

# USED FUEL DISPOSITION CAMPAIGN

## *Addition of Bromide to 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*

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*July 15, 2016*

M4FFT-16PN080302062

PNNL- 25539







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## EXECUTIVE SUMMARY

This report fulfills the M4FT-16-PN080302062 to report on continuing the model integration of the PNNL Radiolysis Model and the ANL Mixed Potential Model for Argillite Disposal. In this work, we demonstrate and approximate the effects of bromide ions on hydrogen peroxide generation under conditions of low oxygen concentration and over pressure of hydrogen. As has been shown these are conditions for which hydrogen peroxide generation is strongly reduced. We find that this reduction is strongly canceled by the presence of even small concentrations of bromide. The full Radiolysis Models seems to be required to accurately predict the effect, but we offer an empirical conservative model for use in the ANL Mixed Potential Model applicable to the prediction of  $\text{UO}_2$  degradation.

Details of the approach are intended to be sufficient for developing a module for calculating radiolytic generation of hydrogen peroxide with known concentration of  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{Br}^-$ . The Listings of the program and reactions considered 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 the effects of bromide and model interface alternatives.



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## 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**

## **Addition of Bromide to 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]

Details of the approach are intended to be sufficient for developing a module for calculating radiolytic generation of hydrogen peroxide with known concentration of  $H_2$ ,  $O_2$  and  $Br^-$ . The listings of the program and reactions considered in this report are given in the appendices.

## 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  $\text{H}_2\text{O}_2$  to one part in  $10^5$ . The intended application of that radiolysis model (RM) was to calculate  $\text{H}_2\text{O}_2$  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 [Shoesmith, D.W., Kolar, M., and King, F., 2003] under disposal conditions where  $\text{O}_2$  is expected to be at low concentrations and  $\text{H}_2$  is generated from oxidation of steel containers. As an initial approximation, that model (MPM) was developed under the assumption that  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  for various water chemistries. As a further step in that direction, this report updates the previously reported steady-state behavior of a full RM under conditions where small concentrations of bromide  $[\text{Br}^-]$  are present.

### 2.1 Model Coupling Definition

The RM coupled kinetics/diffusion rate equations for  $\text{H}_2\text{O}_2$  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  $\text{H}_2\text{O}_2$  generation that is conditional on the local water chemistry. Additionally, because 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  $\text{H}_2\text{O}_2$  production calculation at 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 and how  $[\text{H}_2\text{O}_2]$  is affected by the presence of bromide.







## 2.2 Model Inclusion of Bromide Reactions

This section reviews how a simple analytical function for a conditional  $\text{H}_2\text{O}_2$   $G$ -value compares with the full radiolysis model and shows the added effect of including  $[\text{Br}^-]$  related reactions. The Table 2-1 reactions contain the  $\text{H}_2\text{O}_2$  generating mechanism of the full RM predictions. Without  $\text{Br}^-$  and for low  $\text{O}_2$  concentration, reaction 33 shows how the presence of  $\text{H}_2$  converts the  $\cdot\text{OH}$  radical to the  $\cdot\text{H}$  radical to accelerate  $\text{H}_2\text{O}_2$  destruction lowering its conditional  $G$ -value. At higher  $\text{O}_2$  concentrations,  $\text{O}_2$  effectively competes for  $\cdot\text{H}$  radicals to disable  $\text{H}_2\text{O}_2$  destruction (reaction 27) (reaction numbers are those of the full RM and rate constants are from [Elliot, A.J.; McCracken, D.R. 1990] and [Kelm, M.; Bohnert, E. 2004]).

Table 2-1. Subset of reactions sufficient to represent the primary mechanisms for  $\text{H}_2\text{O}_2$  generation in the full RM.<sup>a</sup>

	Reaction	$k_r$
3	$\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \cdot\text{HO}_2^-$	$1.1 \times 10^{-1}$
4	$\text{H}^+ + \cdot\text{HO}_2^- \rightarrow \text{H}_2\text{O}_2$	$5.0 \times 10^{10}$
15	$\cdot\text{HO}_2^- \rightarrow \text{O}_2^- + \text{H}^+$	$1.3 \times 10^6$
16	$\text{O}_2^- + \text{H}^+ \rightarrow \cdot\text{HO}_2^-$	$5.0 \times 10^{10}$
23	$\text{e}^- + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^-$	$1.1 \times 10^{10}$
26	$\cdot\text{H} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O}$	$9.0 \times 10^7$
27	$\cdot\text{H} + \text{O}_2 \rightarrow \cdot\text{HO}_2^-$	$2.1 \times 10^{10}$
33	$\cdot\text{OH} + \text{H}_2 \rightarrow \cdot\text{H} + \text{H}_2\text{O}$	$4.3 \times 10^7$
34	$\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{HO}_2^- + \text{H}_2\text{O}$	$2.7 \times 10^7$
35	$\cdot\text{HO}_2^- + \text{O}_2^- \rightarrow \cdot\text{HO}_2^- + \text{O}_2$	$8.0 \times 10^7$
36	$\text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \cdot\text{OH}$	$2.5 \times 10^{-7}$
94	$\text{Br}^- + \cdot\text{OH} \rightarrow \text{BrOH}^-$	$1.1 \times 10^{10}$
96	$\text{Br}^- + \cdot\text{H} \rightarrow \text{BrH}^-$	$0.0 \times 10^6$
102	$\text{Br}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{O}_2^- + 2\text{HO}^+$	$2.5 \times 10^9$
138	$\text{BrOH}^- \rightarrow \text{Br}^- + \cdot\text{OH}$	$3.0 \times 10^7$
139	$\text{BrOH}^- \rightarrow \cdot\text{Br} + \text{OH}^-$	$4.2 \times 10^6$

The net effect of this mechanism can be seen in Figure 2-1 where a reduction in  $\text{H}_2\text{O}_2$  generation occurs for small  $\text{O}_2$  and high  $\text{H}_2$  concentration.

<sup>a</sup> Reaction (96) was listed with zero reaction rate in Kelm and Bohnert, 2004.

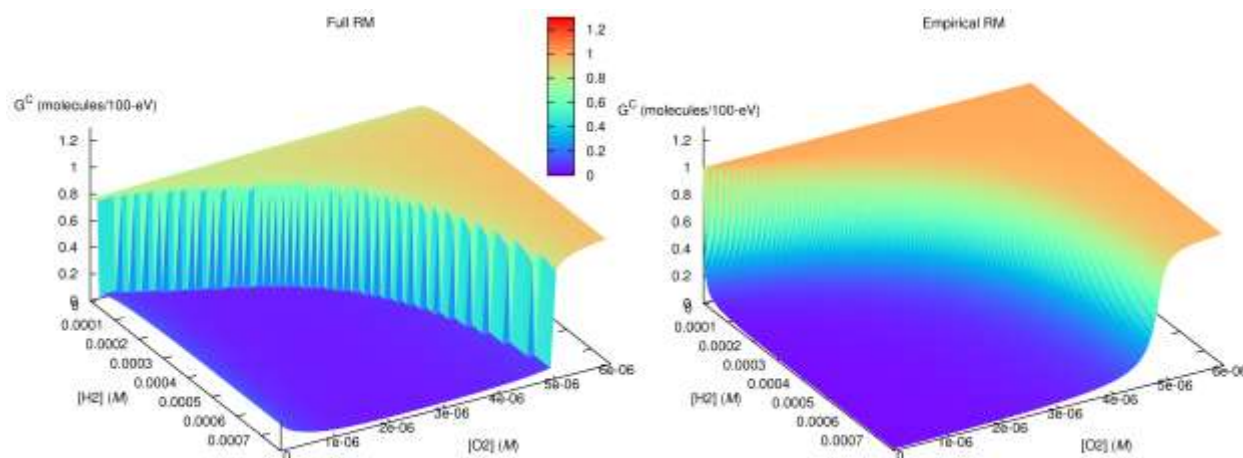


Figure 2-1. Comparison of Full RM and Empirical RM Steady-state conditional  $G$ -values at a dose rate of 160 rad/s.

The effect of even small concentrations of  $\text{Br}^-$  can be seen in Figure 2-2. Figure 2-2 shows a slice through Figure 2-1 where  $[\text{O}_2]$  is fixed at 1  $\mu\text{M}$ . The effect of high  $\text{H}_2$  concentrations to lower the  $\text{H}_2\text{O}_2$  conditional  $G$ -value is nearly removed with the presence of  $\text{Br}^-$ .

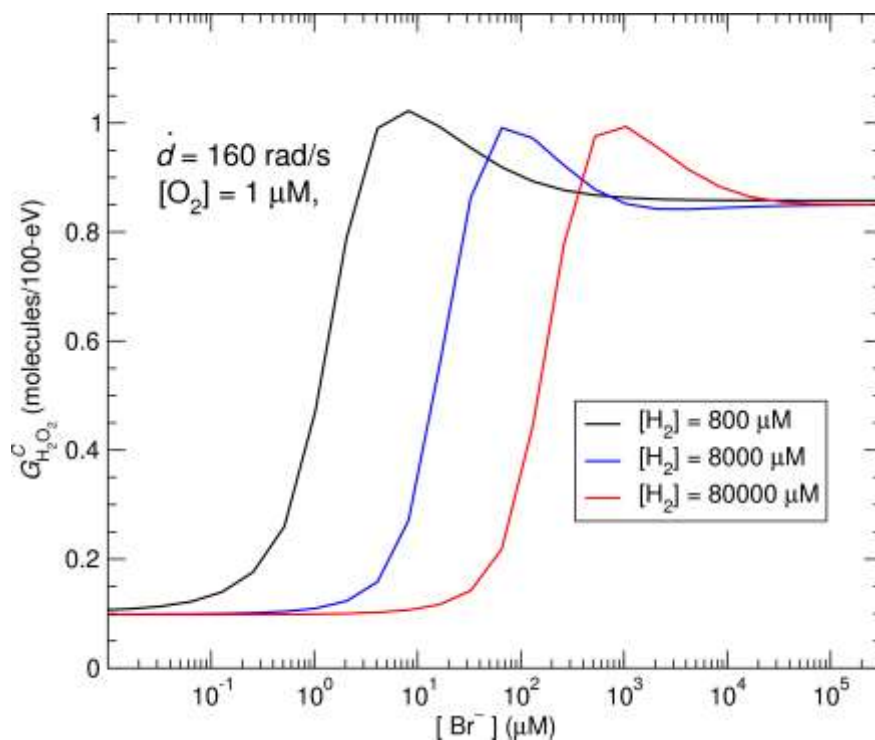


Figure 2-2. Effect of  $[\text{Br}^-]$  on the  $\text{H}_2\text{O}_2$  conditional  $G$ -values in a  $([\text{H}_2], [\text{O}_2])$  region of suppressed  $\text{H}_2\text{O}_2$  generation rate with Full RM.

It is interesting that even at a hydrogen pressure of 100 atm ( $[H_2] = 80000 \mu M$ ) only 100-400  $\mu M$  of  $Br^-$  can bring  $G^C$  from 0.1 to nearly 1.0 molecule/100-eV. The main reason for the effect is reaction 92 in Table 2-1 [Kelm, M.; Bohnert, E. 2004]. By competing for the  $\cdot OH$  radical,  $Br^-$  disables the mechanism for converting  $\cdot OH$  radicals to  $\cdot H$  radical, strongly lowering the rate of destruction of  $H_2O_2$  destruction. It should be mentioned that this mechanism does not operate for the chloride ion because of the smaller rate constant for reaction 39 (see Appendix A).

Based on Table 2.1 an empirical model was previously developed with a minimal number of reactions for use in the MPM. A summary of that model can be described by 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 that incorporate reaction 92 are:

$$\tilde{D}_{H_2O_2}[H_2O_2] = \tilde{G}_{H_2O_2} - k_{26}[\cdot H][H_2O_2] - k_{36}[H_2O_2] \quad (3)$$

$$0 = \tilde{G}_{\cdot H} - k_{27}[\cdot H][O_2] - k_{23}[\cdot H][H_2O] + k_{33}[\cdot OH][H_2] \quad (4)$$

$$0 = \tilde{G}_{\cdot OH} - k_{33}[\cdot OH][H_2] - k_{94}[\cdot OH][Br^-] \quad (5)$$

$$\tilde{D}_{O_2}[O_2] = -k_{27}[\cdot H][O_2] + \tilde{D}_{O_2}[O_2]_B \quad (6)$$

where the bromide concentration is assumed to enter only through reaction 94 [Eq. (5)]. Additionally, if we assume the bromide concentration is the value in the radiation zone as with  $H_2$ , the conditional G-value can be expressed as the solution to a quadratic equation

$$G_{H_2O_2}^C = \frac{-C_1 + (C_1^2 - 4C_0C_2)^{\frac{1}{2}}}{2C_2} \quad (7)$$

where the coefficients are given by:

$$C_0 = -k_{23}k_{27}[H_2O]\tilde{D}_{H_2O_2}^2 \quad (8)$$

$$C_1 = -\tilde{D}_{H_2O_2} \left[ k_{26}k_{27}[O_2]_B\tilde{D}_{O_2} + k_{23}k_{26}[H_2O]\tilde{D}_{O_2} - 2k_{23}k_{27}[H_2O] \left( \tilde{D}_{H_2O_2} + k_{36} \right) \right] + k_{26}k_{27}\tilde{D}_{H_2O_2} \left( \tilde{G}_{\cdot H} + \tilde{G}_{\cdot OH}F_{Br^-} \right) \quad (9)$$

$$C_2 = \left[ k_{26}k_{27}[O_2]_B\tilde{D}_{O_2} + k_{23}k_{26}[H_2O]\tilde{D}_{O_2} - k_{23}k_{27}[H_2O] \left( \tilde{D}_{H_2O_2} + k_{36} \right) \right] \left( \tilde{D}_{H_2O_2} + k_{36} \right) + k_{26} \left( k_{26}\tilde{D}_{O_2} - k_{27}\tilde{D}_{H_2O_2} - k_{27}k_{36} \right) \left( \tilde{G}_{\cdot H} + \tilde{G}_{\cdot OH}F_{Br^-} \right), \quad (10)$$

where

$$F_{Br^-} = \frac{k_{33}[H_2]}{k_{33}[H_2] + k_{94}[Br^-]} \quad (11)$$

Diffusion constants were defined in earlier reports (see Buck et al., 2013). Unlike the pure water system, the presence of bromide introduces an additional dependence on hydrogen through Eq. (11). In this approximation, some of the effect of  $H_2$  is handled empirically by making  $G_H$  and  $G_{OH}$  dependent on  $[H_2]$  according to:

$$G_H = (0.10 \text{ molecules}/100\text{-eV}) \left[ 1 - \exp \left( -\frac{[H_2]F_{Br^-}/0.1 \text{ atm}}{7.8 \times 10^{-4} M/\text{atm}} \right) \right] \quad (12)$$

$$G_{OH} = (0.35 \text{ molecules}/100\text{-eV}) \left[ 1 - \exp \left( -\frac{[H_2]F_{Br^-}/0.3 \text{ atm}}{7.8 \times 10^{-4} M/\text{atm}} \right) \right] \quad (13)$$

Additionally, in this approximation  $k_{23}$  is reduced by a factor of 56,  $k_{94}$  is increased by a factor of 10 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 2-3 shows the conditional  $G$ -value as a function of  $[H_2]$  and  $[O_2]_B$  for the full RM and for the one calculated from Eqs. (7-13).

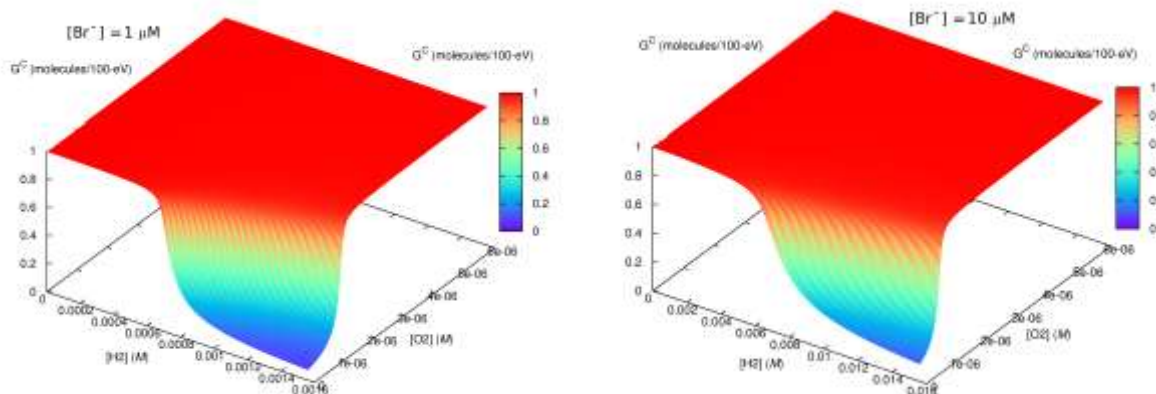


Figure 2-3. Effect of bromide ( $[Br^-] = 1 \mu M$  and  $[Br^-] = 10 \mu M$ ) on Empirical RM Steady-state conditional  $G$ -values at a dose rate of 160 rad/s.

As in the case of Figure 2-1, a scaling behavior still occurs for Figure 2-3 where the shape of the concentration surface remains unchanged with the same scaling of dose rate,  $[H_2]$ ,  $[O_2]_B$  and now of  $[Br^-]$ . The empirical RM with bromide was seen to have less accuracy in comparison with the full RM, but because of the absence of the direct  $H_2O_2$  destructive reaction 102, the prediction of  $G^C$  appears to be normally conservative for regions where a larger  $G^C$  is expected. While it appears that more reactions and further complexity is required for greater accuracy, the Empirical RM is seen to retain the general features of the Full RM (Figure 2-4) and has the advantage of being quickly evaluated.

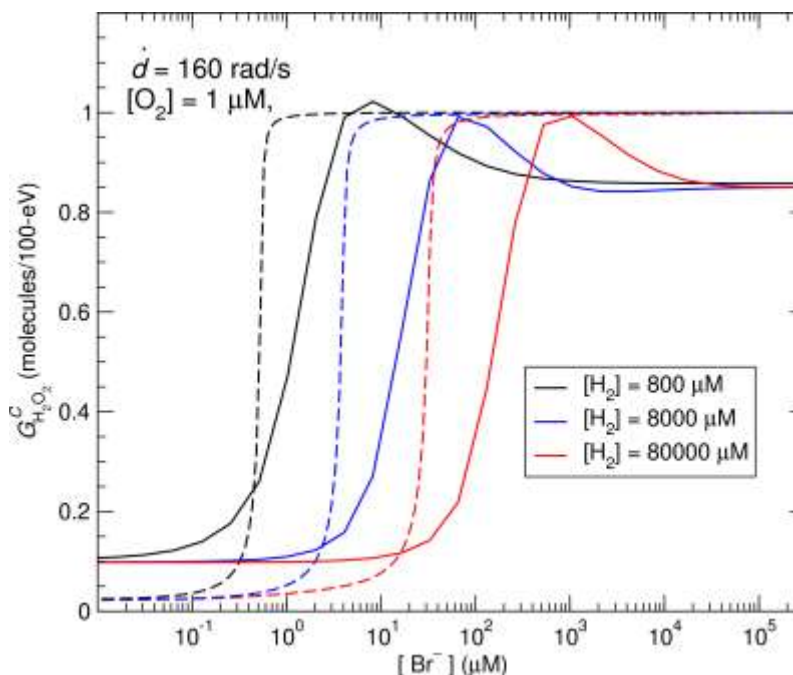


Figure 2-4. Effect of  $[\text{Br}^-]$  on the  $\text{H}_2\text{O}_2$  conditional  $G$ -values in a ( $[\text{H}_2]$ ,  $[\text{O}_2]$ ) region of suppressed  $\text{H}_2\text{O}_2$  generation rate with Empirical RM (dashed) and Fill RM (solid).

## 2.3 Future Work

While a reasonable model for  $\text{H}_2\text{O}_2$  generation with the presence of bromide can be constructed as in the pure water system, an accurate representation of the bromide effect on  $\text{H}_2\text{O}_2$  seems to require the full radiolysis model. Future work will attempt to formulate a reduced model that more closely compares with the full model as well as incorporate carbonate chemistry. A future goal will be to represent a full RM with in the fuel degradation MPM, but as shown here, an empirical model is helpful for both simple calculation and for understanding the most relevant underlying mechanisms that are imbedded in the reactions.





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## APPENDIX A: Reaction Listing for Full RM

Equilibrium constants:

H2O <--> H+ + OH- : RKeq(2) = 10<sup>^(-13.999)</sup>

H2O2 <--> H+ + HO2- : RKeq(3) = 10<sup>^(-11.65)</sup>

OH <--> H+ + O- : RKeq(4) = 10<sup>^(-11.9)</sup>

HO2 <--> H+ + O2- : RKeq(5) = 10<sup>^(- 4.57)</sup>

H <--> H+ + E- : RKeq(6) = 10<sup>^(- 9.77)</sup>

	Reactions	Rate constants (M <sup>-n</sup> /s)
1	H+ + OH- = H2O	1.4d11
2	H2O = H+ + OH-	rk( 2) = rk( 1)*RKeq(2)
3	H2O2 = H+ + HO2-	rk( 3) = rk( 4)*RKeq(3)
4	H+ + HO2- = H2O2	5.0d10
5	H2O2 + OH- = HO2- + H2O	1.3d10
6	HO2- + H2O = H2O2 + OH-	rk( 6) = rk( 5)*RKeq(2)/RKeq(3)
7	E- + H2O = H + OH-	1.9d1
8	H + OH- = E- + H2O	2.2d7
9	H = E- + H+	rk( 9) = rk(10)*RKeq(6)
10	E- + H+ = H	2.3d10
11	OH + OH- = O- + H2O	1.3d10
12	O- + H2O = OH + OH-	rk(12) = rk(11)*RKeq(2)/RKeq(4)
13	OH = O- + H+	rk(13) = rk(14)*RKeq(4)
14	O- + H+ = OH	1.0d11
15	HO2 = O2- + H+	rk(15) = rk(16)*RKeq(5)
16	O2- + H+ = HO2	5.0d10
17	HO2 + OH- = O2- + H2O	5.0d10
18	O2- + H2O = HO2 + OH-	rk(18) = rk(17)*RKeq(2)/RKeq(5)
19	E- + H2O2 = OH + OH-	1.1d10
20	E- + O2- + H2O = HO2- + OH-	1.3d10
21	E- + HO2 = HO2-	2.0d10
22	E- + O2 = O2-	1.9d10
23	H + H2O = H2 + OH	1.1d1
24	H + H = H2	7.8d9
25	H + OH = H2O	7.0d9
26	H + H2O2 = OH + H2O	9.0d7
27	H + O2 = HO2	2.1d10
28	H + HO2 = H2O2	1.8d10
29	H + O2- = HO2-	1.8d10
30	OH + OH = H2O2	3.6d9
31	OH + HO2 = H2O + O2	6.0d9
32	OH + O2- = OH- + O2	8.2d9
33	OH + H2 = H + H2O	4.3d7
34	OH + H2O2 = HO2 + H2O	2.7d7
35	HO2 + O2- = HO2- + O2	8.0d7
36	H2O2 = OH + OH	2.25d-7
37	OH + HO2- = HO2 + OH-	7.5d9
38	HO2 + HO2 = H2O2 + O2	7.0d5
39	OH + Cl- = ClOH-	4.300D+09
40	OH + HClO = ClO + H2O	9.000D+09
41	OH + ClO2- = ClO2 + H2O - H+	6.300D+09
42	E- + Cl = Cl- + H2O	1.000D+10
43	E- + Cl2- = Cl- + Cl- + H2O	1.000D+10
44	E- + ClOH- = Cl- + OH- + H2O	1.000D+10
45	E- + HClO = ClOH-	5.300D+10
46	E- + Cl2 = Cl2-	1.000D+10
47	E- + Cl3- = Cl2- + Cl-	1.000D+10
48	E- + ClO2- = ClO + OH- - H+	4.500D+10
49	E- + ClO3- = ClO2 + OH- - H+	0.000D+00
50	H + Cl = Cl- + H+	1.000D+10

51	H + Cl2- = Cl- + Cl- + H+	8.000D+09
52	H + ClOH- = Cl- + H2O	1.000D+10
53	H + Cl2 = Cl2- + H+	7.000D+09
54	H + HClO = ClOH- + H+	1.000D+10
55	H + Cl3- = Cl2- + Cl- + H+	1.000D+10
56	HO2 + Cl2- = Cl- + HCl + O2	4.000D+09
57	HCl = Cl- + H+	5.000D+05
58	HO2 + Cl2 = Cl2- + H+ + O2	1.000D+09
59	HO2 + Cl3- = Cl2- + HCl + O2	1.000D+09
60	O2- + Cl2- = Cl- + Cl- + O2	1.200D+10
61	O2- + HClO = ClOH- + O2	7.500D+06
62	H2O2 + Cl2- = HCl + HCl + O2-	1.400D+05
63	H2O2 + Cl2 = HO2 + Cl2- + H+	1.900D+02
64	H2O2 + HClO = HCl + H2O + O2	1.700D+05
65	OH- + Cl2- = ClOH- + Cl-	7.300D+06
66	OH- + Cl2 = HClO + Cl-	1.000D+10
67	H+ + ClOH- = Cl + H2O	2.100D+10
68	H2O + Cl2O2 = HClO + ClO2- + H+	2.000D+02
69	H2O + Cl2O2 = O2 + HClO + HCl	0.000D+00
70	H2O + Cl2O = HClO + HClO	1.000D+02
71	H2O + Cl2O4 = ClO2- + ClO3- + H+ + H+	1.000D+02
72	H2O + Cl2O4 = HClO + HCl + O4	1.000D+02
73	O4 = O2 + O2	1.000D+05
74	Cl- + Cl = Cl2-	2.100D+10
75	Cl- + ClOH- = Cl2- + OH-	9.000D+04
76	Cl- + HClO = Cl2 + OH-	6.000D-02
77	Cl- + Cl2 = Cl3-	1.000D+04
78	Cl- + H+ = HCl (assuming pKa = -3.9)	6.295D+01
79	ClOH- = OH + Cl-	6.100D+09
80	Cl2- = Cl + Cl-	1.100D+05
81	Cl2- + Cl2- = Cl3- + Cl-	7.000D+09
82	Cl3- = Cl2 + Cl-	5.000D+04
83	ClO + ClO = Cl2O2	1.500D+10
84	ClO2 + ClO2 = Cl2O4	1.000D+02
85	Cl2O2 + ClO2- = ClO3- + Cl2O	1.000D+02
86	E- + ClO3- = ClR--	1.600D+05
87	ClR-- + OH = OH- + ClO3-	1.000D+10
88	ClR-- + O- = OH- + ClO3- - H+	1.200D+09
89	HClO + HClO = Cl- + ClO2- + H+ + H+	6.000D-09
90	ClO2- + HClO = Cl- + ClO3- + H+	9.000D-07
91	HClO + HClO = O2 + HCl + HCl	3.000D-10
92	HClO4 = H+ + ClO4- (a guess)	1.000D+10
93	H+ + ClO4- = HClO4 (assuming pKa = -7)	1.000D+03
94	Br- + OH = BrOH-	1.100D+10
95	Br- + Br = Br2-	1.000D+10
96	Br- + H = HBr-	0.000D+06
97	Br- + O- = Br + OH- - H+	2.200D+08
98	Br + BrO- = Br- + BrO	4.100D+09
99	Br = BrOH- + H+ - H2O	1.400D+00
100	Br + HO2 = H+ + Br- + O2	1.600D+08
101	Br + OH- = BrOH-	1.300D+10
102	Br + H2O2 = Br- + O2- + H+ + H+	2.500D+09
103	Br2- = Br + Br-	1.900D+04
104	Br2- + Br2- = Br- + Br3-	3.400D+09
105	Br2- + BrO2- = BrO2 + Br- + Br-	8.000D+07
106	Br2- + BrO- = BrO + Br- + Br-	6.200D+07
107	Br2- + ClO2- = Br- + ClO2 + Br-	2.000D+07
108	Br2- + H = H+ + Br- + Br-	1.400D+10
109	Br2- + HO2 = H+ + Br- + Br- + O2	1.000D+08
110	Br2- + O2- = Br- + Br- + O2	1.700D+08
111	Br2- + E- = Br- + Br-	1.100D+10
112	Br2- + H2O2 = Br- + Br- + HO2 + H+	1.900D+06
113	BrO- + OH = BrO + OH-	4.200D+09
114	BrO- + O- = BrO + OH- - H+	3.500D+09

# USED FUEL DISPOSITION CAMPAIGN

## Addition of Bromide to Radiolysis Model Formulation for Integration with the Mixed Potential Model

July 15, 2016

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115	$\text{BrO}^- + \text{E}^- = \text{Br}^- + \text{O}^-$	1.500D+10
116	$\text{BrO}_2^- + \text{OH} = \text{BrO}_2 + \text{OH}^-$	2.300D+09
117	$\text{BrO}_2^- + \text{BrO} = \text{BrO}^- + \text{BrO}_2$	4.000D+08
118	$\text{BrO}_2^- + \text{O}^- = \text{BrO}_2 + \text{OH}^- - \text{H}^+$	1.600D+09
119	$\text{BrO}_2^- + \text{E}^- = \text{BrO} + \text{H}_2\text{O} - \text{H}^+ - \text{H}^+$	1.100D+10
120	$\text{BrO}_3^- + \text{OH} = \text{BrO}_3 + \text{OH}^-$	0.000D+06
121	$\text{BrO}_3^- + \text{H} = \text{BrO}_2 + \text{OH}^-$	2.000D+07
122	$\text{BrO}_3^- + \text{O}^- = \text{BrO}_3 + \text{OH}^- - \text{H}^+$	0.000D+06
123	$\text{BrO}_3^- + \text{E}^- = \text{BrO}_2 + \text{OH}^- + \text{OH}^- - \text{H}_2\text{O}$	3.400D+09
124	$\text{Br}_2 + \text{H} = \text{Br}_2^- + \text{H}^+$	1.000D+10
125	$\text{Br}_2 + \text{HO}_2 = \text{H}^+ + \text{O}_2 + \text{Br}_2^-$	1.300D+08
126	$\text{Br}_2 + \text{O}_2^- = \text{O}_2 + \text{Br}_2^-$	5.000D+09
127	$\text{Br}_2 + \text{Br}^- = \text{Br}_3^-$	9.600D+08
128	$\text{Br}_2 + \text{E}^- = \text{Br}_2^-$	5.300D+10
129	$\text{HOBr} + \text{OH} = \text{BrO} + \text{H}_2\text{O}$	2.000D+09
130	$\text{HOBr} + \text{O}_2^- = \text{O}_2 + \text{Br} + \text{OH}^-$	3.500D+09
131	$\text{BrO}_2 + \text{OH} = \text{BrO}_3^- + \text{H}^+$	2.000D+09
132	$\text{BrO}_2 + \text{BrO}_2 = \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+ + \text{H}^+ - \text{H}_2\text{O}$	4.000D+07
133	$\text{BrO}_2 + \text{ClO}_2^- = \text{BrO}_2^- + \text{ClO}_2$	3.600D+07
134	$\text{Br}_3^- + \text{H} = \text{H}^+ + \text{Br}_2^- + \text{Br}^-$	1.200D+10
135	$\text{Br}_3^- + \text{O}_2^- = \text{O}_2 + \text{Br}_2^- + \text{Br}^-$	1.500D+09
136	$\text{Br}_3^- = \text{Br}_2 + \text{Br}^-$	5.500D+07
137	$\text{Br}_3^- + \text{E}^- = \text{Br}_2^- + \text{Br}^-$	2.700D+10
138	$\text{BrOH}^- = \text{Br}^- + \text{OH}$	3.000D+07
139	$\text{BrOH}^- = \text{Br} + \text{OH}^-$	4.200D+06
140	$\text{BrOH}^- + \text{H}^+ = \text{Br} + \text{H}_2\text{O}$	1.300D+10
141	$\text{BrOH}^- + \text{Br}^- = \text{Br}_2^- + \text{OH}^-$	1.900D+08
142	$\text{BrO} + \text{BrO} = \text{BrO}^- + \text{BrO}_2^- + \text{H}^+ + \text{H}^+ - \text{H}_2\text{O}$	2.800D+09
143	$\text{BrO} + \text{BrO}_2^- = \text{BrO}^- + \text{BrO}_2$	4.000D+08
144	$\text{HOBr} = \text{H}^+ + \text{BrO}^-$	1.580D+01
145	$\text{BrO}^- + \text{H}^+ = \text{HOBr}$	1.000D+10
146	$\text{Br}^- + \text{Cl}_2^- = \text{BrCl}^- + \text{Cl}^-$	4.00D+09
147	$\text{BrCl}^- + \text{Cl}^- = \text{Cl}_2^- + \text{Br}^-$	1.10D+02
148	$\text{BrCl}^- = \text{Cl}^- + \text{Br}$	8.50D+07
149	$\text{Br} + \text{Cl}^- = \text{BrCl}^-$	1.00D+10
150	$\text{BrCl}^- + \text{Br}^- = \text{Br}_2^- + \text{Cl}^-$	8.00D+09
151	$\text{Br}_2^- + \text{Cl}^- = \text{BrCl}^- + \text{Br}^-$	4.30D+06
152	$\text{Br}^- + \text{Cl}_2 = \text{BrCl}_2^-$	6.00D+09
153	$\text{BrCl}_2^- = \text{Cl}_2 + \text{Br}^-$	9.00D+03
154	$\text{BrCl}_2^- = \text{BrCl} + \text{Cl}^-$	1.70D+05
155	$\text{BrCl} + \text{Cl}^- = \text{BrCl}_2^-$	1.00D+06
156	$\text{BrCl}_2^- + \text{Br}^- = \text{Br}_2\text{Cl}^- + \text{Cl}^-$	3.00D+08
157	$\text{BrCl} = \text{HOBr} + \text{H}^+ + \text{Cl}^- - \text{H}_2\text{O}$	3.00D+06
158	$\text{HOBr} + \text{Cl}^- = \text{BrCl} + \text{H}_2\text{O} - \text{H}^+$	2.30D+10
159	$\text{BrCl} = \text{HClO} + \text{H}^+ + \text{Br}^- - \text{H}_2\text{O}$	1.15D-03
160	$\text{HClO} + \text{Br}^- = \text{BrCl} + \text{H}_2\text{O} - \text{H}^+$	1.32D+06
161	$\text{Br}^- + \text{HOBr} = \text{Br}_2 + \text{H}_2\text{O} - \text{H}^+$	3.00D+09
162	$\text{Br}_2 = \text{Br}^- + \text{HOBr} + \text{H}^+ - \text{H}_2\text{O}$	2.00D+00
163	$\text{Br}^- + \text{HBrO}_2 = \text{HOBr} + \text{HOBr} - \text{H}^+$	3.00D+06
164	$\text{HOBr} + \text{HOBr} = \text{Br}^- + \text{HBrO}_2 + \text{H}^+$	2.00D-05
165	$\text{Br}^- + \text{BrO}_3^- = \text{HOBr} + \text{BrO}_2^- - \text{H}^+$	2.500D-7
166	$\text{HOBr} + \text{HBrO}_2 = \text{Br}^- + \text{BrO}_3^- + \text{H}^+ + \text{H}^+$	3.20D+00
167	$\text{HBrO}_2 + \text{HBrO}_2 = \text{HOBr} + \text{BrO}_3^- + \text{H}^+$	3.00D+03
168	$\text{HOBr} + \text{BrO}_3^- = \text{HBrO}_2 + \text{HBrO}_2 - \text{H}^+$	1.00D-08
169	$\text{HBrO}_2 + \text{BrO}_3^- = \text{BrO}_2 + \text{BrO}_2 + \text{H}_2\text{O} - \text{H}^+$	4.20D+01
170	$\text{BrO}_2 + \text{BrO}_2 = \text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ - \text{H}_2\text{O}$	4.20D+07
171	$\text{HBrO}_2 = \text{BrO}_2^- + \text{H}^+$	5.00D+05
172	$\text{BrO}_2^- + \text{H}^+ = \text{HBrO}_2$	1.35D+09
173	$\text{BrCl}^- + \text{BrCl}^- = \text{BrCl} + \text{Br}^- + \text{Cl}^-$	1.20D+09
174	$\text{Br}_2 + \text{Cl}^- = \text{Br}_2\text{Cl}^-$	1.00D+07
175	$\text{Br}_2\text{Cl}^- = \text{Br}_2 + \text{Cl}^-$	7.69D+06
176	$\text{BrCl} + \text{Br}^- = \text{Br}_2\text{Cl}^-$	1.00D+07
177	$\text{Br}_2\text{Cl}^- = \text{BrCl} + \text{Br}^-$	5.56D+02









## APPENDIX B: FORTRAN Listing for Empirical RM

Emp-RM.f

```

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

ddot = 160.d0          ! rad/s

Brex = 1.d-6

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

H2ext = 7.8d-4*dfloat(j)/100.d0      ! mole/L
O2ext = dfloat(i)/2.d7 + 1.d-11      ! mole/L
G2 = Gcond(ddot,O2ext,H2ext,Brex)

write(*,*) H2ext,O2ext,G2

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

STOP
end

FUNCTION Gcond(ddot,O2ext,H2ext,Brex)
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
rk33 = 4.3d7
rk94 = 1.1d10 * 10.
BrFact = rk33*H2ext/(rk33*H2ext + rk94*Brex)
if(Brex.eq.0.) BrFact = 1.d0
GH = 0.100d0*(1.d0-dexp(-(H2ext*BrFact/7.8d-4)/.1d0))      ! molecules/eV
GOH = 0.350d0*(1.d0-dexp(-(H2ext*BrFact/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
GOH = GOH * BrFact

O2 = O2ext + 2.d-6*Brex/(Brex+0.5d-6)
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

```