USED FUEL DISPOSITION CAMPAIGN

Effect of Iron on Radiolytic Hydrogen Peroxide Generation

Fuel Cycle Research & Development

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Used Fuel Disposition Campaign

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EXECUTIVE SUMMARY

This report fulfills the M4FT-16PN080303072 to report on continuing the model integration of the PNNL Radiolysis Model and the ANL Mixed Potential Model for Crystalline Disposal In this work we demonstrate and approximate possible effects of iron from corrosion of surrounding structures on hydrogen peroxide generation. We find that even small concentrations of Fe(II) reduces the steady-state H_2O_2 concentration.

Additionally, suggestions are offered on what further data or measurements would be required for model verification and applicability. The Listings of the reactions considered in this report are given in Appendix.

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 iron chemistry and its applicability to model predictions.

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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

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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. 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]

This report gives the details on the effect of iron chemistry on H_2O_2 decomposition under radiolytic condition at the surface of used nuclear fuel under repository conditions. Additionally, suggestions are offered on what further data or measurements would be required for model verification and applicability. The Listings of the reactions considered in this report are given in Appendix.

2. RADIOLYSIS MODEL WITH IRON REACTIONS

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 [Shoesmith, 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 further step in that direction, this report presents the effect of small concentration of [Fe(II)] on H_2O_2 concentration and explains the mechanism of that effect.

2.1 Effect of Iron on H_2O_2 in Radiation Zone

To better understand how integration of the PNNL Radiolysis Model (RM) can be integrated with the ANL Mixed Potential Fuel Degradation Model in the environment of iron containing species we consider iron reactions in the RM. Since our goal is to consistently account for the chemistry in both models we focus on the mechanism and effect of iron on prediction H_2O_2 decomposition affecting the UO_2 degradation rate.

The main approach is as follows.

- Identify the significant reactions that govern the chemical and radiolytic decomposition of H_2O_2 in water with known dose rate and concentrations of iron species (De Laat, et al., 1999 and Bouniol, 2010).
- Determine if iron chemistry is well understood enough to accurately represent its effects on decomposition of H_2O_2 in the RM.

Progress on Bullet one (above) is summarized here and Bullet two is left as an open question.

Figure 1 of reference (De Laat, et al., 1999) was reproduced by our current kinetics model as a check of the numerical solution and our understanding of the model definition. Assuming 38 water reactions from previous radiolysis model work (Wittman and Buck 2012) and approximately 60 additional iron containing reactions of Refs. (De Laat, et al., 1999 and Bouniol, 2010) we initially find that approximately 60 total reactions are sufficient to reproduce the H_2O_2 concentration.

Figure 1 shows both the radiolytic and iron concentration effects on the H_2O_2 concentration. Without dose, the initial 0.01 molar H_2O_2 concentration is initially catalytically decomposed at a rate of 160 times faster than thermal decomposition (25°) alone. Additionally, at a dose rate of 25 krad/s the steady-state H_2O_2 concentration is about 160 times lower with an initial 1 μM concentration of Fe(II) that is converted to 1 μM of Fe(II). For these comparisons pH is fixed at 7.0 and no constraints were put on oxygen and hydrogen concentrations. The effect of those constraints with diffusion out of the alpha radiation zone is currently being explored.
Further work is in progress to confirm the applicability of the reaction kinetics for pH and iron concentrations required by Mixed Potential UO_2 Fuel Degradation Model. Also, further work is in progress to confirm the applicability of the reaction kinetics for pH and iron concentrations required by Mixed Potential UO_2 Fuel Degradation Model.

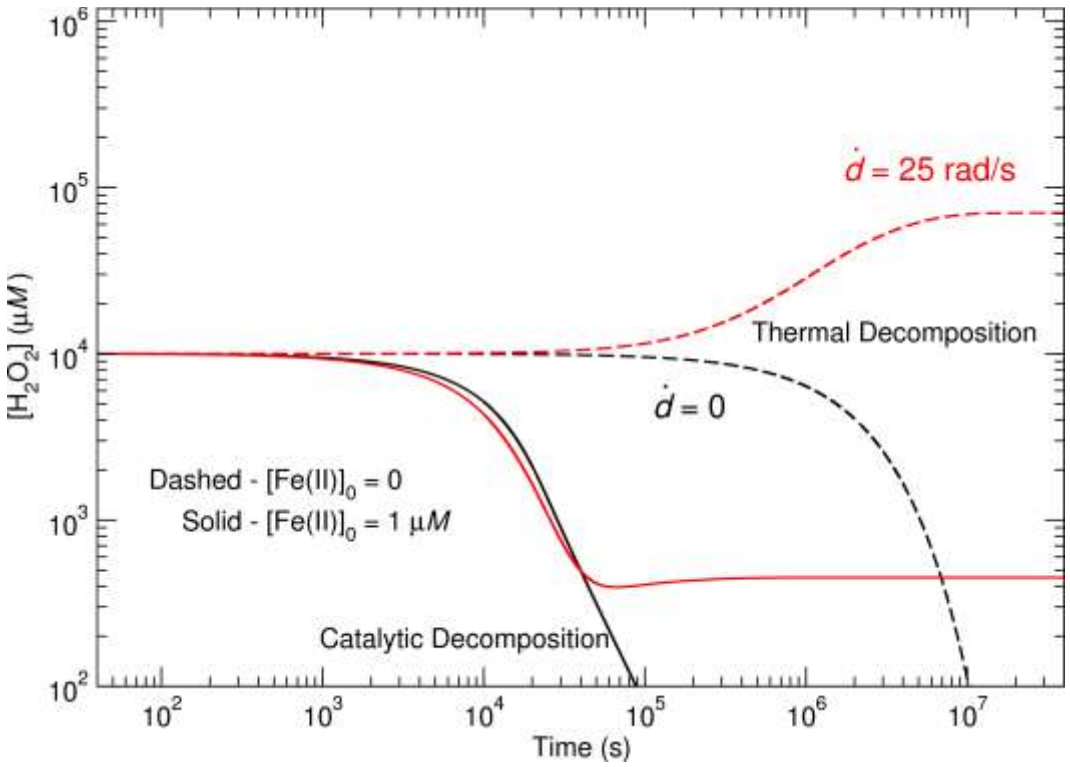

Figure 2-1. Effect of an initial micro-molar concentration of Fe(II) on H_2O_2 generation. Comparison of with and without dose rate (red and black). Comparison of with and without Fe(II) (solid and dashed curves).

Table 2-1 was found to be a sufficient set of reactions to describe the main features of Figure 1 and contains the mechanism that H_2O_2 decomposes or shifts its steady-state concentration. The main process responsible for H_2O_2 decomposition is Fenton's reaction (51 of Table 2-1) (Fenton, H.J.H., (1894) where Fe(II) attains a secular equilibrium with a lower concentration of Fe(III). The effective equilibrium arises because ·OH radicals react with water forming O_2^- which reduces Fe(III) back to Fe(II) (58 and 60 of Table 2-1).

Table 2-1. Subset of reactions sufficient to represent the primary mechanisms for H_2O_2 generation in the full RM (Appendix A) [Iron from Ref. (De Laat, et al., 1999)].

	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	$e^- + H_2O_2 \rightarrow \cdot OH + OH^-$	1.1×10^{10}
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}
41	$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^+ + 2H^+$	1×10^{5}
42	$Fe(OH)_2^+ + 2H^+ \rightarrow Fe^{3+} + 2H_2O$	1.3×10^{11}
51	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^-$	63.0
52	$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$	3.2×10^{8}
58	$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2$	5×10^{7}
60	$Fe(OH)_2^+ + O_2^- \rightarrow Fe^{2+} + O_2 + 2OH^-$	5×10^{7}

The mechanism can be understood by focusing on a few species during H_2O_2 decomposition (Figure 2-2). Figure 2-2 shows that without the reducing reactions (58 and 60 of Table 2-1) the Fe(II) quickly oxidized to Fe(III) resulting in little or no decomposition of H_2O_2. Depending on solution pH the Fe(III) will remain or precipitate from solution. The solid lines show that the iron reducing reaction create an effective fixed concentration of Fe(II) which enables decomposition – while both Fe(II) and Fe(III) participate in reactions, the Fe(II)/Fe(III) equilibrium effective acts like a catalyst. Therefore the decomposition mechanism requires the Fe(III) reduction reactions to preserve even a small concentration of Fe(II). It's this last point that make the inclusion of this mechanism unclear for the RM because if Fe(III) drops out of solution at a rate faster than it can be reduced back to Fe(II) the RM will non-conservatively predict lower than actual H_2O_2 production rates. The current fuel degradation model assumption is that Fe(III) precipitates on formation without subsequent reduction to Fe(II). While Figure 2-2 shows that the concentration of Fe(III) is almost 10X less than Fe(II), the solubility of Fe(III) and its precipitation rate is an open question for conditions (pH, etc.) appropriate for UO_2 degradation.

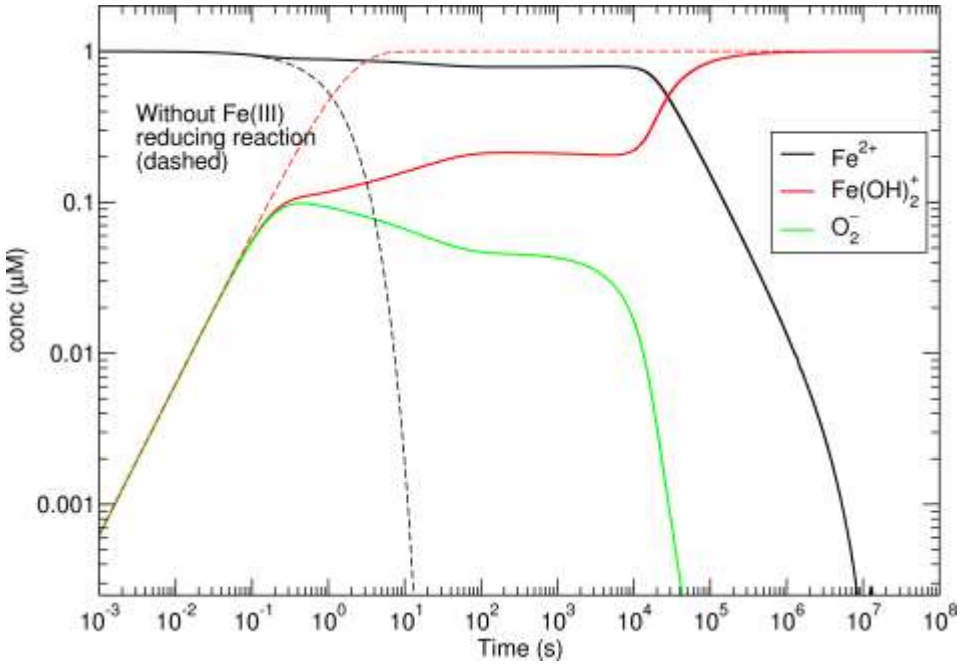

Figure 2-2. Concentrations of Fe(II), Fe(III) and O_2^- during H_2O_2 decomposition.

2.2 Future work

While this work identifies for mechanism for an effective Fe(II)/Fe(III) equilibrium to catalytically reduce H_2O_2 production rates, it cannot guarantee that the mechanism operates under the repository conditions of spent nuclear fuel. Future work that would measure Fe(III) solubility and precipitation rates, ideally under radiolytic conditions, are necessary for a confident inclusion of iron reaction in the RM.

3. REFERENCES

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APPENDIX A:
Reaction Listing for Full RM

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Equilibrium constants:
H2O  <--> H+  +  OH- : RKeq(2) = 10^(-13.999)
H2O2 <--> H+  +  HO2-: RKeq(3) = 10^(-11.65)
OH   <--> H+  +  O-  : RKeq(4) = 10^(-11.9)
HO2  <--> H+  +  O2- : RKeq(5) = 10^(- 4.57)
H    <--> H+  +  E-  : RKeq(6) = 10^(- 9.77)
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	Reactions	Rate constans (M^{-n}/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	
38	HO2 + HO2 = H2O2 + O2	7.0d5	
39	Fe+3 + H2O = FeOH+2 + H+	1d5	
40	FeOH+2 + H+ = Fe+3 + H2O	0.d0	
41	Fe+3 + H2O + H2O = Fe(OH)2+ + H+ + H+	1d5	
42	Fe(OH)2+ + H+ + H+ = Fe+3 + H2O + H2O	0.d0	
43	Fe+3 + Fe+3 + H2O + H2O = Fe2(OH)2+4 + H+ + H+		1d5
44	Fe2(OH)2+4 + H+ + H+ = Fe+3 + Fe+3 + H2O + H2O		0.d0
45	Fe+3 + H2O2 = Fe(HO2)+2 + H+		1d5
46	Fe(HO2)+2 + H+ = Fe+3 + H2O2		0.d0
47	FeOH+2 + H2O2 = Fe(OH)(HO2)+ + H+		1d5
48	Fe(OH)(HO2)+ + H+ = FeOH+2 + H2O2		0.d0
49	Fe(HO2)+2 = Fe+2 + HO2		2.7e-3
50	Fe(OH)(HO2)+ = Fe+2 + HO2 + OH-		2.7e-3
51	Fe+2 + H2O2 = Fe+3 + OH + OH-		63.0

52	Fe+2 + OH = Fe+3 + OH-	3.2e8
53	Fe+2 + HO2 = Fe(HO2)+2	1.2e6
54	Fe+2 + O2- + H+ = Fe(HO2)+2	1.0e7
55	Fe+3 + HO2 = Fe+2 + O2 + H+	1.9e3
56	FeOH+2 + HO2 = Fe+2 + O2 + H2O	1.9e3
57	Fe(OH)2+ + HO2 = Fe+2 + O2 + H2O + OH-	1.9e3
58	Fe+3 + O2- = Fe+2 + O2	5e7
59	Fe2(OH)2+4 + O2- = 2Fe+2 + O2 + OH-	5e7
60	Fe(OH)2+ + O2- = Fe+2 + O2 + OH- + OH-	5e7