A Multiphase Interfacial Model for the Dissolution of Spent Nuclear Fuel

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Abstract

The Fuel Matrix Dissolution Model (FMDM) is an electrochemical reaction/diffusion model for the dissolution of spent uranium oxide fuel. The model was developed to provide radionuclide source terms for use in performance assessment calculations for various types of geologic repositories. It is based on mixed potential theory and consists of a two-phase fuel surface made up of UO_2 and a noble metal bearing fission product phase in contact with groundwater. The corrosion potential at the surface of the dissolving fuel is calculated by balancing cathodic and anodic reactions occurring at the solution interfaces with UO_2 and NMP surfaces. Dissolved oxygen and hydrogen peroxide generated by radiolysis of the groundwater are the major oxidizing agents that promote fuel dissolution. Several reactions occurring on noble metal alloy surfaces are electrically coupled to the UO_2 and can catalyze or inhibit oxidative dissolution of the fuel. The most important of these is the oxidation of hydrogen, which counteracts the effects of oxidants (primarily H_2O_2 and O_2). Inclusion of this reaction greatly decreases the oxidation of U(IV) and slows fuel dissolution significantly. In addition to radiolytic hydrogen, large quantities of hydrogen can be produced by the anoxic corrosion of steel structures within and near the fuel waste package.

The model accurately predicts key experimental trends seen in literature data, the most important being the dramatic depression of the fuel dissolution rate by the presence of dissolved hydrogen at even relatively low concentrations (e.g., less than 1 mM). This hydrogen effect counteracts oxidation reactions and can limit fuel degradation to chemical dissolution, which results in radionuclide source term values that are four or five orders of magnitude lower than when oxidative dissolution processes are operative. This paper presents the scientific basis

of the model, the approach for modeling used fuel in a disposal system, and preliminary calculations to demonstrate the application and value of the model.

1. Introduction

The geologic disposal of nuclear wastes utilizes multiple natural and engineered barriers to isolate radionuclides from the biosphere. The nuclear waste form is the core barrier to radionuclide mobilization, as its dissolution rate will determine the radionuclide source terms for near- and far-field transport calculations.

Of particular importance to current nuclear waste management strategies are the large inventories of used uranium oxide fuel from power plants. For example, in the U.S. there is approximately 23 billion curies of long-lived radioactivity in commercial used oxide fuel stored at 75 sites in 33 states [1]. The direct disposal of existing inventories of used oxide fuel in geologic repositories is a primary waste management strategy throughout the global community [2],[3]. Used fuel destined for direct disposal in a repository is referred to as “spent fuel” in this paper.

A number of process-oriented models that can be used to calculate the radionuclide source term in a geologic repository have been developed and tested against experimental data. For example, five models quantifying the dissolution behavior of the spent fuel matrix were selected for comparison to a central experimental data base as part of the European Commission MICADO project on quantifying model uncertainties [4]. These models included: (1) the matrix alteration model (MAM), which was developed as part of the European Union Spent Fuel Stability project, and accounts for water radiolysis, solution chemistry and surface complexation kinetics, (2) a model developed by KTH Royal Institute of Technology, Sweden

that accounts for water radiolysis, diffusion and homogeneous kinetics at the spent fuel surface, (3) a model developed by SUBATECH, Ecole des Mines de Nantes, France, which also accounts for water radiolysis and diffusion, but deals with interfacial reactions using electrochemistry rather than surface complexation, (4) a model developed by CEA, France, which accounts for oxidizing radiolytic species produced near the fuel surface, but neglects reducing species and the recombination of radicals, and (5) another CEA model consisting of a complete radiolytic model and accounts for dose rate gradients and diffusion similar to the SUBATECH model [4-10]. Additionally, there is the well-established Mixed Potential Model (MPM) developed as part of Canadian repository program [11-15]. The MPM accounts for radiolytic hydrogen peroxide generation, diffusion, the role of secondary phases and describes interfacial reactions at the fuel surface using mixed potential theory [12].

One of the key results from these previous experimental and modeling studies has been that the dissolution rate of spent fuel can be strongly influenced by the so-called “hydrogen effect” (e.g., [4-10, 16-31]). This term refers to the dramatic decrease in the dissolution rates of spent fuel and simulated fuels observed when tests are performed with various concentrations of dissolved hydrogen (e.g., [4-10], [16-31]). As will be discussed below, the hydrogen effect can dominate all the other processes affecting spent fuel dissolution.

Since hydrogen has been shown to decrease fuel dissolution rates, it is conservative to neglect this effect in source term models. However, based on the large amount of experimental data demonstrating the importance of this effect [16-31], ignoring the role hydrogen may prove to be overly conservative and unrealistic for some repository scenarios. Of the models mentioned above, three account for role of hydrogen in determining the

dissolution rate of the fuel [4]: the MAM accounts for the hydrogen effect as homogeneous reactions in solution [6], the SUBATECH model accounts for hydrogen through its electrochemical effects at the fuel surface [4], and the KTH model contains catalytic reaction sites for hydrogen, which are associated with the fission product alloy phase (epsilon phase) present on the fuel surface [9].

In this report we discuss the development of a new spent fuel dissolution model that is based on the Canadian MPM of Shoesmith et al., [11] and King and Kolar [12 - 14]. This new model, referred to as the Fuel Matrix Dissolution Model (FMDM), was first described by Frey and Jerden [32, 33] and was developed based on fundamental principles to quantify the effects of dose rate, temperature, and important chemical species on spent fuel dissolution rates. As discussed below, the FMDM accounts for hydrogen reactions by quantifying their effects on the electrochemical corrosion potential of the fuel. This is accomplished by including hydrogen reactions on both the UO_2 fuel grains and the noble metal fission product alloy particles also referred to as the epsilon phase or noble metal particles (NMP).

The FMDM is being developed as part of the U.S. Department of Energy (DOE), Used Fuel Disposition Program (UFD). The initial version of the model has been integrated into the UFD program's generic repository performance analysis framework to facilitate further development of the FMDM as a science-based, source term model [34].

Since the FMDM is based on fundamental thermodynamic and electrochemical principles, it can be applied to a diverse range of geologic and engineered environments, provided the pertinent redox reactions and rate parameter values are included. This paper

presents FMDM results for redox reactions and environmental conditions expected for clay/shale and crystalline rock repositories.

2. Model Development and Implementation

2.1. Thermodynamic Basis

Radionuclides in spent fuel can be defined in terms of two inventory fractions: (1) the gap and grain boundary fraction, which is often assumed to become available for transport instantaneously when the fuel is contacted by groundwater, and (2) a matrix fraction, which becomes available for transport at the same fractional rate that the fuel dissolves. The FMDM calculates the fuel dissolution rate that controls the release of radionuclides in the matrix fraction. An instant release fraction model is used to calculate release of radionuclides in the gap and grain boundary fraction. The two models are coupled through the area of the matrix and grain boundaries that are contacted by groundwater over time. The releases calculated by the two models are combined to provide radionuclide source terms that can be used in performance assessment calculations [34].

In the absence of oxidants, uranium dioxide spent fuel is sparingly soluble, and the dissolution rate is low. When oxidants are present, fuel matrix degradation proceeds by a faster oxidative dissolution mechanism. The oxidative dissolution of spent fuel has been measured to be approximately four orders of magnitude higher than chemical dissolution in relatively dilute, near-neutral aqueous solutions [35]. The primary value calculated in the MPM and FMDM is the corrosion potential at the fuel surface that is established by the contributing

redox reactions. The value of the corrosion potential is used to determine if the matrix dissolves by oxidative dissolution in addition to chemical dissolution.

The FMDM accounts for both oxidative and chemical dissolution and determines which is operative based on the surface potential. The reactions used in the FMDM to quantify the oxidative and chemical dissolution processes are shown in Table 1 (reactions A and L). These include reactions affecting the dissolved hydrogen concentration that are not included in the MPM. Figures 1 and 2 provide part of the thermodynamic basis for the FMDM and were plotted using the program “the Geochemist’s Workbench” (GWB) [36], with the thermochemical database “data0.ympr5” [37]. The thermodynamic driving force (free energy change) for the oxidative dissolution of spent fuel and the electrochemical threshold for the transition between oxidative dissolution and chemical dissolution are shown in Figure 1. The E_{CORR} labels in the schoepite and uraninite fields indicate extreme values for the range of fuel corrosion potentials, depending on which processes are dominant. If H_2 oxidation dominates, the fuel E_{CORR} falls below the threshold for oxidative dissolution in the uraninite field, and dissolution is slow. If the reduction of radiolytic oxidants dominates, the fuel E_{CORR} falls within the schoepite field due to oxidative dissolution, and dissolution is relatively fast. The change in free energy and the threshold for oxidative dissolution are quantified in terms of electrochemical potential relative to a standard hydrogen electrode (Eh) using the Nernst equation. Figure 2 shows the aqueous speciation of uranium and the solubility-controlling mineral phases.

The measured Eh and pH values for groundwaters at the crystalline Forsmark and Grimsel repository study sites (Sweden and Switzerland, respectively) and the Callovo-

Oxfordian claystone repository study site (France) are shown as examples on Figure 1 [38, 39].

The data indicate that under undisturbed conditions in a granitic disposal system, the spent fuel matrix would be restricted to slow chemical dissolution. However, as will be discussed in more detail below, the Eh near the fuel surface will be much higher than that in the surrounding geology due to radiolytic hydrogen peroxide and dissolved oxygen produced by peroxide decomposition (these are two key reactions included in the FMDM).

The U(VI) phases schoepite and studtite are secondary precipitates that can influence the rate of fuel dissolution by forming corrosion layers on the fuel surface that block radiation from reaching the groundwater and moderate the diffusion of oxidants (H_2O_2 and O_2) and reductants (H_2 and Fe^{2+}) to and from the reacting surface. These effects are included in the FMDM. As shown in Figure 2, both uranyl oxy-hydroxide (schoepite/metaschoepite) and uranyl peroxide (studtite/metastudtite) can be present in the corrosion layer. This is because studtite formation is limited by the supply of hydrogen peroxide and uranium, whereas schoepite formation is limited only by uranium.

Figure 2 shows that the Eh threshold for the oxidative dissolution of UO_2 decreases from around 0.05 to -0.18 V with a pH increase from 7 to 10, and that the aqueous speciation of U(VI) changes with pH. At pH 7, the dominant species are $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ (curves a and b on Figure 2), whereas at pH 10 the dominant species are $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{UO}_2(\text{OH})_3^-$ (curves e and f on Figure 2). The dependencies of the oxidative dissolution threshold on the aqueous speciation and pH are both important in determining the overall dissolution rate of spent fuel in an evolving chemical system, such as a breached waste package within a geologic repository.

The main source of hydrogen in a geologic repository will be the anoxic corrosion of iron and steel hardware that makes up the spent-fuel waste package shell and internal structures. The slow oxidation of Zircaloy cladding and water radiolysis will also produce hydrogen, but at lower levels than that for iron and steel corrosion [40]. As much as 10 MPa hydrogen was estimated to accumulate within a breached spent fuel canister at the proposed Forsmark repository site due to the hydrostatic and lithostatic pressures (repository level is around 500 m deep) and the slow transport of H₂ through the bentonite backfill material [40]. Similarly, at possible repository sites in the Opalinus Claystone (Switzerland) and the Callovo-Oxfordian Claystone (France), hydrogen partial pressures of 5 to 10 MPa are expected to persist for as long as corrosion of steel materials in the waste package and near field continues, which is projected to be around 100,000 years [40]. Based on these gas pressures in both crystalline and claystone repositories at around 500-m depths, the dissolved hydrogen concentrations will be in the 10 to 100 mM range [4].

The homogeneous reaction of dissolved hydrogen with redox sensitive species is kinetically inhibited at near-surface ambient temperatures [39]. Therefore, the mechanisms for the hydrogen effect likely involve heterogeneous catalytic activation or interactions with highly reactive radicals produced by radiolysis [26, 40, 42, 43]. Three mechanisms by which hydrogen decreases the rate of fuel dissolution have been described [26, 42, 43]. The first is a radiolytic mechanism involving the homogeneous destruction of hydrogen peroxide as summarized in the following reactions [10, 44]:

This mechanism is favored in high beta- and gamma-radiation fields due to the relatively high yield of $\text{OH}\bullet$. Consumption of H_2O_2 by this reaction decreases the corrosion potential at the fuel surface, but not to a value that is below the threshold potential for oxidative dissolution [30]. Jonsson [43] also notes that this mechanism can be counteracted by the presence of other species that preferentially react with $\text{OH}\bullet$, such as carbonate and bicarbonate:

This homogeneous, radiolytic mechanism is not yet included in the FMDM, but will be built into the code in future versions as the radiolysis module is expanded [45].

The second and third mechanisms for the hydrogen effect are included in the FMDM and are shown conceptually in Figure 3. The second mechanism involves the catalytic activation of hydrogen at surface defect sites [26] and reactions between U(IV)/U(V) sites with H_2O_2 and H_2 [27]. These reactions are shown schematically in Figure 3 as the reduction of H_2O_2 involving $\text{H}\bullet$ and the oxidation of H_2 involving $\text{OH}\bullet$ [Equations (1) and (2)]. The current densities from these reactions (quantifying the flow of electrons in Figure 3) contribute to the fuel corrosion potential and influence whether the fuel dissolves by relatively rapid oxidative dissolution or only by slow chemical dissolution.

The third mechanism for the hydrogen effect is the activation of hydrogen to $\text{H}\bullet$ catalyzed on the surface of the NMP. This reaction is shown schematically in the lower half of Figure 3 along with the reduction of H_2O_2 . Experimental evidence suggests that the NMP is an effective catalyst for H_2 oxidation, and that the anodic current density (e^- in Figure 3) produced

by millimolar concentrations of H_2 is sufficient to lower the corrosion potential enough to shut down oxidative dissolution [7,9,16 - 31].

The FMDM also accounts for the role of Fe^{2+} (from corroding steels) as an H_2O_2 and O_2 scavenger in bulk solution (reactions U and V in Table 2); however, the importance of Fe^{2+} in decreasing the rate of fuel dissolution is considerably less than that of hydrogen (in the FMDM) due to the low solubility of Fe^{2+} in solution. For example, the solubility calculations performed as part of this study (using the thermochemical database “data0.ympr.R5” [37]) show that near-neutral dilute groundwaters with an Eh of -0.2 V (typical of repository groundwater, Figure 1) become saturated with respect to magnetite at micromolar concentrations of dissolved iron.

2.2. Model Implementation

The FMDM was coded in MATLAB [46] using the same fundamental electrochemical relationships employed by King and Kolar to implement the original MPM [12]. The FMDM is a one-dimensional reaction-diffusion model consisting of a variable-length diffusion path (chosen to be 10 cm for the present study), extending out from a spent fuel surface which serves as a reactive model boundary. The opposite boundary is presently defined by constant concentrations of environmental species, but that will be replaced by a surface representing a corroding canister in the future. No advection or sorption occurs, but a surface layer develops when the U solubility limit is reached. The reaction scheme and model layout are shown in Figure 4. The model diffusion length is discretized by using log space such that there are 24 calculation points within the 35- μm irradiated zone and 576 in the rest of the 10-cm distance. The spacing and number of calculation points near the fuel surface and irradiated zone are shown as tick marks at the bottom of the two schematics in Figure 4.

The mathematical representation of the system shown in Figure 4 involves a set of coupled partial differential equations (one for every component), which are solved as a fixed-boundary problem by the approach described by King and Kolar [12]. The coupled partial differential equation solved for each component i is based the Fickian diffusion equation and takes the following generic form:

$$\varepsilon \frac{\partial C_i(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon \tau D_i(x, T(t)) \frac{\partial C_i(x,t)}{\partial x} \right) + R(C_i(x, t), x, t) \quad (5)$$

where t is time, x is linear distance, and T is temperature. The fraction of the fuel surface that is reacting is denoted as ε which, in the FMDM, physically corresponds to the porosity or surface coverage of a corrosion layer that may form as the fuel undergoes oxidative dissolution (the U(VI) precipitate layer in Figure 4b). Also in the above equation, $C_i(x,t)$ denotes all dependent variables (i.e., concentration of species i as a function of distance and time), D_i is the diffusivity of species i in solution, and τ is the tortuosity factor for diffusion through the corrosion layer, which moderates the diffusion of species i at all values of x that fall within the thickness of the corrosion layer. This layer is assumed to consist of parallel pores, thereby making its porosity (ε) equivalent to its surface coverage (Figure 4b). This assumption simplifies the calculation by representing the diffusion coefficient in the layer as an attenuation of the diffusion coefficient in the solution by the term $\varepsilon \tau$. The R corresponds to the summation of reaction terms, which are non-linear functions of the concentrations C_i in time t and space x . The complete lists of interfacial and bulk reactions are given in Tables 1 and 2.

As depicted in Figure 4, the spent fuel surface in the FMDM consists of a UO_2 phase that surrounds the NMP phases, and surface reactions involving both phases contribute to the overall mixed potential calculation. The NMP is electrically coupled to the fuel matrix phase

through a resistance set by the user (R in Figure 4). For this study, a low value of R (e.g., 1×10^{-3} V/A) was used such that the two phases were at about the same potential for all simulations.

The reactions and fundamental constants used in the FMDM are shown in Tables 1 and 2, while the diffusion coefficients and saturation concentrations are shown in Table 3. To ensure internal model consistency, all thermodynamic constants (equilibrium constants, standard potentials, and saturation concentrations) were calculated from data0.ymp.R5 [37]. Kinetic constants and coefficients were taken from the literature (see references in Tables 1-3). The rate constants for the interfacial reactions have the largest impact on the predicted corrosion potential and dissolution rate (Table 1 and Figure 4). The rate constants for fuel oxidative dissolution and oxidant reduction on the fuel are from King and Kolar [14], and the rate constant for the oxidation of hydrogen is from Trummer et al. [30]. The rate constants for oxidant reduction on the NMP surfaces were estimated by assuming that they are a factor of 100 higher than those on uranium oxide. This assumption is based on qualitative observations about the superior efficiency of noble metal catalysts over oxide catalysts [47] and remains to be verified for spent fuel dissolution.

The central premise of the FMDM is that the rate of fuel oxidative dissolution depends directly on the fuel corrosion potential (E_{CORR}), which is established by the kinetic balance of cathodic and anodic reactions at the surface. The value of E_{CORR} at the fuel surface can be quantified on the basis of the electrochemical axiom that the net total current at the fuel surface (i) is always zero. This axiom can be stated mathematically in terms of the reactions A-K in the FMDM (see Table 1) as follows:

$$(i_A + i_B + i_C + i_D + i_E + i_H + i_I)_{\text{anodic}} + (i_F + i_G + i_J + i_K)_{\text{cathodic}} = 0 \quad (6)$$

For a given simulation, the FMDM solves a set of ordinary differential equations, where the dissolved concentrations are the state variables. Given initial concentrations at the interface with the fuel surface, E_{CORR} is calculated such that the total current flow at the fuel surface is zero. This value of E_{CORR} is used to determine current densities that represent the individual reaction rates. The rates of the surface reactions control the flux of chemical species from the surface, including UO_2 from chemical dissolution (reaction L) and UO_2^{2+} from oxidative dissolution (reactions A, B, and C), if it occurs. Chemical fluxes from the fuel surface are used to update the solution concentrations, and the cycle of calculations is repeated for the desired simulation time (set at 1×10^5 years for this study).

The relationship between the rate of each reaction shown in Table 1 (quantified as current densities (i) in units of $A\ m^{-2}$) and the fuel corrosion potential (E_{CORR} in V) is determined by the equation:

$$Rate\ (i_A) = f k_{A_j} \exp\left(\frac{\Delta H}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) \exp\left(\frac{\alpha F}{RT} (E_{CORR} - E_{A_j}^0)\right) \prod_j [C]^{a_j} \quad (7)$$

where f is the fractional surface coverage of NMP, k_{A_j} is the rate constant for the half reaction A_j , ΔH is the activation enthalpy for the reaction, α is the charge transfer coefficient for reaction A_j , $E_{A_j}^0$ is the standard potential for reaction A_j , C is concentration of species i , and a_j is the reaction order for reaction j . In addition, T_{ref} , T , R , F are the thermodynamic reference temperature (25°C), actual temperature, gas constant, and the Faraday constant. The temperature dependence of the standard potentials is also accounted for (Table 1) and was determined from the equilibrium data given in data0.ymp.R5 [37]. Faraday's law is used to convert reaction current densities to mass concentrations.

The treatment of radiolysis within the FMDM is based on the assumption that the fuel will have aged around 3000 years by the time it is exposed to groundwater (i.e., the waste package is assumed to remain intact for a few thousand years [40]). At these decay times, the fuel decay is dominated by reactions generating alpha particles of long-lived fission products (e.g., Np-237, Pu-239, and Am-241) [48]. Therefore, in the FMDM, the irradiation zone extending 35 μm from the fuel surface (Figure 4) consists of only alpha energy deposition. The width of the irradiation zone (alpha penetration depth) was determined by the energy of the alpha particles emitted from the fuel surface. The 2013 version of the well-established and validated code “The Stopping and Range of Ions in Matter” was used to determine the relationship between alpha particle energy and penetration depth in water [49]. The results show that the alpha penetration depth can vary from 35 μm to 55 μm for a reasonable range of alpha energies (5.0–6.5 MeV was used in the calculation). Based on the used-fuel energy spectra shown in Radulescu [50], a reasonable argument can be made for choosing an energy value of 5.0 MeV for used-fuel alpha particles. Furthermore, Radulescu found that the alpha energy spectra does not change dramatically with time; therefore, it is also reasonable to use a constant alpha penetration depth of 35 μm throughout the duration of the FMDM simulations.

Another key physical quantity that determines the amount of radiolytic oxidants and the local solution oxidative potential is the dose rate within the alpha penetration zone. The MPM from King and Kolar [12] used a constant dose rate (step function) across the entire alpha irradiation zone. This assumption produced the maximum amount of radiolytic oxidants but was physically unrealistic and overly conservative. This step function was replaced in the FMDM with an alpha dose rate that decreases exponentially across the alpha penetration zone

according to the geometrical dose distribution presented by Nielsen and Jonsson [51]. The FMDM dose rate profile extending from the surface is shown in Figure 5.

The points shown on the curves in Figure 5 are the individual calculation nodes for the model (there are 24 calculation points within the 35- μm irradiation zone). Figure 5b shows examples of hydrogen peroxide concentration profiles that were calculated by the FMDM using the dose rate profile from Figure 5a, with and without a corrosion layer. The concentration profiles highlight the effect that the U(VI) precipitate layer can have on species concentrations near the interface relative to the dose rate.

The radiolysis module of the FMDM for crystalline and argillite systems is relatively simple because it is assumed that the only relevant radiolytic species that reacts with the fuel over the time scales of interest is hydrogen peroxide. For dilute groundwaters, this assumption is supported by results from radiolysis codes that account for the full series of relevant radical reactions [52]. This assumption does, however, preclude radiolytic processes that may decrease the overall hydrogen peroxide production rate, such as those summarized in the reactions given in equations 1–4 above. There is an ongoing effort, however, to expand the radiolysis module of the FMDM to include these reactions

The following relationship describes the basic equation for hydrogen peroxide yield as a function of space and time used in the FMDM:

$$H_2O_2 \text{ Yield } (x, t) = G_{H_2O_2} \times R_D(x, t) \times g(x) \quad (8)$$

where $G_{H_2O_2}$ is the generation value for hydrogen peroxide for constant alpha energy of $1.02 \times 10^{-7} \text{ mol L}^{-1} \text{ Gy}^{-1}$ [53]; R_D is the dose rate in Gy s^{-1} , which varies in time (as fuel decays) and space

(Figure 5a); and $g(x)$ is a geometrical factor for the fraction of the fuel surface that is blocked from emitting alpha radiation into solution by the U(VI) precipitate layer.

3. Results and Discussion

The FMDM was run for a number of simplified cases to compare model predictions with experimental data. This comparison was not a parameter fitting exercise or quantitative uncertainty analyses, but an overall assessment of the model's ability to predict the major trends seen in laboratory data and verify that it provides a conservatively bounding fuel dissolution rate. The constants and parameters used are given in Tables 1–3. The dose rate at the fuel surface was varied from run to run, as specified for each calculation discussed below, although the dose rate profile was the same for all simulations (Figure 5a).

3.1. Effect of H_2O_2 Concentrations

Figure 6 shows the predicted corrosion potential, dissolution rate, and dominant reaction current densities with increasing hydrogen peroxide concentrations at the fuel surface. The dose rate at the fuel surface was varied from 1×10^{-3} to $1 \times 10^3 \text{ Gy s}^{-1}$ to produce this large range of hydrogen peroxide values in the model. For this simulation, the temperature was held constant at 25°C ; the environmental concentration (constant concentrations at model boundary) of oxygen was $1 \mu\text{M}$; and the concentrations of hydrogen, carbonate, and iron were all set at $1 \times 10^{-9} \text{ M}$. The curves for the FMDM deviate from the King and Kolar [14] MPM because different values were used for key parameters (Tables 1–3).

The FMDM captures the general trend of how the measured fuel/ UO_2 corrosion potential and dissolution rate increase with increasing hydrogen peroxide (Figure 6b). The

FMDM model is reasonably conservative in that it over-predicts the measured dissolution rates by less than a factor of three. An interesting feature of the model prediction is that the corrosion potential and corresponding dissolution rate approach limiting values at hydrogen peroxide concentrations greater than 0.1 mM. The reason for this effect is revealed in the current density plot (Figure 6c), which shows that the rate of hydrogen peroxide oxidation (reaction E in Table 1) is about the same as the rate of hydrogen peroxide reduction (reaction F in Table 1) at hydrogen peroxide concentrations greater than 0.1 mM. This condition inhibits further increase in the corrosion potential by balancing the cathodic current with an anodic current (H_2 oxidation) for a reaction other than uranium oxidation.

The increase in corrosion potential and dissolution rate when the NMP phase is included (with no H_2) is due to the catalysis of the hydrogen peroxide and oxygen reduction reactions on the NMP surface (reactions J and K in Table 1). The effect is relatively small because the oxidation of hydrogen peroxide (reaction I in Table 1), which is also assumed to be catalyzed by the NMP, partially counterbalances the reductive reactions (Figure 4).

3.2. Effects of Carbonate and Temperature

Figure 7 compares the FMDM fuel dissolution rates with experimental trends for a range of carbonate concentrations and temperatures. For the carbonate variation diagram (Figure 7a), the temperature was a constant $25^{\circ}C$, and for the temperature variation diagram (Figure 7b), the carbonate concentration was 1 mM. For both diagrams the dose rate was a constant 0.01 Gy s^{-1} , oxygen was $1 \mu\text{M}$, and both hydrogen and iron were $1 \times 10^{-9} \text{ M}$.

The FMDM indicates that the rate of fuel dissolution increases about two orders of magnitude over a range of 1 mM to 0.1 M carbonate, which is consistent with the general trend

in the experimental data (Figure 7a). In general, the model is conservative by about a factor of five, though there is considerable scatter in the experimental data due to the different properties of the materials used. The FMDM-predicted total dissolution rate (sum of currents from reactions A, B, and C in Table 1, which is shown by the dashed line on Figure 7a) is two orders of magnitude greater than the FMDM-predicted dissolution rate in the presence of carbonate (sum of reactions B and C in Table 1). The predicted variation of dissolution rate with increasing temperature (Figure 7b) is also consistent with experimental data; the temperature dependencies of most of the reaction rate constants in Table 1 are estimates based on analogies with similar reactions [14].

3.3 Effect of H₂ Concentration

The effect of the dissolved concentration of hydrogen on the corrosion potential, dissolution rate, and key reaction current densities is shown in Figure 8. The results of four model runs are represented in Figure 8a and b: (1) no carbonate and no NMP (dotted curves), (2) no carbonate and 1% surface coverage of NMP (solid curves), (3) 1% NMP and 1 mM carbonate (short-dash curve) and, (4) hydrogen concentration at 1 μM , increasing ferrous iron c along the x-axis at the same molarities listed for H₂, and no carbonate (long-dash curve) (Figure 8b). For all four runs the surface dose rate was 0.25 Gy s⁻¹, and the dissolved oxygen was 1 μM . Except for run 4, no ferrous iron was present. The reaction current density plot (Figure 8c) is for run 3, 1% NMP and 1 mM carbonate.

The results shown in Figure 8 indicate that the FMDM accurately predicts the trend and order of magnitude of the hydrogen effect discussed in Section 1.1. For example, the predicted corrosion potential roughly matches measured values from Broczkowski et al. [24] (Figure 8a).

Run 1 (no NMP) predicts that the oxidation of hydrogen on the fuel surface causes an approximately three orders of magnitude drop in the fuel dissolution rate when dissolved hydrogen increases from 0.1 to 100 mM (Figure 8b), which roughly corresponds to a H_2 pressure increase from 0.01 to 10 MPa. For run 2 (solid curve in Figure 8b, no carbonate and 1% NMP), the dissolution rate drops six orders of magnitude over the range of 10 μM to 10 mM hydrogen. The curve for run 3 (short dash curve in Figure 8b, 1 mM carbonate with 1% NMP) shows a dissolution rate decrease of about four orders of magnitude over the range of 10 μM to 10 mM hydrogen. These results indicate that, based on the reactions included in the FMDM, the complexation of uranium by carbonate partially counteracts the protection of the fuel by hydrogen. The Fe(II) curve from run 4 can be used to compare the hydrogen effect with the reductive effect of Fe(II). Iron acts as an oxidant scavenger in bulk solution (reactions U and V in Table 2), and as shown in Figure 8b, its effect is not nearly as great as the hydrogen effect on the overall dissolution rate of the fuel.

Figure 8c shows how individual half-cell reaction rates contribute to the hydrogen effect as calculated in the FMDM. These reactions include oxidation and reduction catalyzed separately on the NMP and fuel surfaces. The anodic dissolution of fuel proceeds at a rate determined by the balance between U(IV) oxidation and hydrogen peroxide reduction until a hydrogen concentration of 3 μM , at which point the reduction of hydrogen peroxide and oxygen on the fuel and NMP is balanced by the oxidation of hydrogen on the NMP, which “protects” U(IV) from oxidation. A continued increase in hydrogen concentration progressively accentuates this effect until the corrosion potential decreases below the threshold for oxidative dissolution, and the fuel degrades only by slow chemical dissolution.

3.4. Effect of Time

To demonstrate the applicability of the FMDM to the time scale of interest, the dose rate and temperature histories relevant to long-term geologic disposal were used as the basis for 1×10^5 year simulations. The dose rate history (Figure 9a) was assumed to conform to a power law fit to Nielsen and Jonsson's [51] table of average alpha dose rates for a 55 MWd kg⁻¹ fuel for different times. The temperature history (Figure 9b) was assumed to conform to a power law fit to the cooling calculations for a 60 MWd kg⁻¹ fuel in a hypothetical granite repository presented by Greenberg [54]. The environmental carbonate, surface coverage of NMP, and hydrogen concentrations were varied for these simulations. Note that the purpose of the model runs in which the dose rate and temperature time histories were used was not to simulate any particular repository design, but simply to apply the model to reasonable time evolutions of these key variables. The effect of time on the potentials and rates calculated with the current version of the FDMD is a secondary effect occurring through the temporal changes in dose and temperature.

Figure 10 shows results from simulations using the dose rate history from Figure 9 constant temperature of 25°C. Four cases were run: (1) no hydrogen and 1% NMP, (2) 0.1 mM hydrogen and no NMP, (3) 0.1 mM hydrogen and 1% NMP, and (4) 0.01 mM hydrogen and 1% NMP. All of these cases were run with 1 μM environmental dissolved hydrogen peroxide and no carbonate or iron. This simulation highlights how decreasing dose rate accentuates the hydrogen effect.

The dark solid line in Figure 10a shows the corrosion potential history in the absence of hydrogen (run 1). It decreases from 0.315 to 0.175 V over the 1×10^5 year simulation due to

the decrease in dose rate (see Figure 9a). Correspondingly, the fuel dissolution rate decreases from around 3 to $0.02 \text{ g m}^{-2} \text{ yr}^{-1}$ (Figure 10b) due to the change in dose rate that occurs over time. When 0.1 mM hydrogen is present with no NMP (run 2, upper dashed curve), the dissolution rate is depressed by a factor of three (at end of simulation) relative to the “no hydrogen” case due to the oxidation of hydrogen on the fuel surface. Including the catalytic effect of NMP for the 0.1 mM hydrogen case (run 3) depresses the corrosion potential by a factor of three and the dissolution rate by three orders of magnitude relative to the “no NMP” case. Comparing the results for 0.1 mM hydrogen and 1% NMP (Run 3) with the results for 0.01 mM hydrogen and 1% NMP (run 4) shows that the magnitude of the hydrogen effect is strongly dose dependent. For example, in the first 10 years of the simulation, when the dose rate is greater than 1 Gy s^{-1} , the presence of 0.01 mM hydrogen has only a small effect on the fuel dissolution rate relative to the “no hydrogen” case. However, as the dose rate drops from 1 to 0.01 Gy s^{-1} over the next 1000 years or so, the hydrogen reactions cause a three orders of magnitude decrease in the fuel dissolution rate relative to the “no hydrogen” case. As shown in Figure 10c, dose dependence of the hydrogen effect is due to the decrease in the amount of hydrogen peroxide being generated. The cathodic reduction of hydrogen peroxide dominates all reactions at times less than 10 years, but as time increases and the dose rate drops below 1 Gy s^{-1} , the current density for the hydrogen peroxide reduction decreases, and oxygen becomes the dominant oxidant after a few thousands of years (Figure 10c).

Figure 11 shows results from simulations using both the dose rate and temperature histories from Figure 9. Six cases were run for this simulation: (1) no carbonate and no hydrogen; (2) 1 mM carbonate and no hydrogen; (3) 1 μM hydrogen and no carbonate; (4) 1

mM carbonate and 1 μ M hydrogen; (5) 0.1 mM hydrogen and no carbonate; and (6) 1 mM carbonate and 0.1 mM hydrogen. These simulations demonstrate the role of carbonate in counteracting the hydrogen effect at low dose rates (Figure 11). The individual reaction currents contributing to the fuel dissolution rate in the solution with 1 mM carbonate and 1 μ M hydrogen are shown in Figure 11b.

In calculations that account for both the temperature and dose rate histories (both curves in Figure 9), the predicted dissolution rates for all six runs decrease significantly with time (Figure 11a). In the “no hydrogen, no carbonate” case (run 1) shown in Figure 11a, the fuel dissolution rate decreases from around $20 \text{ g m}^{-2} \text{ yr}^{-1}$ initially under high temperature and high dose rate conditions down to $0.02 \text{ g m}^{-2} \text{ yr}^{-1}$ at 1×10^5 years under low temperature and low dose conditions. Although the conditions differ, the FMDM results are consistent with the maximum fuel dissolution rates calculated by Nielsen et al. [55] (data points in Figure 11a). The addition of 1 μ M hydrogen (run 3) depresses the fuel dissolution rate by around a factor of 100, but only after the dose rate has dropped below 0.03 Gy s^{-1} (>1000 years). The presence of 1 mM carbonate (run 2) counteracts the hydrogen effect for low hydrogen concentrations (dashed lines in Figure 11a).

The fuel dissolution rate (Figure 11a) decreases by greater than a factor of 100 for the 0.1 mM hydrogen case (run 5) relative to the “no hydrogen” case. An important observation, however, is that 1 mM carbonate counteracts the hydrogen effect such that the dissolution rate with 0.1 mM hydrogen and 1 mM carbonate (run 6) is a factor of 30 greater than the dissolution rate with 0.1 mM hydrogen and no carbonate (run 5). Figure 11b shows that approximately 200 years into the simulation the absolute current density for the oxidation of

hydrogen on NMP equals that of hydrogen peroxide reduction and exceeds the uranium oxidation current density. Beyond about 700 years, the reaction of oxygen with the fuel surface becomes more important than that of hydrogen peroxide reduction due to less H_2O_2 being produced at the lower dose rates (Figure 11b). Another important observation highlighted in Figure 11b is that the carbonate-accentuated oxidative dissolution (reactions B and C in Table 1) dominates the corrosion current at times greater 2000 years, which is reflected in the dissolution rate plot (Figure 11a) as a factor of 20 higher dissolution rate in the presence of 1 mM carbonate (run 2).

4. Uncertainty and Applicability

In the original MPM model of King and Koler [12], the constants and parameters used were specific to a pH 9.5 groundwater typical of the Canadian Shield. This specificity has been retained in the present version of the FMDM because, based on the sources used to compile Tables 1 and 2, most of these constants do not change significantly within the pH range of 7 – 10. The threshold for oxidative dissolution does change over this pH range (Figure 1), however. This change is accounted for in the FMDM through the use of E_{CORR} to determine the overall dissolution rate (e.g., Figure 1, Equation 6). Furthermore, the FMDM accurately captures general trends in experimental results performed over a range of pH values even though the pH dependence of the redox reactions is not taken into account (i.e., data points shown in Figures 6 – 8, were from tests with pH values ranging from 6.7 to 10).

Overall, the results show that the FMDM is applicable to the types of groundwaters that are typical of most crystalline rock and claystone/shale repository concepts (i.e., relatively dilute, near-neutral carbonate solutions). However, there remains a need for experiments to

better quantify model uncertainties and provide kinetic and electrochemical parameter values. In particular, because the relative surface areas of each will change as the fuel corrodes, experiments are needed to quantitatively distinguish between the interdependent roles of the UO_2 and NMP surfaces. Also, the FMDM can be expanded to represent other environments by including relevant redox reactions. For example, brine conditions typical of salt repository sites would require the addition of aqueous speciation and radiolysis modules for radiolytic oxidants other than hydrogen peroxide (e.g., Cl_2^- , ClO_2^- , ClO_3^- , ClOH^- , HClO) [56].

Although a quantitative uncertainty analysis of the FMDM has not yet been completed, the results presented in this paper show that the model captures key trends and is generally conservative by a factor of 2 to 5 in terms of the predicted dissolution rates for relevant conditions (dose rate, temperature, and chemistry). However, there remains a need for continued experimental work to optimize model parameterization (especially for temperature dependencies) and to fully validate the code. A specific need that is being addressed by ongoing work is the role that relevant noble metal catalyst poisons (e.g., halides and sulfides) play in counteracting the hydrogen effect.

5. Conclusions

The Fuel Matrix Degradation Model (FMDM), which is being developed to quantify the long-term dissolution behavior of spent fuel, accurately represents the dominant trends seen in relevant experimental data. The model is designed for easy expansion to any disposal systems by including redox reactions for important radiolysis products. The reactions and parameters in the current version of the FMDM are applicable to relatively dilute carbonate-bearing

groundwaters typical of most crystalline rock and claystone/shale repository concepts. While further parameter optimization is needed through electrochemical experiments, the simulations presented in this paper demonstrate application of the model to quantify some important trends and quantify the effects of even relatively low concentrations of dissolved hydrogen on the corrosion potential of spent fuel and its dissolution rate. The most important results are as follows:

- The hydrogen oxidation half reaction balances the hydrogen peroxide reduction reactions to lower the corrosion potential and “protect” the fuel from oxidative dissolution at even sub-millimolar concentrations.
- The presence of carbonate counteracts the hydrogen effect by favoring the U(IV) → U(VI) transition at low hydrogen concentrations and low dose rate. However, at hydrogen concentrations greater than 0.1 mM, the hydrogen effect shuts down oxidative dissolution of the fuel, even in the presence of 1 mM carbonate.
- At hydrogen concentrations greater than 1 mM, the radionuclide source term associated with matrix dissolution is predicted to be 4 or 5 orders of magnitude lower than that for the oxidative dissolution case in typical crystalline and clayrock/shale repository settings.
- The presence of a U(VI) precipitate/corrosion layer consisting of schoepite and/or studtite can decrease the dissolution rate of the fuel by a factor of two or more depending on the porosity of the layer. This effect is due to the layer blocking alpha particles emitted from the fuel surface and moderating the diffusion of species in the interfacial region.

Acknowledgments

This work was supported by the US Department of Energy, Office of Nuclear Energy. The report was prepared at Argonne National Laboratory as part of the Used Fuel Disposition (UFD) Campaign. The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. This work benefited greatly from discussions with Edgar Buck, James Cunnane, Carlos Jove-Colon, David Sassani and Rick Wittman.

References

- [1] D. Sassani et al., Evaluation of Options for Permanent Geologic Disposal of Spent Nuclear Fuel and High-Level Radioactive Waste in Support of a Comprehensive National Nuclear Fuel Cycle Strategy, Prepared for U.S. Department of Energy, Used Fuel Disposition Campaign, FCRD-UFD-2013-000371, Revision 1, April 15, 2014.
- [2] Nuclear Waste Technical Review Board, Survey of National Programs for Managing High-Level Radioactive Waste and Spent Nuclear Fuel, a Report to Congress and the Secretary of Energy, Arlington, VA, www.nwtrb.gov, 2009.
- [3] M. Nutt, M. Voegelé, C. Jove-Colon, Y. Wang, R. Howard, J. Blink, H.H. Liu, E. Hardin, K. Jenni, Used Fuel Disposition Campaign Disposal Research and Development Roadmap, Prepared for, U.S. Department of Energy, Used Fuel Disposition Campaign, FCR&D-USED-2011-000065 REV 0, March 2011.
- [4] B. Grambow, J. Bruno, L. Duro, J. Merino, A. Tamayo, C. Martin, G. Pepin, S. Schumacher, O. Smidt, C. Ferry, C. Jegou, J. Quiñones, E. Iglesias, N. Rodríguez Villagra, J. M. Nieto, A. Martínez-Esparza, A. Loida, V. Metz, B. Kienzler, G. Bracke, D. Pellegrini, G. Mathieu, V. Wasselin-Trupin, C. Serres, D. Wegen, M. Jonsson, L. Johnson, K. Lemmens, J. Liu, K. Spahiu, E. Ekeröth, I. Casas, J. de Pablo, C. Watson, P. Robinson, D. Hodgkinson, Model Uncertainty for the Mechanism of Dissolution of Spent Fuel in Nuclear Waste Repository, European Commission, Final Report for MICADO Project, EUR 24597, 2010.
- [5] B. Grambow, A. Loida, A. Martínez-Esparza Valiente, P. Díaz-Arocas, J. de Pablo, J.L. Paul, G. Marx, J.-P. Glatz, K. Lemmens, K. Ollila, H. Christensen, Source Term for Performance Assessment of Spent Fuel as a Waste Form, European Commission Report, Nuclear Science and Technology, EUR 19140 EN, 2000.
- [6] C. Poinssot, C. Ferry, M. Kelm, B. Grambow, A. Martínez-Esparza Valente, L. Johnson, Z. Andriambololona, J. Bruno, C. Cachoir, J.-M. Cavendon, H. Christensen, C. Corbel, C. Jegou, K. K. Lemmens, A. Loida, P. Lovera, F. Miserque, J. De Pablo, A. Poulesquen, J. Quinones, V. Rondinella, K. Spahiu, D.H. Wegen, Spent Fuel Stability Under Repository Conditions - Final Report of the European Project, European Commission, 5th EURATOM Framework Programme 1998-2002, 104 p.
- [7] Lemmens, A. Loida, P. Lovera, F. Miserque, J. de Pablo, A. Poulesquen, J. Quinones, V. Rondinella, K. Spahiu, D. Wegen, Final Report of the European Project Spent Fuel Stability under Repository Conditions, European Commission Report CEA-R-6093, 2005.
- [8] C. Poinssot, C. Ferry, P. Lovera, C. Jegou, J. Gras, J. Nucl. Mat. 346 (2005) 66–77
- [9] M. Trummer, M. Jonsson, J. Nucl. Mat. 396 (2010) 163–169.

- [10] T.E. Eriksen, D.W. Shoesmith, M. Jonsson, J. Nucl. Mat. 420 (2012) 409–423.
- [11] D. W. Shoesmith, F. King, A Mixed-Potential Model for the Prediction of the Effects of Alpha-Radiolysis, Precipitation and Redox Processes on the Dissolution of Used Nuclear Fuel, Ontario Hydro, Nuclear Waste Management Division Report 06819-REP-01200-MPM-R00, 1998.
- [12] F. King, M. Kolar, Mathematical Implementation of the Mixed-Potential Model of Fuel Dissolution Model Version MPM-V1, Ontario Hydro, Nuclear Waste Management Division Report No. 06819-REP-01200-10005 R00, 1999.
- [13] F. King, M. Kolar, 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, 2002.
- [14] F. King, M. Kolar, The Mixed-Potential Model for UO₂ Dissolution MPM Versions V1.3 and V1.4, Ontario Hydro, Nuclear Waste Management Division Report No. 06819-REP-01200-10104 R00, 2003.
- [15] D. W. Shoesmith, M. Kolar, F. King, Corrosion 59 (2003) 802-816.
- [16] F. King, M.J. Quinn, N.H. Miller, The Effect of Hydrogen and Gamma Radiation on the Oxidation of UO₂ in 0.1-1 mol L⁻¹ NaCl, Swedish Nuclear Fuel and Waste Management Company Report TR-99-27, 1999.
- [17] K. Spahiu, L. Werme, U-B. Eklund, Radiochim. Acta 88 (2000) 507-511.
- [18] L. Liu and I. Neretnieks, Nuclear Technology 138 (2002) 69-77.
- [19] K. Spahiu, U.-B. Eklund, D. Cui, M. Lidstrom, Mater. Res. Soc. Symp. Proc. 13 (2002) 633.
- [20] Y. Ollila, V. Albinsson, M. Oversby, M. Cowper, Dissolution Rates of Unirradiated UO₂, UO₂ Doped with ²³³U, and Spent Fuel under Normal Atmospheric Conditions and under Reducing Conditions Using an Isotope Dilution Method, Swedish Nuclear Fuel and Waste Management Company Technical Report TR-03-13, 2003.
- [21] D. Cui, P. Nilsson, K. Spahiu, The Influence of Hydrogen on Spent Fuel Leaching and Possible Mechanisms, Presented at MRS Spring Meeting, San Francisco, CA, April 12-15, 2004.
- [22] D. Cui, J. Low, C.J. Sjöstedt, K. Spahiu, Radiochim. Acta 92 (2004) 551–555.
- [23] K. Spahiu, J. Devoy, D. Cui, M. Lindstrom, Radiochim. Acta 92 (2004) 597.
- [24] M.E. Broczkowski, J.J. Noël, D.W. Shoesmith, J. Nucl. Mat. 346 (2005) 16-23.

- [25] T.Eriksen, M. Jonsson, The Effect of Hydrogen on Dissolution of Spent Fuel in 0.01 mol dm⁻³ NaHCO₃ Solution, Swedish Nuclear Fuel and Waste Management Co., TR-07-06, August 2007.
- [26] S. Nilsson, M. Jonsson, J. Nucl. Mat. 372 (2008) 160-163.
- [27] D.W. Shoesmith, The Role of Dissolved Hydrogen on the Corrosion/Dissolution of Spent Nuclear Fuel, Nuclear Waste Management Organization, Toronto, Ontario, Canada, TR-2008-19, November 2008.
- [28] P. Carbol, P. Fors, T. Gouder, K. Spahiu, Geochim. Cosmochim. Acta 73 (2009) 4366-4375.
- [29] P. Fors, P. Carbol, S. Van Winckel, K. Spahiu, J. Nucl. Mat. 394 (2009) 1–8.
- [30] M. Trummer, O. Roth, M. Jonsson, J. Nucl. Mat. 383 (2009) 226-230.
- [31] D. Cui, J. Low, V.V. Rondinella, K. Spahui, Appl. Catal. B Environ. 94 (2010) 173–178.
- [32] K. Frey, K., J. Jerden, Multi-Domain Mixed Potential Model for Spent Fuel Dissolution, American Institute of Chemical Engineers, Annual Meeting, Conference Proceedings, Advances in Numerical Simulations Bridging Chemical and Nuclear Engineering Phenomena or Processes, 2012.
- [33] J. Jerden, K. Frey, T. Cruse, ANL Mixed Potential Model with Experimental Results: Implementation of Noble Metal Particle Catalysis Module, Prepared for U.S. Department of Energy Used Fuel Disposition Campaign, FCRD-UFD-2013-000305, September 10, 2013.
- [34] D.C. Sassani, J.C. Jove-Colon, P. Weck, J.L. Jerden, K.E. Frey, T. Cruse, W.L. Ebert, E.C. Buck, R.S. Wittman, F.N. Skomurski, K.J. Cantrell, B.K. McNamara, C.Z. Soderquist, Integration of EBS Models with Generic Disposal System Models, FCRD-UFD-2012-000277, SAND2012- 7762 P, 2012.
- [35] S. Rollin, K. Spahiu, U.B. Eklund, J. Nucl. Mater. 297, (2001) 231-243.
- [36] C.M. Bethke, S. Yeakel, The Geochemist's Workbench User's Guides, Version 10.0, Aqueous Solutions LLC, Champaign, Illinois, 2014.
- [37] T. Wolery, C. Jove-Colon, Qualification of Thermodynamic Data for Geochemical Modeling of Mineral–Water Interactions in Dilute Systems, Prepared for U.S. Department of Energy Office of Civilian Radioactive Waste Management Office of Repository Development, ANL-WIS-GS-000003 REV 01, June 2007.
- [38] A. Vinsot, S. Mettler, S. Wechner, Phys. Chem. Earth 33 (2008) S75–S86.

- [39] J. Guimerà, L. Duro, A. Delos, Changes in Groundwater Composition as a Consequence of Deglaciation Implications for Performance Assessment, Swedish Nuclear Fuel and Waste Management Co, SKB, R-06-105, November 2006.
- [40] H. He, M. Broczkowski, K. O’Neil, D. Ofori, O. Semenikhin, D. Shoesmith, A Review of Research Conducted under the Industrial Research Chair Agreement Between NSERC, NWMO and Western University (January 2006 to December 2010), NWMO TR-2012-09, May 2012.
- [41] D.W. Shoesmith, Used Fuel and Uranium Dioxide Dissolution Studies – A Review, Nuclear Waste Management Organization, Canada, NWMO TR-2007-03, 2007.
- [42] L.H. Johnson, D.W. Shoesmith. In W. Lutze , R. C. Ewing (Eds.), Radioactive Waste Forms for the Future, North-Holland, Amsterdam, 1988, pp. 645–657.
- [43] M. Jonsson, Radiation Effects on Materials Used in Geological Repositories for Spent Nuclear Fuel, International Scholarly Research Network, ISRN Materials Science Volume, Article ID 639520, doi:10.5402/2012/639520, 2012.
- [44] J.W.T. Spinks, R. J.Woods, An Introduction to Radiation Chemistry, John Wiley & Sons, New York, 3rd edition, 1990.
- [45] E. Buck, J. Jerden, W. Ebert, R. Wittman, Coupling the Mixed Potential and Radiolysis Models for Used Fuel Degradation, Prepared for U.S. Department of Energy Used Fuel Disposition Campaign FCRD-UFD-2013-000290, 2013.
- [46] MATLAB Release 2013b, MathWorks, Inc., Natick, MA, 2013.
- [47] L.W. Niedrach, Corrosion 47 (1991) 163-169.
- [48] M.I. Ojovan, W.E. Lee, An Introduction to Nuclear Waste Immobilization, Elsevier, Amsterdam, 2005.
- [49] J. F. Ziegler, M.D. Ziegler, J.P. Biersack, Nucl. Instr. Meth. Phys. Res. B 268 (2010) 1818–1823.
- [50] G. Radulescu, Repository Science/Criticality Analysis, Oak Ridge National Laboratory, Reactor and Nuclear Systems Division, FTOR11UF0334, ORNL/LTR-2011, August 2011.
- [51] F. Nielsen, M. Jonsson, J. Nucl. Mat. 359 (2006) 1-7.
- [52] R.S. Wittman, E.C. Buck, Sensitivity of UO₂ Stability in a Reducing Environment on Radiolysis Model Parameters, MRS Proceedings, Vol. 1444, Materials Research Society, 2012.

- [53] H. Christensen, S. Sunder, Current State of Knowledge in Radiolysis Effects on Spent Fuel Corrosion, Studsvik Material Report, STUDSVIK/M-98/71, 1998.
- [54] H.R. Greenberg, M. Sharma, M. Sutton, Investigations on Repository Near-Field Thermal Modeling, Used Fuel Disposition Campaign, LLNL-TR-609935, January 11, 2013.
- [55] F. Nielsen, K. Lundahl, M. Jonsson, J. Nucl. Mater. 372 (2008) 32–35.
- [56] M. Kelm, E. Bohnert, A Kinetic Model for the Radiolysis of Chloride Brine, Its Sensitivity Against Model Parameters and a Comparison with Experiments, Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft, Wissenschaftliche Berichte, FZKA 6977, April 2004.
- [57] J.J.T.T. Vermeijien, L.J.J. Janssen, G.J. Visser, J. Appl. Electrochem. 27 (1997) 497-506.
- [58] K. Kinoshita, Electrochemical Oxygen Technology, John Wiley, New York, Chapter 2, 1992.
- [59] E. Ekeröth, M. Jonsson, T. E. Eriksen, K. Ljungqvist, S. Kovacs, I. Puigdomenech, J. Nucl. Mater. 334 (2004) 35–39.
- [60] J. Bruno, I. Casas, I. Puigdomenech, Geochim. Cosmochim. Acta 55 (1991) 647–658.
- [61] J. Takagi, K. Ishigure, Nucl. Sci. Eng. 89 (1985) 177-186.
- [62] K.H. Gayer, L.C. Thompson, Can. J. Chem. 36 (1958) 1649-1652.
- [63] K. Kubatko, K.B. Helean, A. Navrotsky, P.C. Burns, Science 302 (2003) 1191-1193.
- [64] B.D. Hanson, B. McNamara, E.C. Buck, J.I. Friese, E. Jenson, K. Krupka, B.W. Arey, Radiochim. Acta 93 (2005) 159–168.
- [65] S. Planteura, M. Bertranda, E. Plasarib, B. Courtaudc, J. P. Gaillarda, Procedia Chem. 7 (2012) 725 – 730.
- [66] S. Kerisit, C. Liu, Geochim. Cosmochim. Acta 74 (2010) 4937-4952.
- [67] H. Christensen, S. Sunder, J. Nucl. Mater. 238 (1996) 70-77.
- [68] Y. Marcus, Ion Properties, Marcel Dekker, New York, 1997.
- [69] D. Langmuir, Aqueous Environmental Geochemistry, Prentice Hall, Upper Saddle River, NJ, 2007.
- [70] F. Clarens, J. de Pablo, I. Casas, J. Giménez, M. Rovira, J. Merino, E. Cera, J. Bruno, J. Quiñones, A. Martínez-Esparza, J. Nucl. Mater. 345 (2005) 225–231

- [71] J. de Pablo I. Casas, J. Giménez, M. Moleraa, M. Rovira, L. Duro, J. Bruno, *Geochimica et Cosmochimica Acta*, 63, (1999) 3097–3103.
- [72] I. Casas, J. de Pablo, F. Clarens, J. Giménez, J. Merino, J. Bruno, A. Martinez-Esparza, *Radiochim. Acta*, 97, (2009) 485–490.
- [73] S. Stroes-Gascoyne, F. Garisto, J.S. Betteridge, *J. Nucl. Mater.* 346 (2005) 5-15.
- [74] J.C. Tait, J.M Luht, Dissolution rates of uranium from unirradiated UO₂ and uranium and radionuclides from used CANDU fuel using the single-pass flow-through apparatus. Ontario Hydro Report No: 06819-REP-01200-0006-R00, 1997.
- [75] S.A. Steward, H.C. Weed, *Mat. Res. Soc. Symp. Proc.* Vol. 333, A Barkatt and R A Van Konynenburg, eds., (1994) 409–416,
- [76] W.J. Gray, H.R. Leider, S.A. Steward, *J. Nucl. Mat.* 190 (1992) 46–52.

Figure 1. Eh vs. pH (Pourbaix) diagram for 1 mM total uranium over a pH range for typical clayrock/shale and crystalline rock groundwaters. Black circles show Eh-pH values of groundwaters from crystalline rock at the Forsmark site, Sweden [38]; the crystalline rock at the Grimsel test site, Switzerland [38]; and claystone at the Callovo-Oxfordian site, France [39]

Figure 2. Concentration vs. Eh diagram for 1 mM total uranium and 1 mM total carbonate for pH 7 (left) and pH 10 (right). The Eh units are volts vs. SHE. These plots show the dominant aqueous species and indicate the solubility of the key mineral phases: a = $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, b = $\text{UO}_2(\text{CO}_3)_2^{2-}$, c = $\text{UO}_2(\text{OH})_2(\text{aq})$, d = $\text{UO}_2\text{CO}_3(\text{aq})$, e = $\text{UO}_2(\text{CO}_3)_3^{4-}$, f = $\text{UO}_2(\text{OH})_3^-$.

Figure 3. Schematic diagram summarizing the flow of electrons to and from key oxidation and reduction reactions included in the FMDM. The NMP is assumed to be electrically coupled to the fuel matrix.

Figure 4. Summary of the FMDM reaction current paths and model layout without (top) and with (bottom) a surface layer. The bracketed letters in the top diagram correspond to the reactions in Table 1. The complete lists of interfacial and bulk reactions are given in Tables 1 and 2, respectively.

Figure 5. Dose rate profile within the irradiated zone (alpha penetration zone) used in FMDM assuming a fuel surface dose of 1 Gy s^{-1} . The function used is based on the geometrical alpha dose profile presented in Ref. [51]. The bottom plot shows examples of H_2O_2 concentration profiles with and without the U(VI) precipitate layer. Diffusion within the layer is slowed by tortuosity, leading to an accumulation of H_2O_2 within the 10–30 μm of the fuel surface.

Figure 6. FMDM-calculated (a) corrosion potential, (b) fuel dissolution rate, and (c) absolute current density as function of peroxide concentration on the fuel surface. Experimental values added for comparison. To produce the range of H_2O_2 values, the dose rate at the fuel surface was varied from 1×10^{-3} to $1 \times 10^3 \text{ Gy s}^{-1}$, while the temperature was constant at 25°C , and the initial dissolved concentrations of oxygen, hydrogen, carbonate, and iron were set at $1 \times 10^{-9} \text{ M}$.

Figure 7. Comparison of FMDM-predicted fuel dissolution rate trends with experimental trends as a function of (a) total carbonate concentration at 25°C and (b) temperature at carbonate concentration of 1 mM. For these runs the dissolved concentrations of oxygen, hydrogen, and iron were $1 \times 10^{-9} \text{ M}$, and the dose rate was 0.01 Gy s^{-1} .

Figure 8. Results from FMDM for (a) corrosion potential, (b) fuel dissolution rate, and (c) absolute current density at isothermal (25°C) conditions with a constant dose rate of 1 Gy s^{-1} and increasing dissolved concentration of H_2 . The data points shown in (a) assume a Henry's law constant for H_2 in water of $7.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$ [7]. The Fe(II) curve in (b) shows how the concentration of $[\text{Fe}^{2+}]$ (on x-axis) depresses the fuel dissolution rate. Data in (b) are from Rollin et al. [35], who measured UO_2 dissolution rates in solutions bubbled with H_2 ($\sim 0.78 \text{ mM}$ dissolved H_2) and 0.03% CO_2 over Pt foil at pH 8–9.5.

Figure 9. (a) Fuel surface dose rate and (b) temperature histories used in examples of 100,000-year FMDM simulations. The dose rate history (a) is a power law fit to Nielsen and Jonsson's [51] table of average alpha dose rates for a 55 MWd kg⁻¹ fuel for different times. The dose rate decreases to near zero over the 35- μ m irradiation zone according the curve shown in Figure 5a. The temperature history (b) is a power law fit to the cooling calculations for a 60 MWd kg⁻¹ fuel in a hypothetical granite repository presented by Greenberg [54].

Figure 10 Calculated results from FMDM for (a) corrosion potential, (b) fuel dissolution rate, and (c) absolute current density at isothermal conditions (25°C) with dose rate history shown in Figure 9a.

Figure 11. Calculated FMDM results as function of time for (a) fuel dissolution rate for six simulation runs described in text and (b) absolute current density for run with 1 mM carbonate and 1 μ M hydrogen. The temperature and dose rate decrease with time according to the histories shown in Figure 9.

Table 1. Interfacial half reactions used in the FMDM.

	Reactions on Fuel Surface	Log K_{eq}	Equilibrium Potentials (E^0) (V_{SHE})	Temperature Dependence of E^0	Charge Transfer Coefficients	Interfacial Rate Constants
A	$UO_2^{fuel} \rightarrow UO_2^{2+} + 2e^-$	-15.3283	0.453	$0.0011T + 0.1132$	0.96	$5.0E-08$
B	$UO_2^{fuel} + 2CO_3^{2-} \rightarrow UO_2(CO_3)_2^{2-} + 2e^-$	1.5716	0.046	$3.0E-6T^2 + 0.0011T - 0.0831$	0.82	$1.3E-08$
C	$UO_2^{fuel} + 3CO_3^{2-} \rightarrow UO_2(CO_3)_3^{4-} + 2e^-$	6.217	0.184	$5.0E-6T^2 + 0.0024T - 0.5032$	0.82	$1.3E-08$
D	$H_2(aq) \rightarrow 2H^+ + 2e^-$	1.6555	0.049	$-0.002T^2 - 0.0104T + 0.0767$	0.50	$3.6E-12$
E	$H_2O_2 \rightarrow O_2(aq) + 2H^+ + 2e^-$	24.9277	0.737	$-4E-07T^2 + 0.0001T + 0.7287$	0.41	$7.4E-08$
F	$H_2O_2 + 2e^- \rightarrow 2OH^-$	33.0861	0.979	$-3E-06T^2 + 0.0013T + 0.8588$	-0.41	$1.2E-12$
G	$O_2(aq) + 2H_2O + 4e^- \rightarrow 4OH^-$	30.0235	0.444	$-3E-06T^2 + 0.0013T + 0.3543$	-0.50	$1.4E-12$
Reactions on Noble Metal Particles Surface						
H	$H_2(aq) \rightarrow 2H^+ + 2e^-$	1.6555	0.049	$-0.002T^2 - 0.0104T + 0.0767$	0.50	$1.0E-06$
I	$H_2O_2 \rightarrow O_2(aq) + 2H^+$	24.9277	0.737	$-4E-07T^2 + 0.0001T +$	0.41	$7.0E-06$

	+ 2e ⁻			0.7287		
J	H ₂ O ₂ + 2e ⁻ → 2OH ⁻	33.0861	0.979	-3E-06T ² + 0.0013T + 0.8588	-0.41	1.2E-10
K	O ₂ (aq) + 2H ₂ O + 4e ⁻ → 4OH ⁻	30.0235	0.444	-3E-06T ² + 0.0013T + 0.3543	-0.50	1.4E-10
Chemical Dissolution Reaction						
L	UO ₂ ^{Fuel} + 2H ₂ O → U(OH) ₄ (aq)	-53.621	----	----	----	1.9E-12

Note: The log K_{eq}, E^o, and temperature dependencies were calculated using “the Geochemist’s Workbench” [36], with the thermochemical database “data0.ymp.R5” [37]. The charge transfer coefficients are from King and Kolar [14], except for the H₂ reaction, which is from Ref. [57]. The interfacial rate constants have the following units: mole m⁻² s⁻¹ (reactions A-C), m³ mol⁻¹ s⁻¹ (for reaction D), and m s⁻¹ for reactions (E–L). Due to a lack of experimentally determined values, the activation energies for the rate constants (ΔH) are set as 6.0 x 10⁴ J kg⁻¹: this is a commonly measured value for these types of chemical reactions [58]. The rate constants for reactions A, B, and E-G are from Ref. [14]; the rate constant for reaction C is assumed to be the same as reaction B. The rate constants for reaction D, H, and L are based on the results of Refs. [29, 59, 60], respectively. Rate constants for I, J, and K have not yet been measured; however, based on general comparisons with noble metal and oxide catalysts, these values were assumed to be a factor of 200 greater than the corresponding constants on the oxide surface.

Table 2. Precipitation/dissolution and bulk solution reactions included in the FMDM.

	Precipitation/Dissolution and Bulk Reactions	Log K _{eq}	Rate Constant
M	$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_3 \cdot 2\text{H}_2\text{O} + 2\text{H}^+$	-4.844	1.0E-3 (s ⁻¹)
N	$\text{UO}_2^{2+} + \text{H}_2\text{O}_2 + 4\text{H}_2\text{O} \rightarrow \text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+$	2.873	1.0E-3 (s ⁻¹)
O	$\text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{H}_2\text{O} \rightarrow \text{UO}_3 \cdot 2\text{H}_2\text{O} + 2\text{CO}_3^{2-} + 2\text{H}^+$	-21.744	1.0E-4 (s ⁻¹)
P	$\text{UO}_2(\text{CO}_3)_2^{2-} + 4\text{H}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+ + 2\text{CO}_3^{2-}$	-14.027	1.0E-4 (s ⁻¹)
Q	$\text{UO}_3 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + 2\text{H}_2\text{O}$	4.844	8.6E-7 (mol m ⁻³ s ⁻¹)
R	$\text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O}_2 + 4\text{H}_2\text{O}$	-2.8723	8.6E-7 (mol m ⁻³ s ⁻¹)
S	$\text{UO}_3 \cdot 2\text{H}_2\text{O} + 2\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{H}_2\text{O}$	21.744	8.6E-6 (mol m ⁻³ s ⁻¹)
T	$\text{UO}_2\text{O}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}^+ + 2\text{CO}_3^{2-} \rightarrow \text{UO}_2(\text{CO}_3)_2^{2-} + 4\text{H}_2\text{O} + \text{H}_2\text{O}_2$	14.027	8.6E-6 (mol m ⁻³ s ⁻¹)
U	$\text{H}_2\text{O}_2 + 2\text{Fe}^{2+} + 4\text{OH}^- \rightarrow 3\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	90.926	6.9E-2 (m ³ mol ⁻¹ s ⁻¹)
V	$\text{O}_2 + 4\text{Fe}^{2+} + 8\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 2\text{Fe}_2\text{O}_3$	145.703	5.9E-1 (m ³ mol ⁻¹ s ⁻¹)
W	$\text{UO}_2^{2+} + 2\text{Fe}^{2+} + 6\text{OH}^- \rightarrow \text{UO}_2^{\text{precip}} + 3\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	73.168	1.0E-2 (m ³ mol ⁻¹ s ⁻¹)
X	$\text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{Fe}^{2+} + 6\text{OH}^- \rightarrow \text{UO}_2^{\text{precip}} + 2\text{CO}_3^{2-} + 3\text{H}_2\text{O} + \text{Fe}_2\text{O}_3$	56.268	1.0E-3 (m ³ mol ⁻¹ s ⁻¹)
Y	$\text{H}_2\text{O}_2 \rightarrow 0.5\text{O}_2 + \text{H}_2\text{O}$	18.074	4.5E-7 (s ⁻¹)

Note: The log K_{eq} were calculated using “the Geochemist’s Workbench” [36], with the thermochemical database “data0.ympr.R5” [37]. Due to a lack of experimentally determined values, the activation energies for the rate constants (ΔH) are set as 6.0 x 10⁴: this is a commonly measured value for these types of chemical reactions [58]. All rate constants are from Ref. [14], except for reaction Y, which is from Ref. [61]. The rate constants for reactions N, P, R, and T are assumed to be the same as M, O, Q, and S from Ref. [14], based on relatively rapid precipitation and dissolution kinetics (similar to schoepite) as observed in a number of experiments (e.g., Refs. [62 – 65]).

Table 3. Diffusion coefficients and saturation concentrations used in the FMDM.

Reactive species	UO_2^{2+}	$\text{UO}_2(\text{CO}_3)_2^{2-}$	$\text{U}(\text{OH})_4(\text{aq})$	CO_3^{2-}	$\text{O}_2(\text{aq})$	H_2O_2	Fe^{2+}	$\text{H}_2(\text{aq})$
Diffusion coeff. (m^2/s)	7.59E-10	6.67E-10	6.00E-10	8.12E-10	2.50E-09	1.90E-09	7.19E-10	6.00E-09
Saturation conc. (mol/L)	1.0E-5	1.0E-4	4.0E-10	----	----	----	5.0E-06	----

Note: Sources for diffusion coefficients: uranium and carbonate species are from Ref. [66]; O_2 , H_2O_2 and H_2 are from Ref. [67]; and $\text{Fe}(\text{II})$ is from Ref. [68]. The saturation concentrations were calculated using “the Geochemist’s Workbench” [36], with the thermochemical database “data0.ympr.R5” [37]. Due to a lack of experimentally determined values, the activation energies (ΔH) for the diffusion coefficients and saturation concentrations are set at $1.5 \times 10^4 \text{ J kg}^{-1}$ and $6.0 \times 10^4 \text{ J kg}^{-1}$, respectively: these are commonly measured values for these types quantities (e.g., Ref. [69]).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Graphical abstract