilde{G}_{H_2O_2} - k_{26}[\cdot H][H_2O_2] - k_{36}[H_2O_2] \quad (15)$$

$$0 = \tilde{G}_{\cdot H} - k_{27}[\cdot H][O_2] - k_{23}[\cdot H][H_2O] + k_{33}[\cdot OH][H_2] \quad (16)$$

$$0 = \tilde{G}_{\cdot OH} - k_{33}[\cdot OH][H_2] \quad (17)$$

$$\tilde{D}_{O_2}[O_2] = -k_{27}[\cdot H][O_2] + \tilde{D}_{O_2}[O_2]_B \quad (18)$$

The conditional G -value can be expressed as the solution to a quadratic equation

$$G_{H_2O_2}^C = \frac{-C_1 + (C_1^2 - 4C_0C_2)^{\frac{1}{2}}}{2C_2} \quad (19)$$

Where the coefficients are given by:

$$C_0 = -k_{23}k_{27}[H_2O]\tilde{D}_{H_2O_2}^2 \quad (20)$$

$$C_1 = -\tilde{D}_{H_2O_2} \left[k_{26}k_{27}[O_2]_B\tilde{D}_{O_2} + k_{23}k_{26}[H_2O]\tilde{D}_{O_2} - 2k_{23}k_{27}[H_2O] \left(\tilde{D}_{H_2O_2} + k_{36} \right) \right] + k_{26}k_{27}\tilde{D}_{H_2O_2} \left(\tilde{G}_{\cdot H} + \tilde{G}_{\cdot OH} \right) \quad (21)$$

$$C_2 = \left[k_{26}k_{27}[O_2]_B\tilde{D}_{O_2} + k_{23}k_{26}[H_2O]\tilde{D}_{O_2} - k_{23}k_{27}[H_2O] \left(\tilde{D}_{H_2O_2} + k_{36} \right) \right] \left(\tilde{D}_{H_2O_2} + k_{36} \right) + k_{26} \left(k_{26}\tilde{D}_{O_2} - k_{27}\tilde{D}_{H_2O_2} - k_{27}k_{36} \right) \left(\tilde{G}_{\cdot H} + \tilde{G}_{\cdot OH} \right) \quad (22)$$

In this approximation the effect of H₂ is handled empirically by making G_{·H} and G_{·OH} dependent on [H₂] according to:

$$G_{\cdot H} = (0.10 \text{ molecules}/100\text{-eV}) \left[1 - \exp \left(-\frac{[H_2]/0.1 \text{ atm}}{7.8 \times 10^{-4} M/\text{atm}} \right) \right] \quad (23)$$

$$G_{\cdot OH} = (0.35 \text{ molecules}/100\text{-eV}) \left[1 - \exp \left(-\frac{[H_2]/0.3 \text{ atm}}{7.8 \times 10^{-4} M/\text{atm}} \right) \right] \quad (24)$$

Additionally, in this approximation k₂₃ is reduced by a factor of 56 and x_B is adjusted between 0.4 and 0.5~cm to compare reasonably well with the full radiolysis model kinetics-diffusion result. Appendix B gives the FORTRAN listing for evaluating the empirical RM. Figure 2-5 shows the conditional G-value as a function of [H₂] and [O₂]_B for the full RM and for the one calculated from Eq. (19-24).

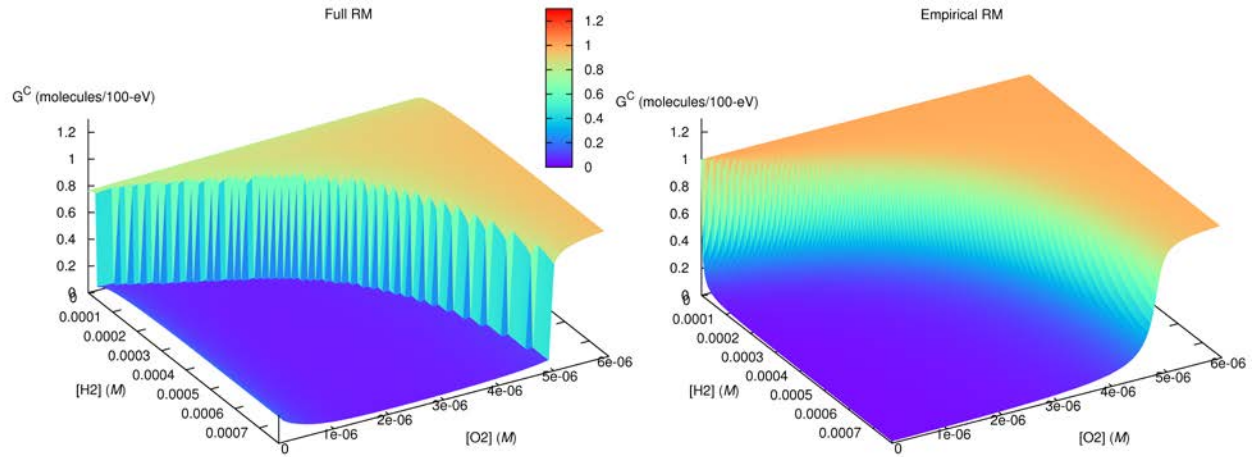


Figure 2-5. Comparison of Full RM and Empirical RM Steady-state conditional G-values.

2.3 Future Work

While the results of this work are applicable to radiolysis for the pure water system, future work will attempt to formulate a reduced model that includes chloride and carbonate chemistry. At some point it may be advantageous to represent a full RM within the fuel degradation MPM, but as shown here, a reduced model is helpful for both simple calculation and for understanding the most relevant underlying mechanisms that are imbedded in the reactions.

The role of bromine is of great interest as it appears to have a significant effect on used fuel in a disposal environment although the mechanisms are unclear. A computational study examining the role of bromine would be a useful exercise when run in the same manner as this investigation has been done.

Lastly, experimental validation of the radiolysis model is necessary to confirm many of the important findings. Accelerator based methods will be the most suitable to rapidly determine the effects of alpha radiolysis under various conditions combined with detailed chemical and solid phase analysis.

3. REFERENCES

Brown PN, and AC Hindmarsh. 1989. "Reduced storage matrix methods in stiff ODE systems." *Journal of Applied Mathematics and Computing*, 31(May 1989):40-91.

Buck, E.C, J.L. Jerden, W.L. Ebert, R.S. Wittman, (2013) "Coupling the Mixed Potential and Radiolysis Models for Used Fuel Degradation," FCRD-UFD-2013-000290, M3FT-PN0806058.

Christensen, H., Sunder, S. (1996) An evaluation of water layer thickness effective in oxidation of UO₂ fuel due to radiolysis of water, *Journal of Nuclear Materials* 238: 70-77.

Elliot, A.J.; McCracken, D.R. 1990, "Computer modelling of the radiolysis in an aqueous lithium salt blanket: Suppression of radiolysis by addition of hydrogen," *Fusion Eng. Des.*, 13, 21.

Freeze, G., Mariner, P., Houseworth, J., Cunnane, J., and F. Caporuscio, F. (2010). *Used Fuel Disposition Campaign Features, Events, and Processes (FEPs): FY10 Progress Report*, August 2010.

Hindmarsh AC. 1983. "ODEPACK, A Systematized Collection of ODE Solvers." In *Scientific Computing*, IMACS Transactions on Scientific Computation, Volume 1 edited by RS Stepleman, M Carver, R Peskin, WF Ames and WF Vichnevetsky, North-Holland, Amsterdam, pp 55-64.

Jerden, J., Frey, K., Cruse, T., and Ebert, W. (2012). *Waste Form Degradation Model Status Report: Electrochemical Model for Used Fuel Matrix Degradation Rate*. FCRD-UFD-2012-000169.

Jerden, J., Frey, K., Cruse, T., and Ebert, W. (2013). *Waste Form Degradation Model Status Report: ANL Mixed Potential Model, Version 1*. Archive. FCRD-UFD-2013-000057.

King, F. and Kolar, M. (1999) *Mathematical Implementation of the Mixed-Potential Model of Fuel Dissolution Model Version MPM-VI.0*, Ontario Hydro, Nuclear Waste Management Division Report No. 06819-REP-01200-10005 R00.

King, F. and Kolar, M. (2002) *Validation of the Mixed-Potential Model for Used Fuel Dissolution Against Experimental Data*, Ontario Hydro, Nuclear Waste Management Division Report No. 06819-REP-01200-10077-R00.

King, F. and Kolar, M. (2003) *The Mixed-Potential Model for UO₂ Dissolution MPM Versions VI.3 and VI.4*, Ontario Hydro, Nuclear Waste Management Division Report No. 06819-REP-01200-10104 R00.

Pastina, B. and LaVerne, J. A. (2001) Effect of Molecular Hydrogen on Hydrogen Peroxide in Water Radiolysis, *Journal of Physical Chemistry* A105: 9316-9322.

Poinsot, C. Ferry, C. M. Kelm, B. Grambow, A. Martinez, A., Johnson, L., Andriamoloolona, Z., Bruno, J., Cacho, C., Cavedon, J.M., Christensen, H., Corbel, C., Jegou, C., Lemmens, K., Loida, A., Lovera, P., Miserque, F. de Pablo, J., Poulesquen, A., Quinones, J. Rondinella, V., Spahiu, K., and D. H. Wegen, (2004) *Spent Fuel Stability under Repository Conditions: Final Report of the European Project*, European Commission, 5th EURATOM FRAMEWORK PROGRAMME, 1998-2002.

Radulescu, G. (2011) *Radiation Transport Evaluations for Repository Science*, ORNL/LTR-2011/294, LETTER REPORT, Oak Ridge National Laboratory, August, 2011.

Sassani et al., 2012 *Integration of EBS Models with Generic Disposal System Models*, U.S. Department of Energy, Used Fuel Disposition Campaign milestone report: M2FT-12SN0806062, September, 7 2012

Shoesmith, D.W., Kolar, M., and King, F. (2003). A Mixed-Potential Model to Predict Fuel (Uranium Dioxide) Corrosion Within a Failed Nuclear Waste Container, *Corrosion*, 59, 802-816.

Wittman RS and EC Buck. 2012. "Sensitivity of UO₂ Stability in a Reducing Environment on Radiolysis Model Parameters." In *Actinides and Nuclear Energy Material, MRS Spring 2012 Proceedings*, vol. 1444, 3-8, ed. D Andersson, et al. Cambridge University Press, Cambridge, United Kingdom. DOI:10.1557/opl.2012.1449.

APPENDIX A: FORTRAN Listing for Analytical RM

SS-Bisec-L2-NODiff.f

```
common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,  
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm  
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2
```

C Physical constants

```
Av = 6.0221415e23 ! mole^{-1}  
echrg = 1.602176462e-19 ! J/eV  
dk7 = 19.  
dk8 = 0. !2.2e7  
dk19 = 1.1e10  
dk22 = 0. ! 1.9e10  
  
dk23 =1.1e1  
dk26 =9.0e7  
dk27 =2.1e10  
dk34 =2.7e7  
dk36 =2.25e-7  
dk33 =4.3e7  
gH = 0.100 ! 0.66 ! 0.100 !  
gH2O2 = 1.000 ! 0.70 ! 1.000 !  
gHO2 = 0.100 ! 0.02 ! 0.100 !  
gOH = 0.350 ! 2.70 ! 0.350 !  
gEm = 0.000 ! 2.60 ! 0.150 !  
gO2m = 0.  
gHO2m = 0.  
  
xR1 = 35.e-4  
xR2 = 1.5*35.e-4  
xB = 0.5  
dkH = 0* 1.500e-05/(xR1*xR2)  
dkOH = 0* 2.300e-05/(xR1*xR2)  
dkH2O2 =0* 1.900e-05/(xR1*xB)  
dkO2 =0* 2.500e-05/(xR1*xB)  
H2O = 1000./18.  
OHm = 1.01e-7  
  
ddotR = 160. ! rad/s  
  
ddot = ddotR/(Av * echrg * 100.d0 * 100.d0) ! Unit conversion  
  
do i1 = 0,200  
do i2 = 0,200  
  
H2 = 7.800E-2*float(i1) /200.  
O2 = .6e-4*float(i2) /200. + 1.e-10  
  
H2O21 = 0.  
zero1 = fzero(H2,O2,H2O,H2O21,OHm,ddot)  
  
do i=0,10000  
  
c H2O2 = float(i)/10000.  
c Det = fDet(H2,O2,H2O,H2O2)  
c write(*,*) H2O2,Det  
  
H2O22 = float(i)/10000. + 1.e-6  
zero2 = fzero(H2,O2,H2O,H2O22,OHm,ddot)  
if(zero1*zero2.lt.0.) goto 50  
  
H2O21 = H2O22  
zero1 = zero2
```

```

c      H2O22 = float(i)/1000000.
c      zero2 = fzero(H2,O2,H2O,H2O22,OHm,ddot)

      enddo

50 continue

      do ibisec=1,10
      H2O2 = (H2O21+H2O22)/2.
      zero = fzero(H2,O2,H2O,H2O2,OHm,ddot)
      if(zero1*zero.le.0.) then
        zero2 = zero
        H2O22 = H2O2
      else
        zero1 = zero
        H2O21 = H2O2
      endif
      enddo

c      Det= fDet(H2,O2,H2O,H2O2,OHm,ddot)
      H = fH(H2,O2,H2O,H2O2,OHm,ddot)/Det
      O2B = O2*(dkO2 + dk27*H)/dkO2
c      OH = fOH(H2,O2,H2O,H2O2,OHm,ddot)/Det
c      Em = fEm(H2,O2,H2O,H2O2,OHm,ddot)/Det
c      write(*,*) H2,O2,bndy(H2,O2)!H2O2!*dkH2O2/ddot ! ,H,OH,Em
      write(*,*) H2,O2,H2O2!*dkH2O2/ddot ! ,H,OH,Em

      enddo
      write(*,"(lx)")
      enddo

      STOP
      end

      function fH(H2,O2,H2O,H2O2,OHm,ddot)
      common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2

      A11 = -dk26*H2O2 - dkH/2.
      A12 = -dk34*H2O2 - dkOH/2.
      A21 = -dk27*O2-dk26*H2O2-dk23*H2O - dkH
      A22 = dk33*H2

      B1 = -(gOH/2.+gO2m/2.+gHO2m+gHO2/2.+gH2O2+gH/2.)*ddot
1 + dkH2O2*H2O2
      B2 = -(gH)*ddot

      Det = A11*A22 - A12*A21

      fH = (B1*A22 - A12*B2) /Det

      RETURN
      end

      function fOH(H2,O2,H2O,H2O2,OHm,ddot)
      common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2

      A11 = -dk26*H2O2 - dkH/2.
      A12 = -dk34*H2O2 - dkOH/2.
      A21 = -dk27*O2-dk26*H2O2-dk23*H2O - dkH
      A22 = dk33*H2

      B1 = -(gOH/2.+gO2m/2.+gHO2m+gHO2/2.+gH2O2+gH/2.)*ddot
1 + dkH2O2*H2O2
      B2 = -(gH)*ddot

```

```

Det = A11*A22 - A12*A21

fOH =(A11*B2 - B1*A21)/Det

RETURN
end

function fzero2(H2,O2,H2O,H2O2,OHm,ddot)
common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2

A11 = -dk26*H2O2 - dkH/2.
A12 = -dk34*H2O2 - dkOH/2.
A21 = -dk27*O2-dk26*H2O2-dk23*H2O - dkH
A22 = dk33*H2

H = fH(H2,O2,H2O,H2O2,OHm,ddot)
OH = fOH(H2,O2,H2O,H2O2,OHm,ddot)

B1 = -(gOH/2.+gO2m/2.+gHO2m+gHO2/2.+gH2O2+gH/2.)*ddot
1 + dkH2O2*H2O2
B2 = -(gH)*ddot

Det = A11*A22 - A12*A21

fzero =
1 - dk34*H2O2*OH - dk33*H2*OH + dk26*H*H2O2 +
2 2.*dk36*H2O2 + dk23*H*H2O + gOH*ddot - dkOH*OH

RETURN
end

function fzero(H2,O2,H2O,H2O2,OHm,ddot)
common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2

a0 = ((dk27*dk33*H2*O2 + dk27*dkOH*O2 + dk23*dkOH*H2O
1 + dk33*dkH*H2 + dkH*dkOH)*(gH2O2 + gHO2/2)
2 + (dk27*dk33*H2*O2 + dk27*dkOH*O2)*gH/2
3 + dk27*dk33*H2*O2*gOH/2 )*ddot

a1 = - (2*dk27*dk33*dkH2O2*H2*O2 + 2*dk27*dkH2O2*dkOH*O2
1 + 2*dk27*dk36*dkOH*O2 + 2*dk23*dkH2O2*dkOH*H2O
2 + 2*dk23*dk36*dkOH*H2O + 2*dk33*dkH*dkH2O2*H2
3 + 2*dk33*dk36*dkH*H2 + 2*dkH*dkH2O2*dkOH + 2*dk36*dkH*dkOH)/2
4 + ( dk27*dk34*O2 + dk23*dk34*H2O + dk26*dkOH + dk34*dkH)
5 *(gH2O2 + gHO2/2)
6 + (dk27*dk34*O2 - dk23*dk34*H2O - 2*dk26*dk33*H2 - 2*dk26*dkOH)
7 *gH/2
8 - (dk27*dk34*O2 + dk23*dk34*H2O + 2*dk26*dk33*H2 + dk34*dkH)
9 *gOH/2 )*ddot

a2 = - (dk27*dk34*dkH2O2*O2 + 2*dk27*dk34*dk36*O2
1 + dk23*dk34*dkH2O2*H2O + 2*dk23*dk34*dk36*H2O
2 + 2*dk26*dk33*dk36*H2 + dk26*dkH2O2*dkOH
3 + dk34*dkH*dkH2O2 + 2*dk34*dk36*dkH)
4 - dk26*dk36*dkOH
5 + dk26*dk34*(gH2O2 + gHO2/2 - 3*gH/2 - gOH/2)*ddot

a3 = - dk26*dk34*dkH2O2 - 2*dk26*dk34*dk36

fzero = a0 + a1*H2O2 + a2*H2O2**2 + a3*H2O2**3

RETURN
end

```

```

function bndy(H2,O2)
common /const/ dk7,dk8,dk19,dk22,dk23,dk26,dk27,dk33,dk34,dk36,
1 gH,gH2O2,gHO2,gOH,gHO2m,gO2m,gEm
1 ,xR1,xR2,xB,dkH,dkOH,dkH2O2,dkO2

S1 = -2*dk26*dk33*(sqrt((gOH-2*gH2O2+gH)*(gOH-2*gH2O2+3*gH)
1 * (gOH+2*gH2O2+gH)*(3*gOH+2*gH2O2+gH) )
2 + 2*gOH**2 - 2*gH2O2*gOH
3 + 4*gH*gOH - 4*gH2O2**2 + 2*gH*gH2O2 + 2*gH**2)
4 /(dk27*dk34*(gOH-2*gH2O2-gH)**2)

S2 = 2*dk26*dk33*(sqrt((gOH-2*gH2O2+gH)*(gOH-2*gH2O2+3*gH)
1 * (gOH+2*gH2O2+gH)*(3*gOH+2*gH2O2+gH) )
2 - 2*gOH**2 + 2*gH2O2*gOH
3 - 4*gH*gOH + 4*gH2O2**2 - 2*gH*gH2O2 - 2*gH**2)
4 /(dk27*dk34*(gOH-2*gH2O2-gH)**2)

bndy = 0.
if((O2.ge.S1*H2).and.(O2.le.S2*H2)) bndy = 0.25

RETURN
end

```

APPENDIX B: FORTRAN Listing for Empirical RM

Emp-RM.f

```
implicit real*8 (a-h,o-z)

ddot = 160.d0          ! rad/s

do j=0,200
do i=0,200

H2ext = 7.8d-4*dfloat(j)/200.d0      ! mole/L
O2ext = dfloat(i)/2.d7 + 1.d-11      ! mole/L
G = Gval(ddot,O2ext,H2ext)
G2 = Gcond(ddot,O2ext,H2ext)

write(*,*) O2ext,H2ext,G2

enddo
write(*,"(1x)")
enddo

STOP
end

FUNCTION Gval(ddot,O2ext,H2ext)
implicit real*8 (a-h,o-z)

rk27 = 2.1d10          ! L/mole-s
rk23 = 1.1d1/56.d0     ! L/mole-s   divided by 56
rk26 = 9.0d7           ! L/mole-s
rk36 = 0.0             ! L/mole-s
GH = 0.100d0*(1.d0-dexp(-(H2ext/7.8d-4)/.1d0))      ! molecules/eV
GOH = 0.350d0*(1.d0-dexp(-(H2ext/7.8d-4)/.3d0))     ! molecules/eV
CH2O = 1.d3/18.d0     ! mole/L
DO2 = 2.500d-05       ! cm^2/s
DH2O2 = 1.900d-05    ! cm^2/s
dx = 3.5d-3           ! cm
dN = 0.475d0/dx
A = rk27/(rk23*CH2O) ! L/mole
dlam0 = rk27*ddot*(GH + GOH)*
1      (1.d0/(1.602d-19*1.d4*6.022d23))/(rk23*CH2O) ! 1/s
dk = DO2/dx**2        ! 1/s
dkH2O2 = DH2O2/dx**2 ! 1/s
ratk = rk26/rk27

C0 = O2ext + 1.d-11   ! mole/L
CALL NLconc(C1p,C1m,C0,dlam0,A,dN,dk)
dlam = dlam0/(1.d0 + A*C0*C1p)
Gval = dkH2O2/(dkH2O2 + ratk*dN*dlam)

RETURN
end

FUNCTION Gcond(ddot,O2ext,H2ext)
implicit real*8 (a-h,o-z)

rk27 = 2.1d10          ! L/mole-s
```

```

rk23 = 1.1d1/56.d0      ! L/mole-s   divided by 56
rk26 = 9.0d7            ! L/mole-s
rk36 = 0.0d0            ! L/mole-s
GH   = 0.100d0*(1.d0-dexp(-(H2ext/7.8d-4)/.1d0))      ! molecules/eV
GOH  = 0.350d0*(1.d0-dexp(-(H2ext/7.8d-4)/.3d0))      ! molecules/eV
CH2O = 1.d3/18.d0      ! mole/L
DO2  = 2.500d-05       ! cm^2/s
DH2O2 = 1.900d-05      ! cm^2/s
dx   = 3.5d-3          ! cm
dN   = 0.475d0/dx

      O2 = O2ext
      H2 = H2ext
      H2O = CH2O
      dk27 = rk27
      dk23 = rk23
      dk26 = rk26
      dk36 = rk36
      dkO2 = DO2/(dN*dx**2)      ! 1/s
      dkH2O2 = DH2O2/(dN*dx**2) ! 1/s
      dot = ddot*(1.d0/(1.602d-19*1.d4*6.022d23))

      A0 =      -dk23*dk27*H2O*dkH2O2**2

      A1 = -dkH2O2*(dk26*dk27*dkO2*O2+dk23*dk26*dkO2*H2O
1 - 2.d0*(dk23*dk27*H2O)*(dkH2O2+dk36) )
2 + dot*(gH+gOH)*dk26*dk27*dkH2O2

      A2 = (dkH2O2+dk36)*(dk26*dk27*dkO2*O2+dk23*dk26*dkO2*H2O
1 - (dk23*dk27*H2O)*(dkH2O2+dk36) )
2 + dot*(gH+gOH)*dk26*(dk26*dkO2-dk27*dkH2O2-dk27*dk36)

      Gcond = (-A1 + dsqrt(A1**2 - 4.d0*A2*A0))/(2.d0*A2)
c      Gcond = dkH2O2/(dkH2O2+dk36+dk26*dot*(gOH+gH)/
c      1      (dk23*H2O+dk27*O2))

      RETURN
      end

      SUBROUTINE NLconc(C1p,C1m,C0,dlam0,A,dN,dk)
      implicit real*8 (a-h,o-z)

      B = -(1.d0 - 1.d0/(A*C0) - dN*dlam0/(dk*A*C0))
      C = -1.d0/(A*C0)

      C1p = ( -B + dsqrt(B**2 - 4.d0*C) )/2.d0
      C1m = ( -B - dsqrt(B**2 - 4.d0*C) )/2.d0

      RETURN
      end

```