USED FUEL DISPOSITION CAMPAIGN

Chloride/Bromide System Radiolysis Model for Integration with the Mixed Potential Model

Fuel Cycle Research & Development

Submitted by:

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EXECUTIVE SUMMARY

This report fulfills the M4 milestone (M4FT-15PN0804011) to report on the model integration of the PNNL Radiolysis Model and the ANL Mixed Potential Model (MPM). The approach taken is to formulate a simplified analytical model that retains the main feature and predictions of a full chloride/bromide system Radiolysis Model applicable to the prediction of UO_2 degradation.

From nuclear reactor chemistry it has been established that dissolving H_2 into the pressurized cooling water limits radiolysis that might otherwise be deleterious to various components in the reactor. Similar effects have been observed in long-term dissolution experiments with used UO_2 nuclear fuel under anoxic conditions. Including such processes over the lifetime of a geologic nuclear waste repository, is facilitated by understanding the mechanism of the protective effect more precisely and for a variety of anoxic disposal scenarios. We have been modeling radiolysis chemistry for simple systems relevant to UO_2 disposal, such as pure water. In this report, we examine the possible radiolysis effects in a chloride/bromide system.[a]

The main approach detailed in this report is as follows.
- Identify the significant environment reactions that govern the radiolytic generation of oxidants ($HClO$, H_2O_2 and Cl_2^-) in water with known chloride/bromide ion concentrations.[b]

- Define and demonstrate a solvable simplified analytical model of $HClO$, H_2O_2 and Cl_2^- generation that retains the main physical features and replicate predictions of the full radiolysis model. Bromine reactions are considered in this approach and demonstrated to be extremely important with respect to the final concentrations of species that control the reactivity o UO_2. However, there were no $UO_2 - Br$ species reactions considered in the analysis.

- Present two simplified alternatives: 1) a reduced radiolysis reaction set that replicate the main details of the full set at steady-state and; 2) analytical expressions that are easily evaluated and retain the relevant mechanisms for oxidant generation, but contain empirical adjustments. This type of equation is required for implementation into the MPM.

Details of the approach are intended to be sufficient for developing a module for calculating radiolytic generation of $HClO$, H_2O_2 and Cl_2^-. Listings of the programs used in this report are given in Appendices.

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[a] The term Cl/Br solutions rather than brines is used in this report. Brines are generally higher concentration solutions (e.g., seawater is about 0.7 molal).

[b] Radiolytic products directly produced from bromine were not considered in this exercise because the concentrations were too low to be considered as important direct radiolysis products.

ACKNOWLEDGMENTS

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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

LET   Linear Energy Transfer

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
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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 (Freeze et al., 2010). 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 (Jerden et al. 2012, 2013, 2015) and the PNNL Radiolysis Model (Buck et al., 2013; Wittman et al. 2014).

This report is in response to the desire to simplify integration of 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 Degradatio*n, FCRD-UFD-2013-000290, M3FT-PN0806058] specifically for the brine environment of the chloride/bromide system. This works stems from the need to determine the long-term behavior of the engineered barrier system for the geologic disposal of used nuclear fuel.

The effects of radiolysis in brines has been investigated by Jenks and Walton (1981); Jain et al., 1985; and, more recently, Mustaree et al. (2014). High Linear Energy Transfer (LET) processes relevant to the disposal of used UO_2 nuclear fuel (i.e., α-radiolysis) in brine repository environments have been conducted by Gray (1988); Gimenez et al., 1996; Kelm and Bohnert (2004, 2005); and Kelm et al. (2011). Furthermore, there have been many studies that have examined the effect of radiolysis in metallic waste packages in brine environments, typically involving low LET processes (i.e., β,γ-radiolysis).

Hence, there is a good understanding of the types of radiolytic products formed in brines with different LET. The objective was not to make necessarily valid predictions but to demonstrate that the RM could be used to develop an analytical expression for radiolysis effects that could be easily linked to the MPM (Jerden et al., 2015), for the development of a consistent model for environments similar to that reported previously (see Buck et al., 2013).

Chloride ions, which are abundant in granitic, argillaceous and saline formation water, readily react with hydroxyl radicals achieving an equilibrium that is in favor of free OH• radicals only at low Cl^- concentrations. In the near-field environment, radiolysis from disposed nuclear materials could impact the mobility of radionuclides in the brine solutions. If the brines are irradiated by contacting the waste package and/or used fuel, radiolytic species such as hypochlorite (ClO-), hypochlorous acid (HClO) or H_2O_2, will be generated; and the pH and Eh of the solutions will be altered. The oxidation and complexation states of released actinides that

might be present in the brine, may change, and therefore, influence their speciation and potential mobility. In addition, these oxidizing species may enhance the corrosion of any canister materials through pitting and other effects. Kelm and Bohnert (2002) conducted studies with ^{238}Pu-doped UO_2 pellets to examine the effects of irradiated brine solutions on the simulant fuel.

Bromine has played a significant role in the development of radiolysis science because the Br^- ion is inert toward the aqueous electron and reacts only slowly with H• but very effectively with OH• (Kelm and Bohnert, 2004; 2011).

$$OH• + Br^- \rightarrow Br• + OH^- \qquad k = 1.1 \times 10^{10} \text{ mol}^{-1}\text{s}^{-1} \qquad (1.1)$$
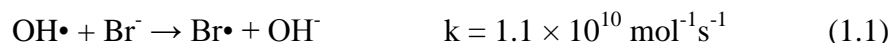
Hence, G_{H2} was initially determined from measuring gas volumes generated in deaerated aqueous KBr because the Br- ion prevents the destruction of H_2 because it consumes the OH• that is the major reactant to use H_2. Radiolysis studies and leaching experiments with spent nuclear fuel and UO_2(s) indicate that molecular hydrogen both impedes radiolytic decomposition of the studied formation water simulates and considerably inhibits corrosion of the UO_2(s) matrix (Bruno and Ewing, 2006). To the present knowledge, a single reaction accounts for the influence of molecular hydrogen on radiolysis of aqueous solution equation (1.2).

Ultimately, this reaction converts oxidizing OH• into reducing H•.

$$OH• + H_2 \rightarrow H_2O + H• \qquad k = 3.8 \times 10^7 \text{ mol}^{-1}\text{s}^{-1} \qquad (1.2)$$
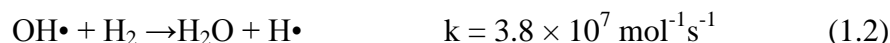
Using pulse radiolysis, Christensen and Sehested (1986) determined the rate constant of reaction (1.2) at 20°C as $k_i=3.4(\pm0.3)\times10^7$ dm^3 mol^{-1} s^{-1}, which is in agreement with results of previous pulse radiolysis studies. Reaction (1.2) is perhaps the most important reaction in the disposal environment as it knocks out the OH• radical that leads to H_2O_2 production. Understanding the role of this process is key to predicting the effects of H_2 on ultimately limiting UO_2 degradation and this is where much of the science of disposal radiolysis is currently focused.

Foreign species incorporated in the brines can change the redox potential under the influence of a radiation field. It is well known that radiolysis of brines produces Cl_2^- and various oxychlorides. The Cl^- ion can react with OH radicals to produce reactive ClO^- ions. The hypochlorite ion is known to adversely affect the corrosion rate of UO_2. Indeed, Giménez et al. (1996) found that a general rate equation for the effect of the oxidants [ClO^-] and [H_2O_2] on the rate (r) of UO_2 dissolution was equally applicable:

$$\log r = (-8.0 \pm 0.2) + \log[Ox]^{0.93\pm0.07} \qquad (1.3)$$

The amount of hydrogen and oxygen formed was proportional to the dose. The gas formation was observed not to depend on pH. While the chlorite concentration remained near 10^{-5} mol/kg, the yield of hypochlorite increased with increasing pH and approached a limiting concentration.
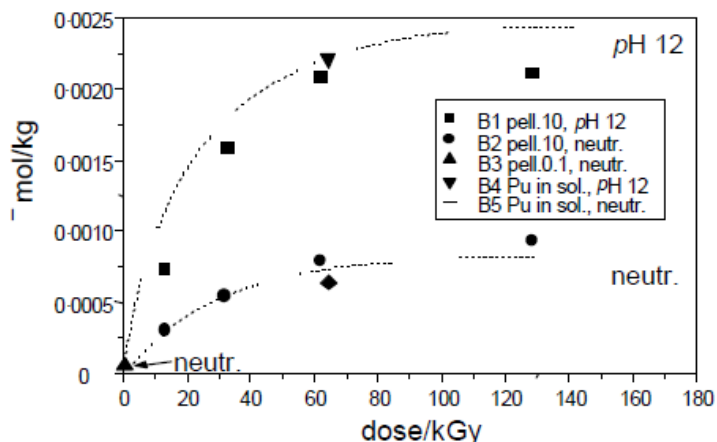
Figure 1

Figure 1.1 Formation of hypochlorite in 5 M NaCl solution in contact with Pu-doped pellets with dose measured in kGy (where 1 Gy = 100 Rad) [from Kelm and Bohnert (2002)]
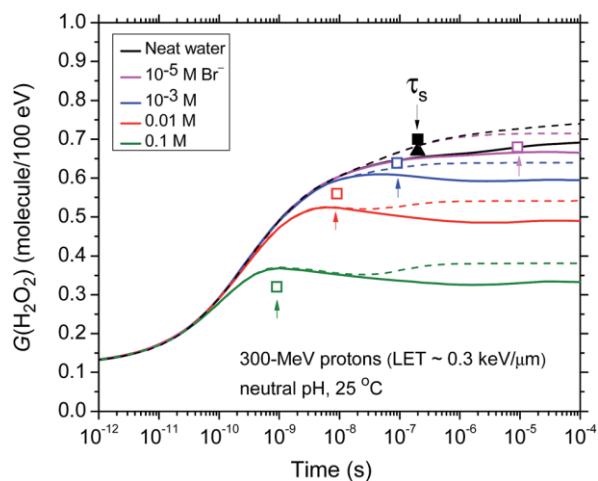
Figure 1.2 Time evolution of G_{H2O2} after 300 MeV proton irradiation of aqueous bromide solutions at neutral pH and 25°C based on Monte Carlo simulations over the interval 10^{-12} to 10^{-4} s [taken from Mustaree et al., 2014].[c]

Monte Carlo track chemistry simulations have been used by Mustaree and co-workers (2014) to determine G_{H2O2} in both water and dilute aqueous bromide solutions with variable LET. In particular, they focused on the influence of Br⁻ ions, as scavengers of •OH (see Equation 1.1 and 1.2), precursors of H_2O_2. They studied this system under a wide range of Br⁻ concentrations (5 × 10^{-7} to 0.1 M) but in the absence of chloride.[d] Simulations showed that the short track geometry of higher LET tritium β-electrons in both water and aqueous bromide solutions favored a clear

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[c] The lifetime of a radiation spur (τ_s) is the time required for the change-over from non-homogeneous spur kinetics to homogeneous kinetics in the bulk solution, thus it defines the so-called primary (or 'escape') radical and molecular yields of radiolysis (Sanguanmith et al., 2012).

[d] Solid lines were simulated results for deaerated systems and dashed lines for air-saturated systems. Bromide (Br-) concentrations, 10^{-5}M (magneta), 10^{-3}M (blue), 10^{-2}M (red), 0.1M (red).

increase in $G_{H_2O_2}$ compared to ^{60}Co γ-rays. Moreover, O_2 was observed to scavenge the aqueous electron ($e^-_{(aq)}$) and H• on the 10^{-7} s time-scale, thereby protecting H_2O_2 from further reactions with these species in the homogeneous stage of radiolysis. This protection against $e^-_{(aq)}$ and H• led to an increase in the long time H_2O_2 yields. For both deaerated and aerated solutions, the H_2O_2 yield in H-3 β-radiolysis was found to be more easily suppressed than in the case of γ-radiolysis, and interpreted by the quantitatively different chemistry between spurs and short tracks. These differences in the ability of H_2O_2 to be scavenged were in good agreement with the experimental data.

The Appendixes provide the full radiolysis model reactions and a FORTRAN listing of the computer programs written to evaluate three 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 et al., 2014) showed that of the approximately 100 reactions (Elliot and McCracken, 1990; Christensen and Sunder, 1996; Pastina and LaVerne, 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 et al., 2012, 2013, 2015) developed to calculate the oxidation/dissolution rate of used nuclear fuel (Shoesmith et al., 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 oxidant concentrations for other water chemistries such as a concentrated brine solution. As a step in that direction, this report describes the steady-state behavior of a full RM under conditions relevant to the MPM and formulates analytical expressions that closely approximate the full RM. We apply an analogous approach used in previous work (Buck, et al., 2013) to the generation of the primary oxidants for the chloride/water/bromide system of a brine environment.

2.1   Model Coupling Definition

We solve the coupled kinetics/diffusion rate equations on discrete spatial zones (*n*). For example, the time dependence of the hydrogen peroxide concentration $d[H_2O_2]_n/dt$ can be expressed in terms of all the concentrations, fluxes J_n and dose rate $\dot{d}$ according to

$$\frac{d[\mathrm{H_2O_2}]_n}{dt} + \frac{J_n^{(\mathrm{H_2O_2})} - J_{n-1}^{(\mathrm{H_2O_2})}}{x_n - x_{n-1}} = G_{\mathrm{H_2O_2}}\dot{d}_n + (\text{reaction kinetics})_n \qquad (2.1)$$

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. (2.1) after inserting Fick's Law fluxes containing diffusion constant D and boundary concentration $[H_2O_2]_B$ can be written:

$$\frac{D_{\mathrm{H_2O_2}}}{x_R x_B}[\mathrm{H_2O_2}] = G_{\mathrm{H_2O_2}}\dot{d} + (\text{reaction kinetics}) + \frac{D_{\mathrm{H_2O_2}}}{x_R x_B}[\mathrm{H_2O_2}]_B \equiv G_{\mathrm{H_2O_2}}^C\dot{d} \qquad (2.2)$$

Equation 2.2 serves as the working definition of "conditional" *G*-value ($[H_2O_2]_B = 0$ 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. (2.2) is assumed to define the interface between the RM and MPM − i.e. the MPM evaluates a new conditional *G*-value for its radiolytic oxidant production calculation at each new time-step.

The next sections describe analytical simplifications of the full RM to approximate Eq. (2.2) conditional *G*-values of [H_2O_2], [HCLO] and [Cl_2^-] for use in the MPM for the chloride/water/bromide system

2.2   Model Simplification

This section describes simple analytical functions for conditional *G*-values that could operate as an interface (Buck et al. 2013) between the Radiolysis Model (RM) and the Mixed Potential Model (MPM). Two approaches are given here. The first attempts to retain the effect of the reaction kinetics in a reduced set of reactions at externally fixed Cl^- and Br^- concentrations. The second keeps an even more reduced reaction set that can be solved analytically, but treats a few model parameters empirically to reproduce more closely the full model results. Both seem to give reasonable approximations to the full radiolysis model with 177 reactions (Appendix A).

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). Notice that Table 2-1 retains the key reactions (146 & 152) for Br^- to influence the generation of HCLO and Cl_2^-. The reaction numbers are those of the full RM (Appendix A) and rate constants are from Kelm and Bohnert (2004).

Table 2.1 Subset of reactions with k_r ($mol^n s^{-1}$) sufficient to represent full RM predictions.

	Reaction	k_r
64	$H_2O_2 + HClO \rightarrow HCl + H_2O + O_2$	1.7×10^5
66	$OH^- + Cl_2 \rightarrow HClO + Cl^-$	1.0×10^{10}
75	$Cl^- + ClOH^- \rightarrow Cl_2^- + OH^-$	9.0×10^4
76	$Cl^- + HClO \rightarrow Cl_2 + OH^-$	6.0×10^{-2}
81	$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^-$	7.0×10^9
146	$Br^- + Cl_2^- \rightarrow BrCl^- + Cl^-$	4.0×10^9
147	$BrCl^- + Cl^- \rightarrow Cl_2^- + Br^-$	1.1×10^2
152	$Br^- + Cl_2 \rightarrow BrCl_2^-$	6.0×10^9
153	$BrCl_2^- \rightarrow Cl_2 + Br^-$	9.0×10^3
154	$BrCl_2^- \rightarrow BrCl + Cl^-$	1.7×10^5
155	$BrCl + Cl^- \rightarrow BrCl_2^-$	1.0×10^6
156	$BrCl_2^- + Br^- \rightarrow Br_2Cl^- + Cl^-$	3.0×10^8
173	$BrCl^- + BrCl^- \rightarrow BrCl + Br^- + Cl^-$	1.2×10^9
176	$BrCl + Br^- \rightarrow Br_2Cl^-$	1.0×10^7
177	$Br_2Cl^- \rightarrow BrCl + Br^-$	5.56×10^2

As an example, hypochlorous acid (HClO) is one of the significant oxidants with an alpha radiolysis *G*-value of 1.07 molecules/100-eV at 5 M Cl^-. We find that G_{HClO} is effectively reduced (40%) for even small concentrations (10^{-4} M) of bromide (Br^-) with the mechanism of that effect preserved in the Table 2.1 reactions. Notice that reactions 66 and 76 (Table 2.1) generate an equilibrium concentration of Cl_2 with HClO. With even a small Br^- concentration,

reaction 152 competes for Cl_2 to push the equilibrium away from HClO (reaction 76) reducing both its concentration and effective generation rate. As a comparison between the full and reduced set radiolysis models, Figure 2.1 shows the steady-state HClO concentration for four Br^- concentrations from the radiation zone (< 35 mµ) out to 0.5 cm for a dose rate of 160 rad/s. The black curves of Figure 2-1use the full 177 reactions of Appendix A. The red curves use only 11 reactions of Table 2-1 − only reactions 75, 81, 146, 147 and 174 have significant effect on HClO.
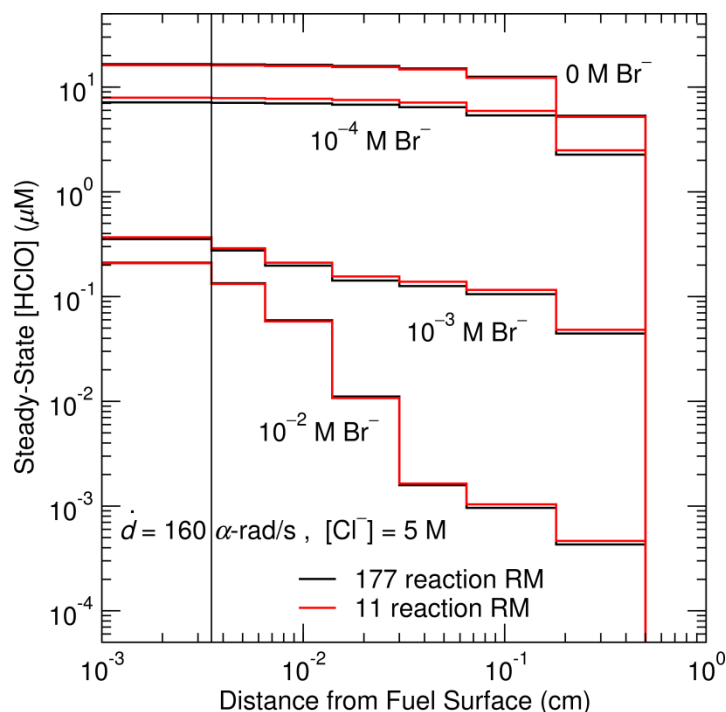
Figure 2.1 Comparison of Full RM (black) with reduced reaction set (only 11) of Table 2.1 (red).

In considering the primary reactions for [HCLO], [Cl_2^-] and [H_2O_2] given in Table 2.1 at a fixed pH and with fixed concentrations of Cl^- and Br^-, we find that even fewer reactions are required to approximate generation rates. Only the four reactions of Table 2-2 significantly influence the generation rates of HClO and H_2O_2.

Table 2.2 Subset of reactions with k_r ($mol^n s^{-1}$) for HClO & H_2O_2 analytical RMs.

	Reaction	k_r
64	$H_2O_2 + HClO \rightarrow HCl + H_2O + O_2$	1.7×10^5
66	$OH^- + Cl_2 \rightarrow HClO + Cl^-$	1.0×10^{10}
76	$Cl^- + HClO \rightarrow Cl_2 + OH^-$	6.0×10^{-2}
152	$Br^- + Cl_2 \rightarrow BrCl_2^-$	6.0×10^9

Additionally, if reactions are considered to 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. (2.1)], the steady-state rate equations in the radiation zone can be expressed as:

$$\tilde{D}_{\mathrm{H_2O_2}}[\mathrm{H_2O_2}] = \tilde{G}_{\mathrm{H_2O_2}} - k_{64}[\mathrm{H_2O_2}][\mathrm{HClO}] \tag{2.3}$$

$$\tilde{D}_{\mathrm{HClO}}[\mathrm{HClO}] = \tilde{G}_{\mathrm{HClO}} - k_{64}[\mathrm{H_2O_2}][\mathrm{HClO}] + k_{66}[\mathrm{OH^-}][\mathrm{Cl_2}] - k_{76}[\mathrm{Cl^-}][\mathrm{HClO}] \tag{2.4}$$

$$\tilde{D}_{\mathrm{Cl_2}}[\mathrm{Cl_2}] = -k_{66}[\mathrm{OH^-}][\mathrm{Cl_2}] + k_{76}[\mathrm{Cl^-}][\mathrm{HClO}] - k_{152}[\mathrm{Br^-}][\mathrm{Cl_2}] \tag{2.5}$$

The three equations (Eqs. 2.3 - 2.5) can be combined to eliminate all unknown species other than HClO to give:

$$A_2[\mathrm{HClO}]^2 + A_1[\mathrm{HClO}] + A_0 = 0 \tag{2.6}$$

where the coefficients (A_0, A_1 and A_2) are given according to:

$$A_2 = k_{64}\left[k_{76}[\mathrm{Cl^-}]\left(\tilde{D}_{\mathrm{Cl_2}} + k_{152}[\mathrm{Br^-}]\right) + \tilde{D}^*\tilde{D}_{\mathrm{HClO}}\right] \tag{2.7}$$

$$A_1 = \tilde{D}_{\mathrm{H_2O_2}}\left[k_{76}[\mathrm{Cl^-}]\left(\tilde{D}_{\mathrm{Cl_2}} + k_{152}[\mathrm{Br^-}]\right) + \tilde{D}^*\tilde{D}_{\mathrm{HClO}}\right] + \tilde{D}^*k_{64}\left(\tilde{G}_{\mathrm{H_2O_2}} - \tilde{G}_{\mathrm{HClO}}\right) \tag{2.8}$$

$$A_0 = -\tilde{D}^*\tilde{D}_{\mathrm{H_2O_2}}\tilde{G}_{\mathrm{HClO}} \tag{2.9}$$

with $\tilde{D}^*$ defined as

$$\tilde{D}^* \equiv \tilde{D}_{\mathrm{Cl_2}} + k_{66}[\mathrm{OH^-}] + k_{152}[\mathrm{Br^-}]. \tag{2.10}$$

The quadratic Eq. (2.6) is easily solved to obtain [HClO] for the conditional G-value of

$$G^C_{\mathrm{HClO}} \equiv \tilde{D}_{\mathrm{HClO}}[\mathrm{HClO}]/\dot{d} \tag{2.11}$$

and to solve Eq. (2.3) for [H$_2$O$_2$] to give the conditional G-value of

$$G^C_{\mathrm{H_2O_2}} \equiv \tilde{D}_{\mathrm{H_2O_2}}[\mathrm{H_2O_2}]/\dot{d} \tag{2.12}$$

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 with rate constants given at 25 °C.

Table 2.3 G-values for α-radiolysis (taken from Kelm and Bohnert, 2004; Elliot and McCracken, 1990)

Species	G-values at 5 MeV (molecules/100-eV)	
	Water	5 M NaCl
H_2O_2	0.98	0.23
$\cdot HO_2$	0.22	0.05
H_2	1.30	1.52
$\cdot H$	0.21	0.26
e^-	0.06	0.06
$\cdot OH$	0.25	0.06
OH^-	0	1.01
$H+$	0.06	0
Cl^-	0	-1.62
Cl_2^-	0	0
$ClOH^-$	0	0.55
$HClO$	0	1.07
H_2O	-2.65	-3.25

For the species that appear in the reduced reaction sets the values for the diffusion constants were all taken to be 1.5×10^{-5} cm^2/s other than H_2O_2 which was 1.9×10^{-5} cm^2/s.

Figures 2.2 and 2.3 compare the full RM (black) conditional G-values with the derived analytical expressions at 160 rad/s. The full RM was run out to steady-state in 10^6 seconds with the LBNL ODE solvers of references (Brown and Hindmarsh, 1989; Hindmarsh 1983), while the analytical RM (violet) simply involved evaluating Eqs. (2.6 − 2.12) with the FORTRAN programs of Appendix B. The red curves are the steady-state solution of the kinetics equation for the reduced reaction set referred to in Figure 2.1 using the actual parameters of the full RM. For the analytical RM (violet) the 64 and 152 are adjusted empirically for better agreement with the full model. Also, because of the approximation of neglecting reaction kinetics outside the radiation zone, an empirical adjustment is also allowed for diffusion constants. The adjustments are constrained to match values equal to or preferentially greater than those predicted by full RM. While the analytical model is shown to perform less well for the H_2O_2 conditional G-values (Figure 2.3), it is remarkable that the main trend is reproduced with a single reaction 64 of Table 2.2. Seven other reactions of Table 2.1 that include bromine containing species are responsible for the rise and fall of the peak structure seen in the kinetics based models (black & red curves) of Figure 2.3.
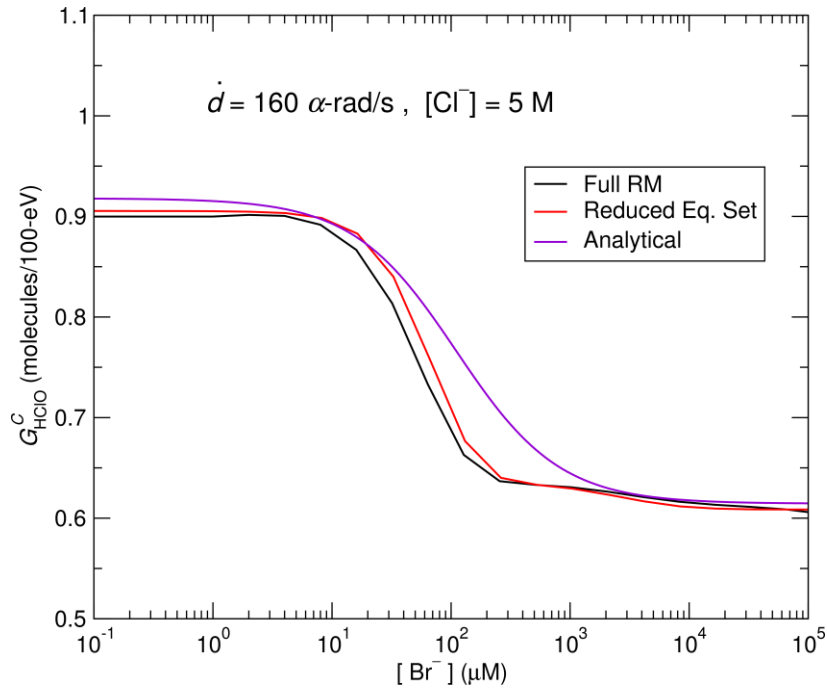
Figure 2.2 Comparison of full RM (black) HClO conditional *G*-values with reduced reaction set of Table 2-2 (red) and simplified analytical model (violet).

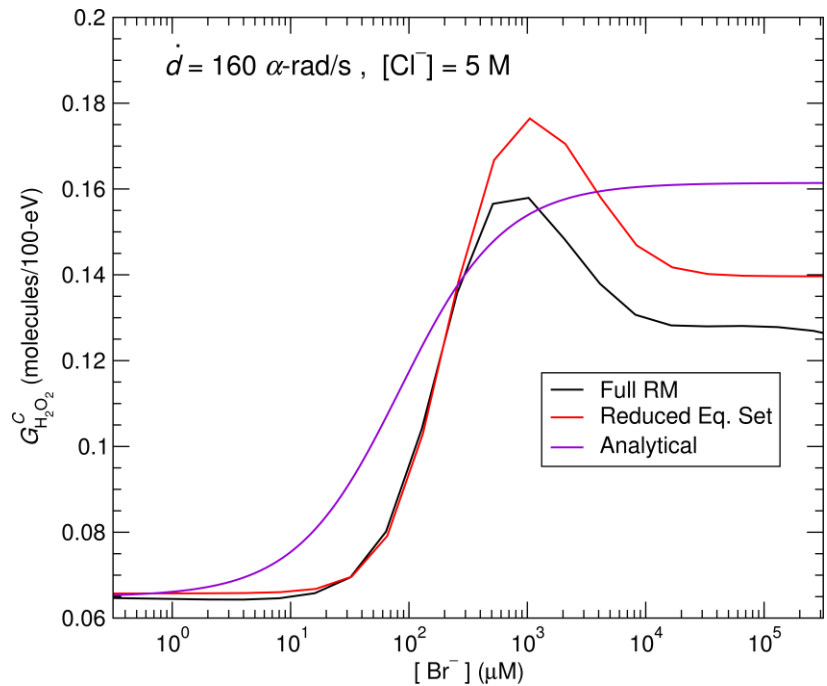Figure 2.3. Comparison of Full RM (black) H_2O_2 conditional *G*-values with reduced reaction set of Table 2-2 (red) and simplified analytical model (violet).

As in the case of HClO, we find that only the four reactions of Table 2.4 are needed to approximate the Cl_2^- generation rate at a fixed pH and with fixed concentrations of Cl^- and Br^-. The specific role of Br^- can be seen in the equilibrium of reactions 146 and 147 which act like as a sink for Cl_2^-. Even though the radiolytic G-value for Cl_2^- is zero (Table 2-2), it is still produced indirectly through reactions with radiolytically generated $ClOH^-$ (reaction 75). Therefore the conditional G-value as defined in Eq. (2.2) is nonzero. Additionally, the Cl_2^- induced oxidation rate of UO_2, as indicated in Kelm and Bohnert (2004), can be 10^7–10^8 times greater than with HClO or H_2O_2 and is likely to dominate.

Table 2.4. Subset of reactions with k_r ($mol^n s^{-1}$) for Cl_2^- analytical RM.

	Reaction	k_r
75	$Cl^- + ClOH^- \rightarrow Cl_2^- + OH^-$	9.0×10^4
81	$Cl_2^- + Cl_2^- \rightarrow Cl_3^- + Cl^-$	7.0×10^9
146	$Br^- + Cl_2^- \rightarrow BrCl^- + Cl^-$	4.0×10^9
147	$BrCl^- + Cl^- \rightarrow Cl_2^- + Br^-$	1.1×10^2

Making the same approximations as in Eqs. (2.3 - 2.5) gives three steady-state rate equations in the radiation zone that can be expressed as:

$$\tilde{D}_{Cl_2^-}[Cl_2^-] = k_{75}[Cl^-][ClOH^-] - k_{146}[Br^-][Cl_2^-] + k_{147}[BrCl^-][Cl^-] - 2k_{81}[Cl_2^-]^2 \tag{2.13}$$

$$\tilde{D}_{ClOH^-}[ClOH^-] = \tilde{G}_{ClOH^-} - k_{75}[Cl^-][ClOH^-] \tag{2.14}$$

$$\tilde{D}_{BrCl^-}[BrCl^-] = k_{146}[Br^-][Cl_2^-] - k_{147}[BrCl^-][Cl^-] \tag{2.15}$$

The three rate equations (Eqs. 2.13 – 2.15) at steady-state can be combined to eliminate all unknown species other than Cl_2^- according to

$$2k_{81}[Cl_2^-]^2 + \left(\tilde{D}_{Cl_2^-} + \frac{\tilde{D}_{BrCl^-} - k_{146}[Br^-]}{\tilde{D}_{BrCl^-} + k_{147}[Cl^-]} \right)[Cl_2^-] - \frac{k_{75}[Cl^-]\tilde{G}_{ClOH^-}}{\tilde{D}_{ClOH^-} + k_{75}[Cl^-]} = 0 \tag{2.16}$$

where $[Cl_2^-]$ is easily solved to obtain the conditional G-value (G^C) of

$$G^C_{Cl_2^-} \equiv \tilde{D}_{Cl_2^-}[Cl_2^-]/\dot{d} \tag{17}$$

Figure 2.4 shows a comparison of the analytical model (violet) of Eqs. (2.16 – 2.17) with the kinetics based Full RM (black) and reduced set model (red). While the maximum G^C for very low Br^- concentrations at 160 rad/s is only 0.019 molecules/100eV, the UO_2 oxidizing potential is likely to be significant. Additionally, the trend in G^C is to increase for lower dose rates to a maximum of 0.53 molecules/100eV for the full RM and 0.55 molecules/100-eV for the analytical model – of course the Cl_2^- generation rate goes to zero at zero dose-rate.
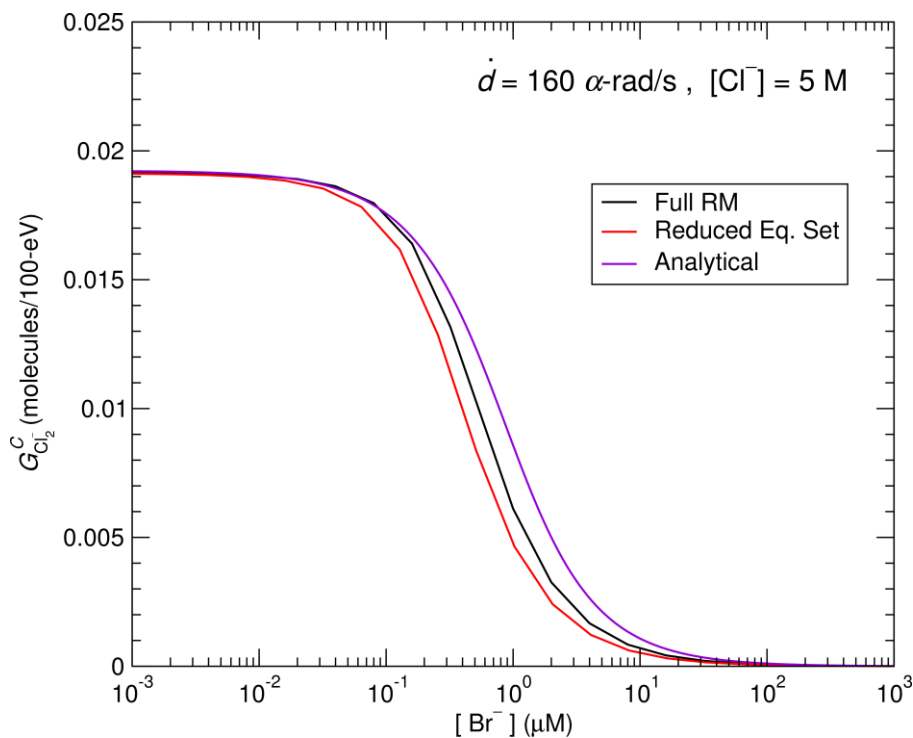
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Figure 2.4. Comparison of full RM (black) Cl_2^- conditional G-values with reduced reaction set of Table 2.4 with the addition of reaction 173 (red) and simplified analytical model (violet).

It is interesting that at 5 M [Cl$^-$] the reactions that describe pure water radiolysis (Appendix A, 1-38) and the their related radicals play practically no role in determining the generation rates of Cl_2^-, HClO and H_2O_2. Additionally, it is striking that the presence of even micro-molar concentrations of Br$^-$ can have such a strong effect.

There is a great deal of interest in the rates of chlorine reactions in atmospheric sciences and approved rate constants are available in the literature for many relevant reactions. For instance, the chlorine hydrolysis reaction:

$$Cl_2(aq) + OH- \rightarrow HOCl + Cl^-$$
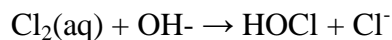
has a rate reported by Gershenzon et al. (2002) that is two orders of magnitude faster than the one used in this study and commonly reported. However, there is less information available for bromine reactions which may have significant impact with respect to fuel disposal chemistry.

2.3 Future Work

While the results of this work show that very simple expressions can be useful to approximate radiolysis for the chloride/water/bromide system, future work will attempt to formulate a reduced model that accounts for a variation of [Cl$^-$] from 5 M and at least partially accounts for reaction kinetics outside the radiation zone. At some point it may be advantageous to represent a full RM

with in 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 full set of reactions. Validation of key components of these models with controlled experiments remains an important task to determine if low Br^- concentrations provide a sustained protective H_2 effect under high LET radiation for used nuclear fuel.

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APPENDIX A:
Reactions and rate constants (mol^n/s) for the full RM [from M. Kelm, E. Bohnert (2004)]

No.	Reaction	rate constant
1	H+ + OH- = H2O	1.400E+11
2	H2O = H+ + OH-	1.403E-03
3	H2O2 = H+ + HO2-	1.119E-01
4	H+ + HO2- = H2O2	5.000E+10
5	H2O2 + OH- = HO2- + H2O	1.300E+10
6	HO2- + H2O = H2O2 + OH-	5.820E+07
7	E- + H2O = H + OH-	1.900E+01
8	H + OH- = E- + H2O	2.200E+07
9	H = E- + H+	3.906E+00
10	E- + H+ = H	2.300E+10
11	OH + OH- = O- + H2O	1.300E+10
12	O- + H2O = OH + OH-	1.035E+08
13	OH = O- + H+	1.259E-01
14	O- + H+ = OH	1.000E+11
15	HO2 = O2- + H+	1.346E+06
16	O2- + H+ = HO2	5.000E+10
17	HO2 + OH- = O2- + H2O	5.000E+10
18	O2- + H2O = HO2 + OH-	1.862E+01
19	E- + H2O2 = OH + OH-	1.100E+10
20	E- + O2- + H2O = HO2- + OH-	1.300E+10
21	E- + HO2 = HO2-	2.000E+10
22	E- + O2 = O2-	1.900E+10
23	H + H2O = H2 + OH	1.100E+01
24	H + H = H2	7.800E+09
25	H + OH = H2O	7.000E+09
26	H + H2O2 = OH + H2O	9.000E+07
27	H + O2 = HO2	2.100E+10
28	H + HO2 = H2O2	1.800E+10
29	H + O2- = HO2-	1.800E+10
30	OH + OH = H2O2	3.600E+09
31	OH + HO2 = H2O + O2	6.000E+09
32	OH + O2- = OH- + O2	8.200E+09
33	OH + H2 = H + H2O	4.300E+07
34	OH + H2O2 = HO2 + H2O	2.700E+07
35	HO2 + O2- = HO2- + O2	8.000E+07
36	H2O2 = OH + OH	2.250E-07
37	OH + HO2- = HO2 + OH-	7.500E+09
38	HO2 + HO2 = H2O2 + O2	7.000E+05
39	OH + Cl- = ClOH-	4.300E+09
40	OH + HClO = ClO + H2O	9.000E+09
41	OH + ClO2- = ClO2 + H2O - H+	6.300E+09
42	E- + Cl = Cl- + H2O	1.000E+10
43	E- + Cl2- = Cl- + Cl- + H2O	1.000E+10
44	E- + ClOH- = Cl- + OH- + H2O	1.000E+10
45	E- + HClO = ClOH-	5.300E+10
46	E- + Cl2 = Cl2-	1.000E+10
47	E- + Cl3- = Cl2- + Cl-	1.000E+10
48	E- + ClO2- = ClO + OH- - H+	4.500E+10
49	E- + ClO3- = ClO2 + OH- - H+	0.000E+00
50	H + Cl = Cl- + H+	1.000E+10
51	H + Cl2- = Cl- + Cl- + H+	8.000E+09
52	H + ClOH- = Cl- + H2O	1.000E+10

53	H + Cl2 = Cl2- + H+	7.000E+09
54	H + HClO = ClOH- + H+	1.000E+10
55	H + Cl3- = Cl2- + Cl- + H+	1.000E+10
56	HO2 + Cl2- = Cl- + HCl + O2	4.000E+09
57	HCl = Cl- + H+	5.000E+05
58	HO2 + Cl2 = Cl2- + H+ + O2	1.000E+09
59	HO2 + Cl3- = Cl2- + HCl + O2	1.000E+09
60	O2- + Cl2- = Cl- + Cl- + O2	1.200E+10
61	O2- + HClO = ClOH- + O2	7.500E+06
62	H2O2 + Cl2- = HCl + HCl + O2-	1.400E+05
63	H2O2 + Cl2 = HO2 + Cl2- + H+	1.900E+02
64	H2O2 + HClO = HCl + H2O + O2	1.700E+05
65	OH- + Cl2- = ClOH- + Cl-	7.300E+06
66	OH- + Cl2 = HClO + Cl-	1.000E+10
67	H+ + ClOH- = Cl + H2O	2.100E+10
68	H2O + Cl2O2 = HClO + ClO2- + H+	2.000E+02
69	H2O + Cl2O2 = O2 + HClO + HCl	0.000E+00
70	H2O + Cl2O = HClO + HClO	1.000E+02
71	H2O + Cl2O4 = ClO2- + ClO3- + H+ + H+	1.000E+02
72	H2O + Cl2O4 = HClO + HCl + O4	1.000E+02
73	O4 = O2 + O2	1.000E+05
74	Cl- + Cl = Cl2-	2.100E+10
75	Cl- + ClOH- = Cl2- + OH-	9.000E+04
76	Cl- + HClO = Cl2 + OH-	6.000E-02
77	Cl- + Cl2 = Cl3-	1.000E+04
78	Cl- + H+ = HCl (assuming pKa = -3.9)	6.295E+01
79	ClOH- = OH + Cl-	6.100E+09
80	Cl2- = Cl + Cl-	1.100E+05
81	Cl2- + Cl2- = Cl3- + Cl-	7.000E+09
82	Cl3- = Cl2 + Cl-	5.000E+04
83	ClO + ClO = Cl2O2	1.500E+10
84	ClO2 + ClO2 = Cl2O4	1.000E+02
85	Cl2O2 + ClO2- = ClO3- + Cl2O	1.000E+02
86	E- + ClO3- = ClR--	1.600E+05
87	ClR-- + OH = OH- + ClO3-	1.000E+10
88	ClR-- + O- = OH- + ClO3- - H+	1.200E+09
89	HClO + HClO = Cl- + ClO2- + H+ + H+	6.000E-09
90	ClO2- + HClO = Cl- + ClO3- + H+	9.000E-07
91	HClO + HClO = O2 + HCl + HCl	3.000E-10
92	HClO4 = H+ + ClO4- (a guess)	1.000E+10
93	H+ + ClO4- = HClO4 (assuming pKa = -7)	1.000E+03
94	Br- + OH = BrOH-	1.100E+10
95	Br- + Br = Br2-	1.000E+10
96	Br- + H = HBr-	0.000E+00
97	Br- + O- = Br + OH- - H+	2.200E+08
98	Br + BrO- = Br- + BrO	4.100E+09
99	Br = BrOH- + H+ - H2O	1.400E+00
100	Br + HO2 = H+ + Br- + O2	1.600E+08
101	Br + OH- = BrOH-	1.300E+10
102	Br + H2O2 = Br- + O2- + H+ + H+	2.500E+09
103	Br2- = Br + Br-	1.900E+04
104	Br2- + Br2- = Br- + Br3-	3.400E+09
105	Br2- + BrO2- = BrO2 + Br- + Br-	8.000E+07
106	Br2- + BrO- = BrO + Br- + Br-	6.200E+07
107	Br2- + ClO2- = Br- + ClO2 + Br-	2.000E+07
108	Br2- + H = H+ + Br- + Br-	1.400E+10
109	Br2- + HO2 = H+ + Br- + Br- + O2	1.000E+08
110	Br2- + O2- = Br- + Br- + O2	1.700E+08
111	Br2- + E- = Br- + Br-	1.100E+10
112	Br2- + H2O2 = Br- + Br- + HO2 + H+	1.900E+06
113	BrO- + OH = BrO + OH-	4.200E+09
114	BrO- + O- = BrO + OH- - H+	3.500E+09
115	BrO- + E- = Br- + O-	1.500E+10
116	BrO2- + OH = BrO2 + OH-	2.300E+09
117	BrO2- + BrO = BrO- + BrO2	4.000E+08
118	BrO2- + O- = BrO2 + OH- - H+	1.600E+09

```
119    BrO2- + E- = BrO + H2O - H+ - H+                1.100E+10
120    BrO3- + OH = BrO3 + OH-                          0.000E+00
121    BrO3- + H = BrO2 + OH-                           2.000E+07
122    BrO3- + O- = BrO3 + OH- - H+                     0.000E+00
123    BrO3- + E- = BrO2 + OH- + OH- - H2O              3.400E+09
124    Br2 + H = Br2- + H+                              1.000E+10
125    Br2 + HO2 = H+ + O2 + Br2-                       1.300E+08
126    Br2 + O2- = O2 + Br2-                            5.000E+09
127    Br2 + Br- = Br3-                                 9.600E+08
128    Br2 + E- = Br2-                                  5.300E+10
129    HOBr + OH = BrO + H2O                            2.000E+09
130    HOBr + O2- = O2 + Br + OH-                       3.500E+09
131    BrO2 + OH = BrO3- + H+                           2.000E+09
132    BrO2 + BrO2 = BrO3- + BrO2- + H+ + H+ - H2O      4.000E+07
133    BrO2 + ClO2- = BrO2- + ClO2                      3.600E+07
134    Br3- + H = H+ + Br2- + Br-                       1.200E+10
135    Br3- + O2- = O2 + Br2- + Br-                     1.500E+09
136    Br3- = Br2 + Br-                                 5.500E+07
137    Br3- + E- = Br2- + Br-                           2.700E+10
138    BrOH- = Br- + OH                                 3.000E+07
139    BrOH- = Br + OH-                                 4.200E+06
140    BrOH- + H+ = Br + H2O                            1.300E+10
141    BrOH- + Br- = Br2- + OH-                         1.900E+08
142    BrO + BrO = BrO- + BrO2- + H+ + H+ - H2O         2.800E+09
143    BrO + BrO2- = BrO- + BrO2                        4.000E+08
144    HOBr = H+ + BrO-                                 1.580E+01
145    BrO- + H+ = HOBr                                 1.000E+10
146    Br- + Cl2- = BrCl- + Cl-                         4.000E+09
147    BrCl- + Cl- = Cl2- + Br-                         1.100E+02
148    BrCl- = Cl- + Br                                 8.500E+07
149    Br + Cl- = BrCl-                                 1.000E+10
150    BrCl- + Br- = Br2- + Cl-                         8.000E+09
151    Br2- + Cl- = BrCl- + Br-                         4.300E+06
152    Br- + Cl2 = BrCl2-                               6.000E+09
153    BrCl2- = Cl2 + Br-                               9.000E+03
154    BrCl2- = BrCl + Cl-                              1.700E+05
155    BrCl + Cl- = BrCl2-                              1.000E+06
156    BrCl2- + Br- = Br2Cl- + Cl-                      3.000E+08
157    BrCl = HOBr + H+ + Cl- - H2O                     3.000E+06
158    HOBr + Cl- = BrCl + H2O - H+                     2.300E+10
159    BrCl = HClO + H+ + Br- - H2O                     1.150E-03
160    HClO + Br- = BrCl + H2O - H+                     1.320E+06
161    Br- + HOBr = Br2 + H2O - H+                      3.000E+09
162    Br2 = Br- + HOBr + H+ - H2O                      2.000E+00
163    Br- + HBrO2 = HOBr + HOBr - H+                   3.000E+06
164    HOBr + HOBr = Br- + HBrO2 + H+                   2.000E-05
165    Br- + BrO3- = HOBr + BrO2- - H+                  2.500E-07
166    HOBr + HBrO2 = Br- + BrO3- + H+ + H+             3.200E+00
167    HBrO2 + HBrO2 = HOBr + BrO3- + H+                3.000E+03
168    HOBr + BrO3- = HBrO2 + HBrO2 - H+                1.000E-08
169    HBrO2 + BrO3- = BrO2 + BrO2 + H2O - H+           4.200E+01
170    BrO2 + BrO2 = HBrO2 + BrO3- + H+ - H2O           4.200E+07
171    HBrO2 = BrO2- + H+                               5.000E+05
172    BrO2- + H+ = HBrO2                               1.350E+09
173    BrCl- + BrCl- = BrCl + Br- + Cl-                 1.200E+09
174    Br2 + Cl- = Br2Cl-                               1.000E+07
175    Br2Cl- = Br2 + Cl-                               7.690E+06
176    BrCl + Br- = Br2Cl-                              1.000E+07
177    Br2Cl- = BrCl + Br-                              5.560E+02
```

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APPENDIX B:
FORTRAN Listing for Analytical RM for Cl_2^-

```
      function gClO2m(ddotR,Brm,OHm)
      implicit real*8 (a-h,o-z)

C   Physical constants
      Av    =   6.0221415d23    !  mole^{-1}
      echrg =   1.602176462d-19 !  J/eV


      H2O = 1000.d0/18.d0
c     OHm =  1.005d-7
      Clm =  5.0d0
c     Brm =  1.d-4

C     ddotR = 160.   ! rad/s
      ddot = ddotR/(Av * echrg * 100.d0 * 100.d0) ! Unit conversion

      xR = 35.e-4
      xB  = 0.5

      DH2O2  =  1.900e-5  /3. /(xR*xB)
      Diff   =  1.500e-5  *65./(xR*xB)
C            He      gamma   10 MeV-p   2 MeV-p
      gHClO  =  1.07*ddot !   0.66 ! 0.57  !   0.20   !
      gH2O2  =  0.27*ddot !   0.70 ! 0.74  !   0.76   !
      gClOHm =  0.55*ddot !   0.70 ! 0.74  !   0.76   !

      dk75  =   9.d4
      dk146 =   4.d9  *7.
      dk147 =   1.1d2
      dk81  =   7.d9   /5.21


      AA = 2.d0*dk81
      BB = Diff*(1.d0+dk146*Brm/(Diff+dk147*Clm))
      CC = -dk75*Clm*gClOHm/(Diff+dk75*Clm)

      ClO2m = (-BB+dsqrt(BB**2-4.d0*AA*CC))/(2.d0*AA)

      gClO2m = Diff*ClO2m/(ddot)


      STOP
      end
```

FORTRAN Listing for Analytical RM for HClO

```
      function gHClO(ddotR,Brm,OHm)

C   Physical constants
      Av    =   6.0221415d23    !  mole^{-1}
      echrg =   1.602176462d-19 !  J/eV


      H2O = 1000.d0/18.d0
c     OHm =  1.005d-7
      Clm =  5.0d0
c     Brm =  1.d-4
```

```
c      ddotR = 160.    ! rad/s
       ddot = ddotR/(Av * echrg * 100.d0 * 100.d0) ! Unit conversion

       xR = 35.e-4
       xB  = 0.5

       DH2O2  = 1.900e-5/3./(xR*xB)
       Diff   = 1.500e-5*65./(xR*xB)
C              He        gamma   10 MeV-p   2 MeV-p
       gHClO =   1.07*ddot !    0.66  !  0.57   !   0.20    !
       gH2O2 =   0.27*ddot !    0.70  !  0.74   !   0.76    !

       dk64   =   1.70d5 / 10. ! *0
       dk76   =   6.d-2  !*0
       dk66   =   1.d10 !*100.  !*0
       dk152  =   6.d9  /1d3  !*0

       A =  dk76*Clm
       B =  dk66*OHm
       C =  dk152*Brm


       AA = dk64*(Diff*(C+B+Diff) + A*(C+Diff))
       BB = DH2O2*(Diff*(C+B+Diff) + A*(C+Diff)) -
      1  (C+B+Diff)*dk64*(gHClO - gH2O2)
       CC = - DH2O2*gHClO*(C+B+Diff)

       HClO = (-BB+dsqrt(BB**2-4.d0*AA*CC))/(2*AA)


       gHClO = Diff*HClO/(ddot)

       enddo

       STOP
       end
```

FORTRAN Listing for Analytical RM for H_2O_2

```
       function gH2O2(ddotR,Brm,OHm)

C   Physical constants
       Av   =   6.0221415d23    !  mole^{-1}
       echrg =   1.602176462d-19 !  J/eV


       H2O = 1000.d0/18.d0
c      OHm =  1.005d-7
       Clm =  5.0d0
c      Brm =  1.d-4

c       ddotR = 160.    ! rad/s
       ddot = ddotR/(Av * echrg * 100.d0 * 100.d0) ! Unit conversion

       xR = 35.e-4
       xB  = 0.5

       DH2O2  =  1.900e-5/(xR*xB)
       Diff   =  1.500e-5*8.3/(xR*xB)
C              He        gamma   10 MeV-p   2 MeV-p
       gHClO =   1.07*ddot !    0.66  !  0.57   !   0.20    !
       gH2O2 =   0.27*ddot !    0.70  !  0.74   !   0.76    !

       dk64   =   1.70d5 / 10. ! *0
       dk76   =   6.d-2  !*0
```

```
  dk66  =   1.d10 !*100.  !*0
  dk152 =   6.d9  /1d3  !*0

  A =  dk76*Clm
  B =  dk66*OHm
  C =  dk152*Brm


  AA = dk64*(Diff*(C+B+Diff) + A*(C+Diff))
  BB = DH2O2*(Diff*(C+B+Diff) + A*(C+Diff)) -
1  (C+B+Diff)*dk64*(gHClO - gH2O2)
  CC = - DH2O2*gHClO*(C+B+Diff)

  HClO = (-BB+dsqrt(BB**2-4.d0*AA*CC))/(2*AA)

  H2O2 = gH2O2/(DH2O2 + dk64*HClO)

  gH2O2 = DH2O2*H2O2/(ddot)

  enddo

  STOP
  end
```