

***Fuel Matrix Degradation
Model: Integration with
Performance Assessment
and Canister Corrosion
Model Development***

Used Fuel Disposition

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

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SUMMARY

This work is being performed as part of the DOE NE Used Fuel Disposition (UFD) Campaign Argillite and Crystalline Rock R&D work packages: FT-15AN080601 and FT-15AN080701. This document meets the July 21, 2015 milestone M4FT-15AN0806016 for Argillite R&D and the July 21, 2015 milestone M4FT-15AN0807016 for Crystalline R&D.

The main accomplishments for Argonne's FY2015 work on the Fuel Matrix Degradation Model (FMDM) development project are as follows:

- Completed a model validation study in which results from the state of the art FMDM were compared to experimental data from international geologic repository programs. This study was published in the Journal of Nuclear Materials: "A Multiphase Interfacial Model for the Dissolution of Spent Nuclear Fuel" by J. Jerden, K. Frey and W. Ebert, Volume 462, July 2015, Pages 135-146.
- Completed conversion of the state of the art FMDM (version 2.3) to Fortran to facilitate integration with the Generic Disposal System Analysis (GDSA) repository Performance Assessment (PA) code PFLOTRAN: *Mixed Potential Model for Used Fuel Dissolution-Fortran Code*. FCRD-UFD-2015-000159.
- Worked with SNL scientists to complete and test a prototype integrated PFLOTRAN-FMDM repository model.
- Completed preliminary model runs focused on expanding the FMDM to account for corrosion of the used fuel steel canister.
- Completed scoping experiments investigating the possible poisoning of the Noble Metal Particles (NMP), which are known to catalyze the oxidation of H₂, thus shutting down the oxidative dissolution of used fuel.

The current version of the FMDM has proven effective for quantifying key processes affecting the rate of used fuel degradation; however, the implementation of FMDM within a performance assessment model requires further model development to account for steel corrosion and the possible poisoning of the NMP phase, which is responsible for the protective H₂ effect. Focused experiments are also needed quantify key parameter values and provide data sets for model validation. In order to take advantage of the work that has been done so far on the FMDM, a number of needs have been identified:

- Take next step in integration of FMDM with PFLOTRAN: demonstrate sensitivity of the Crystalline and Argillite PA models to key variables in the FMDM such as burnup, surface area and the dissolved concentrations of H₂, O₂, carbonate and ferrous iron.
- Extend the FMDM to account for the corrosion of the steel waste canister. This will quantify feedbacks between H₂ production at the corroding steel surface and the dissolution rate of the used fuel.

- Perform focused electrochemical experiments to determine the effect of halides and other possible poisons on the catalytic efficiency of the NMP. These tests will quantify processes that may counteract the protective H₂ effect.

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ACRONYMS

DOE	U.S. Department of Energy
FEPs	features, events, and processes
ICPMS	Inductively coupled plasma mass spectrometry
ORNL	Oak Ridge National Laboratory
PA	performance assessment
R&D	Research and development
SNF	spent nuclear fuel
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
UFD	Used Fuel Disposition Campaign
UNF	used nuclear fuel
MCNPX	Monte Carlo N-Particle eXtended

1.0 INTRODUCTION AND OBJECTIVE

The importance of used nuclear fuel (UNF) degradation in a repository safety case is that the fuel itself is the initial and primary barrier in a multiple-barrier waste isolation system that must be represented in a quantitative safety analysis. The fuel degradation rate is used directly to calculate radionuclide source term values in the safety analysis reactive-transport model. High confidence in the performance of the sequential barriers used in the safety case requires an accurate representation of the source term due to fuel degradation and coupling with repository engineered barriers and near-field components of repository-scale transport models. The impact of waste form degradation on the safety analysis could depend on the geologic environment owing to the expected interactions during the relevant performance period and importance of the ground water composition on the fuel dissolution rate (dissolved oxygen and hydrogen, ligands affecting dissolved concentration limits, secondary phase, etc.).

The objective of this project is to develop and implement a fundamentals-based process model for the degradation rate of used fuel that can be readily incorporated into the Generic Disposal System Analyses (GDSA) Performance Assessment (PA) code. This model, referred to as the Fuel Matrix Degradation Model (FMDM), was initially based on the Canadian Mixed Potential Model (King and Kolar, 2003), but has since been expanded and customized for the ongoing UFD Argillite and Crystalline rock disposal projects.

The continued development and implementation of the FMDM addresses two high level Features, Events, and Processes (FEPs) that are recognized as high R&D priorities for the UFD (Wang et al., 2014). The FEPs addressed by this model are 2.1.02 (waste form) and 2.1.03 (waste container), which correspond to the high priority research topics P19 (Development of waste form degradation model) and P20 (Development of new waste package concepts and models for evaluation of waste package performance for long-term disposal) identified by Wang et al., 2014.

The FMDM calculates the dissolution rate of used fuel based the interfacial corrosion potential (E_{corr}) determined by the kinetic balance between anodic and cathodic half reactions at the fuel/solution boundary. The dissolution rate is relatively fast under oxidizing conditions (high E_{corr}) but decreases dramatically at E_{corr} values lower than the U(IV)/U(VI) threshold (where solubility based, chemical dissolution is dominant). The FMDM accounts for:

- the generation of radiolytic oxidants based on fuel burn-up,
- the catalyzed oxidation of H_2 , which protects the fuel from oxidative dissolution,
- the precipitation of secondary phases,
- the complexation of uranyl by carbonate,
- the oxidation of ferrous iron,
- temperature variations (by Arrhenius equations),
- the one-dimensional diffusion of all chemical species.

Of these processes, the catalysis of H_2 oxidation on Nobel Metal Particles (NMP) on the fuel surface and the generation rate of radiolytic oxidants (determined by dose rate, which is related to fuel burn-up) are the most important for determining the degradation rate of the fuel (Jerden et al., 2015).

The dissolution rate calculated by the FMDM accounts for oxidation of the fuel by radiolytic H_2O_2 (and decomposition product O_2) the concentration of which is calculated using an analytical form of the radiolysis model developed at PNNL (Buck et al., 2014) and the burn-up/dose rate function described in Section 2 of this report. Fuel oxidation is counteracted by the catalytic oxidation of H_2 on NMP sites that are present on the fuel surface as a distinct phase. The dominant source of H_2 in the repository will be from the anoxic corrosion of steel (Shoesmith, 2008).

As discussed in Section 3 below, the FMDM is being extended to include steel corrosion thus providing a realistic kinetic source of H_2 for key interfacial reactions. It was shown in Jerden et al., 2015 that the FMDM accurately reproduces the experimental observation that relatively low concentrations of dissolved H_2 ($\sim 0.1\text{mM}$) can completely inhibit the oxidative dissolution of the fuel. In the absence of oxidative dissolution, the fuel degrades by solubility based, chemical dissolution, which is over 4 orders of magnitude slower than oxidative dissolution (Röllin et al., 2001). The FMDM accounts for the surface area of the NMPs and is being extended to account for the effects of species that may poison the catalytic effects of the NMP (see Section 4 below).

The key processes currently accounted for in the FMDM as well as the processes that are to be added in FY 2016 are summarized in Figure 1.

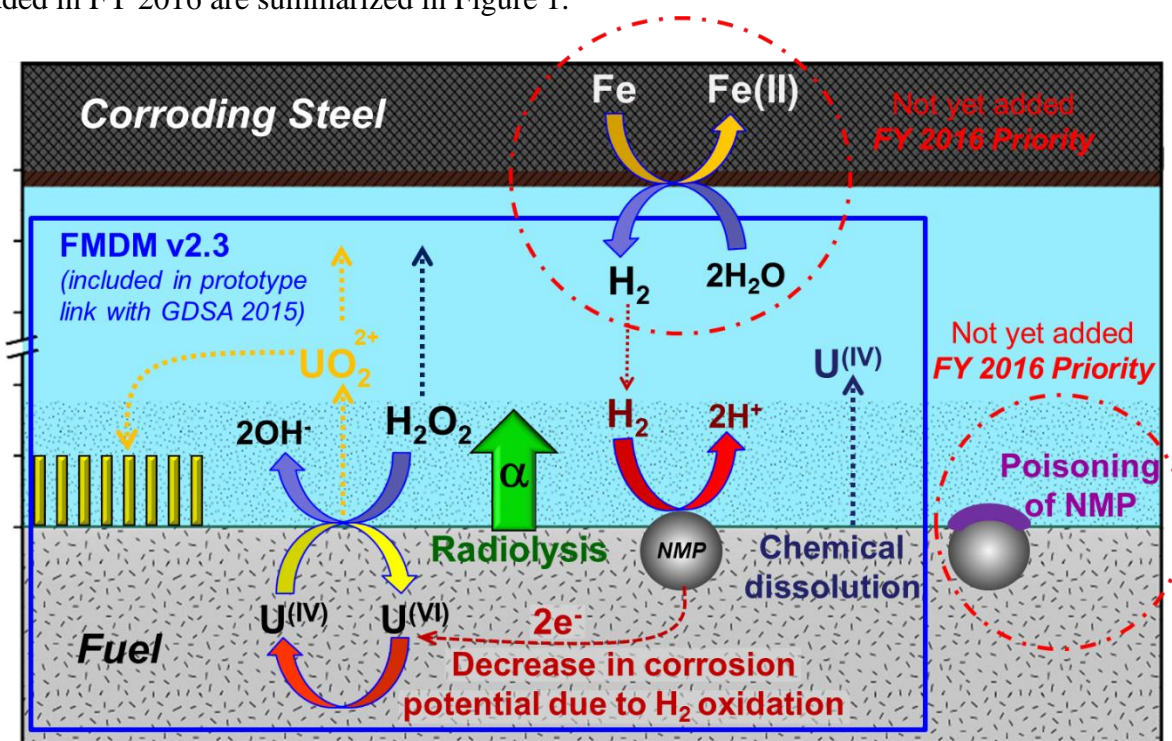


Figure 1. Conceptual diagram identifying the key dissolution rate-determining processes in the FMDM and highlighting the FY 2016 priorities.

2. FUEL MATRIX DEGRADATION MODEL DEVELOPMENT AND INTEGRATION WITH PFLOTRAN

This section documents model development work that focused on integrating the FMDM with the GDSA PA reactive transport code PFLOTRAN. This involved the conversion of the FMDM from MATLAB to Fortran and the addition of an analytical function that calculates the dose rate at the fuel surface based on a user specified fuel burnup and fuel age (out of reactor). The Fortran version of the FMDM was integrated with PFLOTRAN to produce a prototype PFLOTRAN-FMDM working model. This integrated code was demonstrated for a scaled-down and simplified repository example, which is described in Section 2.3 below.

2.1 Conversion of FMDM from MATLAB to Fortran

The first Fortran version of the FMDM [previously referred to as the Mixed Potential Model (MPM)], was completed and distributed to the GDSA team in October 2014 as version number 2.0 and is documented in Jerden et al., 2014. Versions 2.1 and 2.2 were produced and used internally at Argonne but were not distributed. The Fortran FMDM version 2.3 was distributed to the GDSA team in March 2015. The new features of version 2.3 are described in this report.

One of the major changes is that the Fortran FMDM version 2.3 returns the fuel dissolution rate (`fuelDisRate`) in $\text{g m}^{-2} \text{y}^{-1}$ rather than a matrix of fluxes (as the previous version did). This fuel dissolution rate is equal to the sum of the three interfacial fluxes of uranium leaving the fuel surface: uranyl ion, uranyl tricarbonate and aqueous U(IV) (labeled `UO2_2p`, `UCO3_2n`, `UO2` in the code).

The other major addition to the FMDM v2.3 is that the dose rate at the fuel surface, which determines the generation rate of radiolytic oxidants, is calculated internally rather than provided as an input to the model. This is accomplished through an analytical dose rate – burnup function that was derived by fitting the burnup – dose rate – age of fuel data of Radulescu 2011 (discussed in Section 2.2 below).

The original Fortran FMDM was converted from MATLAB to Fortran 90 for integration with the PFLOTRAN code. The only external library used was LAPACK for its linear algebra solver “dgesv” (LAPACK 3.5.0 Windows 32-bit static library). This conversion was a line by line translation of the original MATLAB code. A single call to the FMDM version 2.3 Fortran code requires a call to the subroutine “AMP_step” whose interface is shown below.

```
interface
  subroutine AMP_step ( sTme, conc, initialRun, fuelDisRate, status )
    real ( kind = 8), intent( in ) :: sTme
    real ( kind = 8), intent( inout ), dimension (:,:) :: conc
    logical ( kind = 4), intent( in ) :: initialRun
    real ( kind = 8), intent(out) :: fuelDisRate
    integer ( kind = 4), intent(out) :: status
  end subroutine
end interface
```

The first time the code is called, initialRun must be set to “.true.” and the contents of the concentration matrix “conc” are ignored. In this case, the initial concentrations are defaulted to the values returned by the subroutine “enVals” in file “AMP_class.f90”. In subsequent calls to “AMP_step”, the concentration from the previous AMP_step call must be preserved and used as input to the current AMP_step call.

There are eleven components followed by the FMDM version 2.3 Fortran code and the order is defined in the file “AMP_compList.inc”. The first dimension of the concentration matrix is in this order.

UO2_2p	[symbol for UO_2^{2+}]
UCO3_2n	[symbol for $\text{UO}_2(\text{CO}_3)_2^{2-}$]
UO2	[symbol for $\text{UO}_2(\text{aq})$]
CO3_2n	[symbol for CO_3^{2-}]
O2	[symbol for $\text{O}_2(\text{aq})$]
H2O2	[symbol for H_2O_2]
Fe_2p	[symbol for Fe^{2+}]
H2	[symbol for $\text{H}_2(\text{aq})$]
UO2_s1d	[symbol for U(IV) oxide precipitate]
UO3_s1d	[symbol for U(VI) oxide hydrate precipitate]
UO4_s1d	[symbol for U(VI) peroxide precipitate]

Figure 2 identifies the basic order of calculations within the FMDM, identifies the inputs and outputs from and to PFLOTRAN and indicates the new features of v2.3. This Fortran version of the FMDM has been coupled with PFLOTRAN to form a prototype working integrated model as discussed in Section 2.3 below.

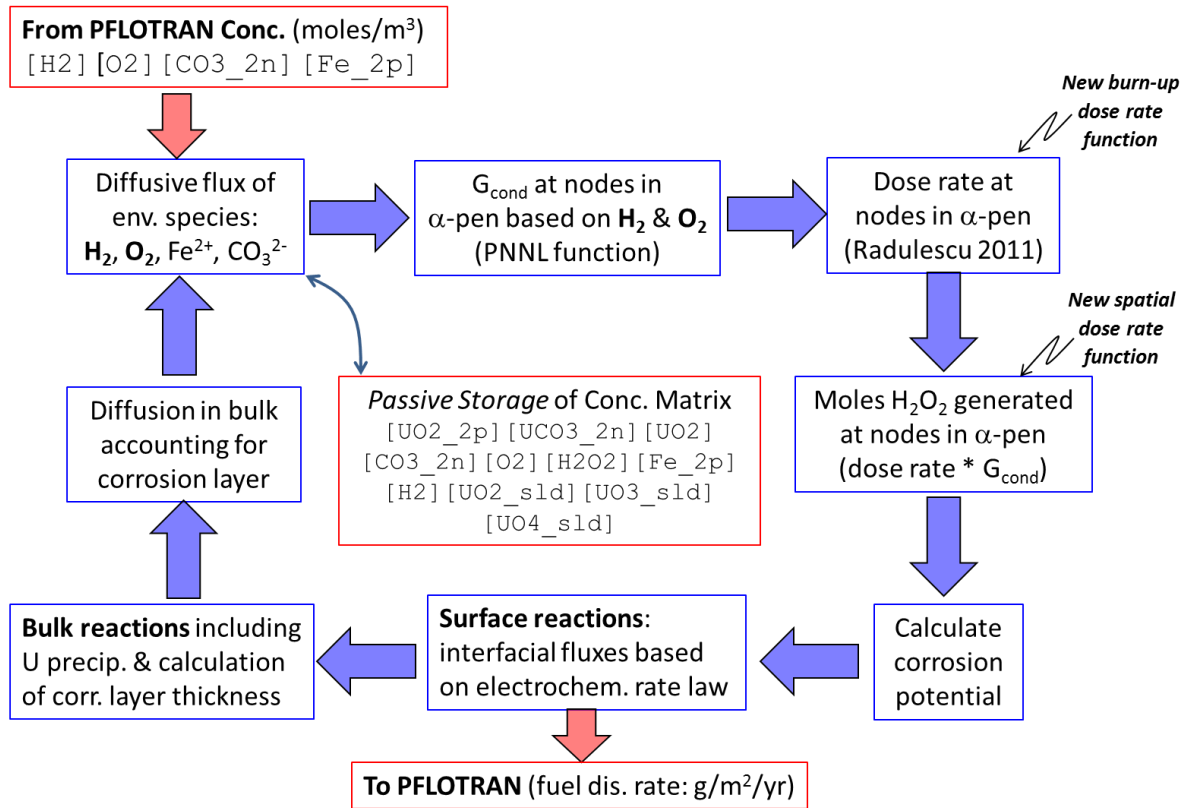


Figure 2. Conceptual flow diagram showing the individual calculations within a single time step of the FMDM. Note that the concentrations of all components must be stored and fed back to the FMDM at the beginning of each new time step. G_{cond} refers to the conditional generation value for H₂O₂, which determines the peroxide generation rate within the alpha radiation zone (α-pen). In the FMDM v.2.3 the conditional H₂O₂ generation value is calculated by an analytical function. (G_{cond} is a function of [H₂] and [O₂]) derived from sensitivity runs of the PNNL radiolysis model (Buck et al., 2014).

2.3 Summary of Technical Changes Made to the FMDM Incorporated into Version 2.3

The following changes are incorporated into the Fortran version 2.3 of the FMDM:

- The does rate function (dose rate as a function of time) was replaced by a function derived from the MCNPX results of Radulescu 2011. The new function calculates the dose rate at the fuel surface as a function of time based on the assumed average burnup of the fuel. The new function is described in Figures 3 and 4.
- The spatial dose rate function, which calculates the dose rate at nodes within the alpha radiation penetration zone (35 micrometers), was replaced with a new function derived from the MCNPX results of Radulescu 2011. The new function is described in Figure 5.

The following is an example section of code showing both the burnup – dose rate function and the spatial dose rate function based on Radulescu 2011. The MATLAB code is shown for clarity – the Fortran implementation is identical except for syntax differences.

```
BU = 60; %Fuel burnup in GWd/MTU
dect = 30; %Decay time of fuel in yr
aof = t/60/60/24/365+dect; %Age of fuel yr

%Relationship between age of fuel, burnup and dose rate (rad0)
%Simple fit from Radulescu 2011 report
f1=log(aof)*log(aof);
f2=log(aof);
f3=1.0/log(aof);
f4=log(aof)/aof;
f5=exp(BU/25.26892627636246);
rad0a = -206.0634818750711-0.7631591788870090*f1...
        +20.97112373957833*f2+678.8463343193430*f3...
        -506.7149017370657*f4+0.1555448893425319*f5;
rad0 = max(exp(rad0a),5.0e-3);

%Constant dose rate option
%rad0 = 1.0; % (J/kg)/s = Gy/s = 100 rad/s

%Dose rate profile with x
rCut = exp(-0.14*(lmat*1.0e6)); %Exponential from Radulescu 2011
%rCut = (max(1 - lmat./penD, 0)); %Linear decrease
%rCut = lmat <= penD; %Step function

rad = rad0.*rCut; %Dose rate used to determine H2O2 generation
```

Simple Fit to Radulescu 2011
Function: $\ln z = a + b(\ln x)^2 + c \ln x + d / \ln x + e \ln x / x + f e^{y/wy}$
 $r^2 = 0.9973546$ DF Adj $r^2 = 0.99680728$ FitStdErr = 0.017963849 Fstat = 2262.0877
 $a = -206.06348$ $b = -0.76315918$ $c = 20.971124$
 $d = 678.84633$ $e = -506.7149$ $f = 0.15554489$

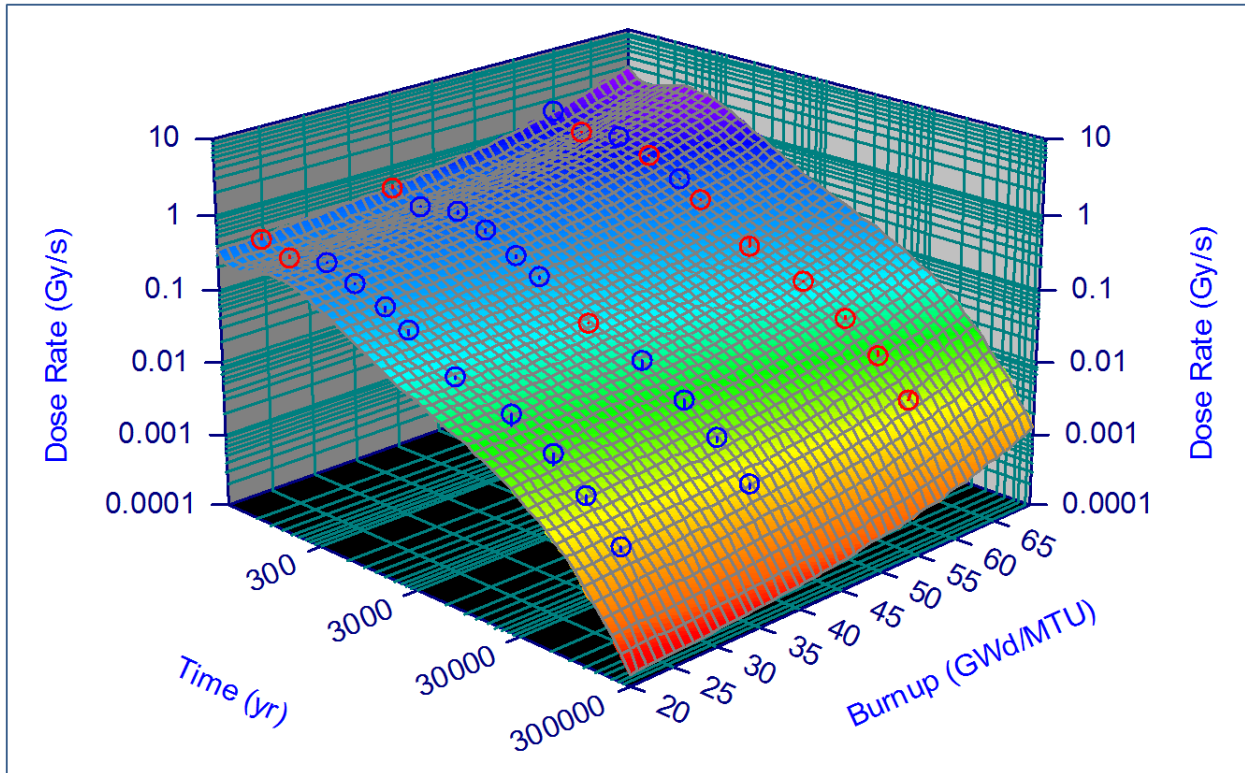


Figure 3. The burnup – dose rate function derived from the MCNPX results of Radulescu 2011 as a polynomial fit. The calculation points from Radulescu 2011 are shown as blue and red circles. Blue indicates that the data point falls below the fit surface and red indicates that the data point is above the fit surface. The derived function is shown as the surface: $x = \text{time}$, $y = \text{burnup}$, $z = \text{dose rate}$, where a , b , c , d , e , f and w are all fitting parameters.

Figure 4 shows a comparison between the new burnup – dose rate function and the MCNPX results of Radulescu, 2011. This figure also shows a comparison between results from the MATLAB version of the FMDM (thin blue line) and the Fortran version (thick red line). This comparison indicates that the Fortran FMDM code accurately reproduces results from the MATLAB FMDM code, which has been validated against experimental data (Jerden et al., 2015).

The results shown in Figure 4 indicate that the burnup – dose rate function accurately reproduces the MCNPX results from Radulescu 2011 and that the Fortran and MATLAB versions of the FMDM produce essentially identical results. It is noted that the increase in dose rate from 100 – 200 years in Figure 4 corresponds with the ingrowth of Am-241.

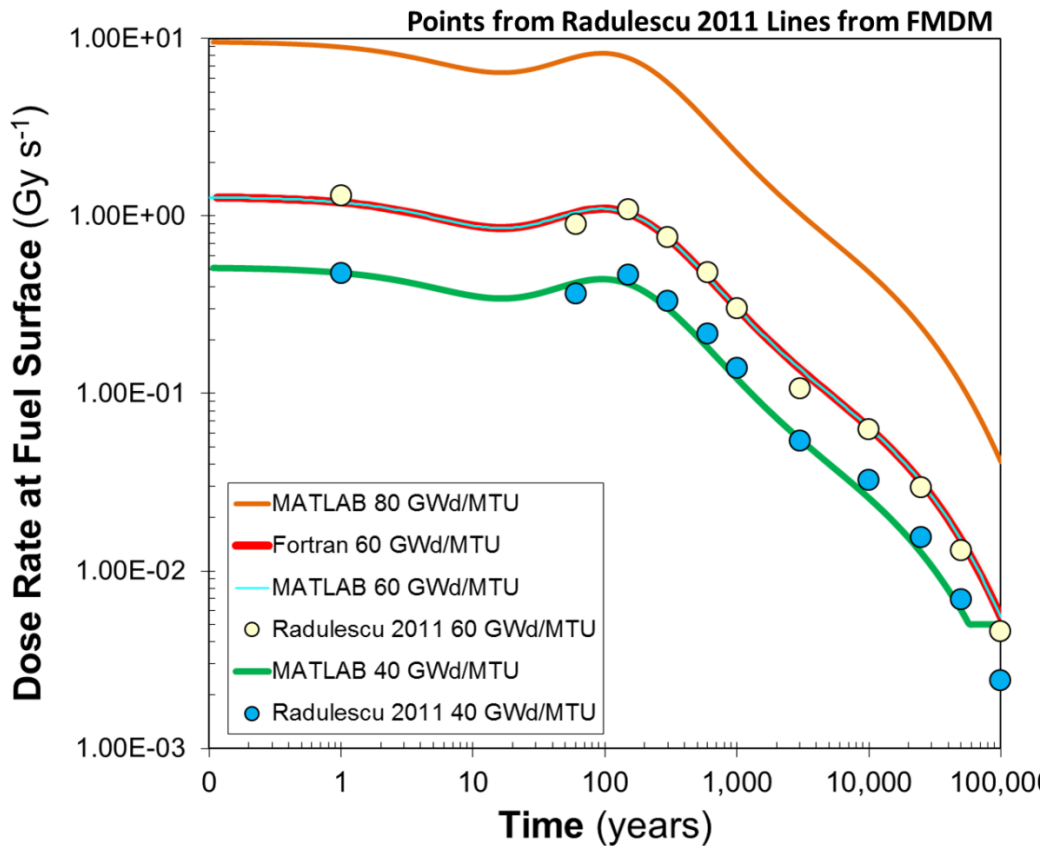


Figure 4. shows three types of results: (1) points from Radulescu 2011, (2) dose rate with time from an example simulation with the Fortran FMDM for 60 GWd/MTU (red), (3) dose rate with time from an example simulation with the MATLAB FMDM for 40, 60 and 80 GWd/MTU.

Figure 5 compares results from the new spatial dose rate function, which calculates the dose rate at each node within the alpha radiation zone, with the MCNPX of Radulescu 2011. The actual function in the code is:

$$\text{Spatial Dose Rate (Gy/hr at } x) = \text{Surface Dose Rate (Gy/hr)} * \exp[-0.14*(x (m)*1.0E+6)]$$

The results shown in Figure 5 indicate that the spatial dose rate function in the FMDM reasonably represents the spatial dose rate calculations of Radulescu 2011.

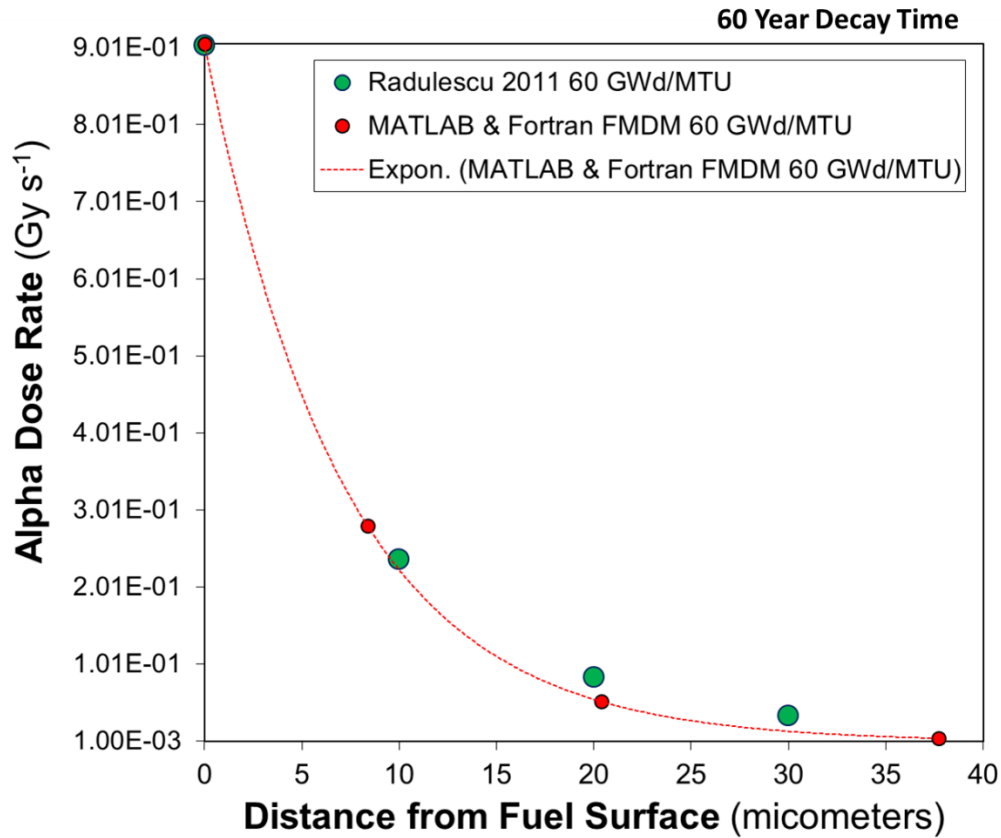


Figure 5. The alpha particle dose rate as a function of distance from the fuel surface. The red line is from example simulations with both the MATLAB and Fortran versions of the FMDM. The green points are from MCNPX calculations presented in Radulescu 2011.

Figure 6 shows direct comparisons of results from the FMDM MATLAB and Fortran versions (v2.3) for cases in which the H₂ concentration is varied. As shown in previous runs with the MATLAB version, the catalyzed oxidation of H₂ on the NMP surfaces at the fuel/solution interface dramatically decrease the fuel dissolution rate at H₂ concentrations around 0.01 mM. This is consistent with experimental investigations as discussed in Jerden et al., 2015.

The runs shown in Figure 6 were performed to confirm that the H₂ catalysis reactions were accurately represented in the Fortran version. The results show that the model outputs are essentially identical and that the breaks in the curves for 0.001mM H₂ and 0.01mM H₂ occur in both MATLAB and Fortran versions of the FMDM. The mathematic cause of these breaks or steps in the results is being studied as part of the continuing model development and optimization work. Note: the increase in dissolution rate at 100 -200 years corresponds with the dose rate increase associated with the ingrowth of Am-241.

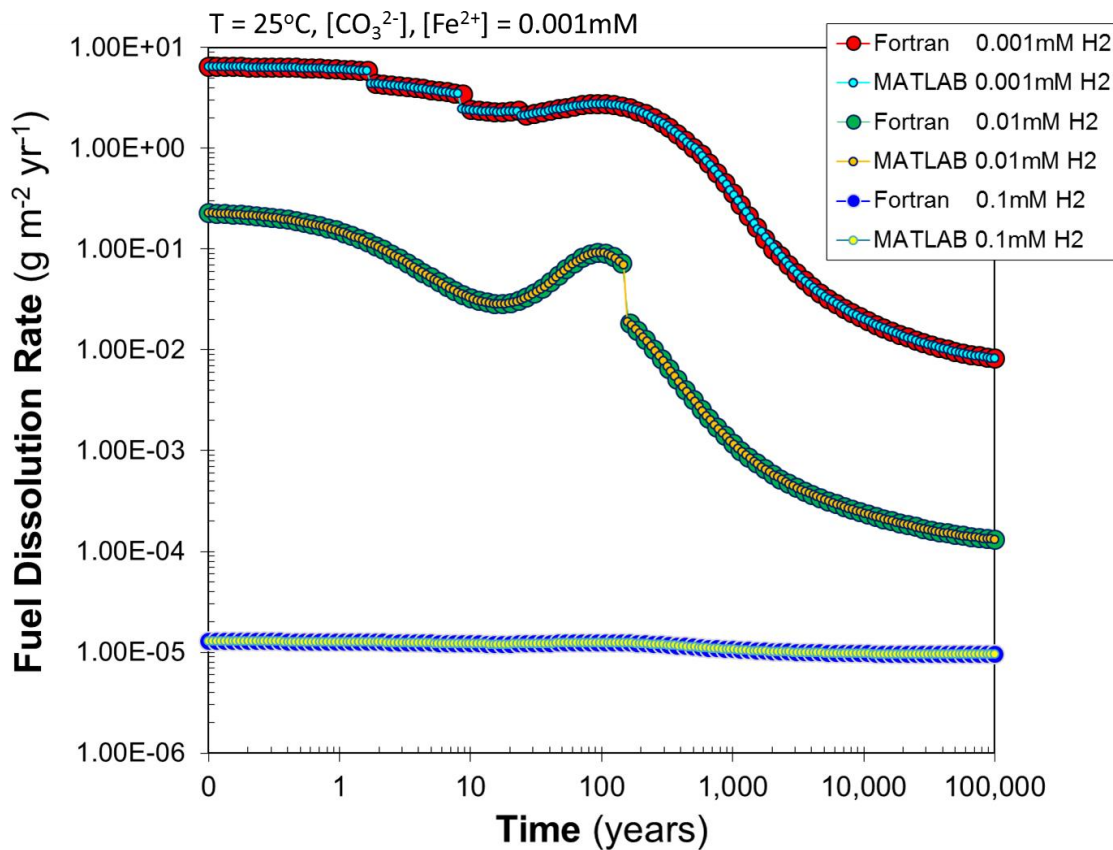


Figure 6. Results from three simulation cases performed with both the MATLAB and Fortran versions of the FMDM. For these cases carbonate and iron were held constant at 1.0×10^{-6} molar while H₂ was varied from 1.0×10^{-6} up to 1.0×10^{-4} . The Fortran simulation used 100 time steps, while the MATLAB run used 200 time steps. The results demonstrate that the Fortran and MATLAB versions of the FMDM give identical results.

2.3 Demonstration of Prototype Integrated PFLOTRAN – FMDM Model for PA

The method of integration of the FMDM Fortran version 2.3 with PFLOTRAN is summarized in Figure 7 (diagrams are from Hammond, 2015). The initial set up that was used to demonstrate the integrated code involved 52 separate 1x1x1 meter fuel bearing cells, each of which degraded at a rate determined by the FMDM (Figure 8). For simplicity, the waste container and fuel cladding were ignored.

Following an initialization step, the PFLOTRAN repository simulation proceeds with energy and mass flow (multiphase flow, heat transfer, reactive transport) calculations, which determine the temperature and solution chemistry inputs for the FMDM (Figure 7 top diagram). The fuel burnup and surface area are currently randomly selected by the code from a relevant range of values. For each time step of the repository simulation, the FMDM returns a fuel dissolution rate for each of the 52 used fuel cells in grams per square meters per year (Figure 7 bottom diagram). This is converted to grams per year using the randomized waste form surface area. This rate is then used to calculate the release of a non-sorbing, non-reacting tracer radionuclide (Figure 8).

The dimensions and conditions used for this initial demonstration of the integrated PFLOTRAN - FMDM code are as follows:

- Spatial discretization: 101x101x21m with 1m resolution (~214K grid cells)
- Temporal discretization: 100 years with 1 year time step (10^{-6} y initial)
- Waste cell spacing: 5m (X), 20m (Y) between 20-80 m
- Prescribed concentrations: $O_2(aq)$, $H_2(aq)$, HCO_3^- , Fe^{2+} all = 1 mM
- Fuel burnup: 55-65 GWd/MTU (random)
- Total fuel reactive surface area: 0.8-1 m² (random)
- Pore water velocity: 1 m/yr (X), 0.14 m/yr (Y)
- Computing performance: 66% of total time (~30 minutes) spent in FMDM

It is important to note that the results of the preliminary run with the PFLOTRAN – FMDM model (Figure 8) was for relatively high burnup values and oxidizing conditions. These factors lead to quite high fuel dissolution rates (on the order of $10 - 50 \text{ g m}^{-2} \text{ yr}^{-1}$) and thus rapid radionuclide release. The results from an on-going series of runs for anoxic conditions with both high and low H_2 concentrations will reveal the impact of the FMDM H_2 effect on radionuclide mobilization and will be used to confirm that the integrated model correctly represents the stand-alone FMDM process model.

Due to the relatively rapid fuel dissolution rate and probably high reactive surface area values, the mobilization of the tracer radionuclide is relatively rapid; and while, there is some variation in the tracer concentration among individual waste cells (e.g., t_2 , Figure 8) the overall plume shapes for the four waste cell rows are nearly identical. As mentioned above, results from on-going runs with the integrated model will reveal sensitivities of radionuclide mobilization to key variables such as H_2 , O_2 and CO_3^{2-} concentrations. Based on this initial model coupling experience a number of near-term improvements for the integrated code have been identified:

- Increase flexibility of coupling
- Ability to customize FMDM discretization from PFLOTRAN side

- Incorporate transient surface area
- Update to FMDM v3.0
- Optimized FMDM serial performance
- Integration into simulation of a repository with many waste packages
- Add increasingly mechanistic geochemistry

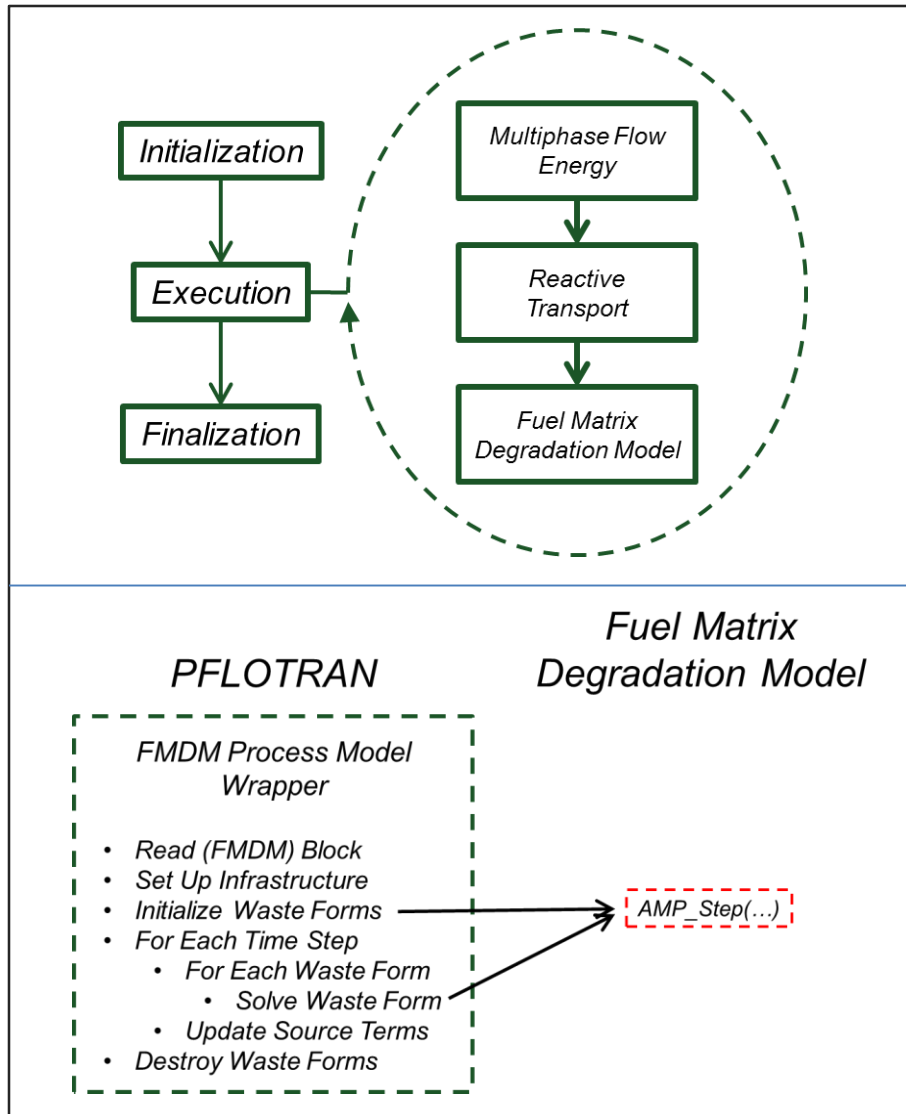
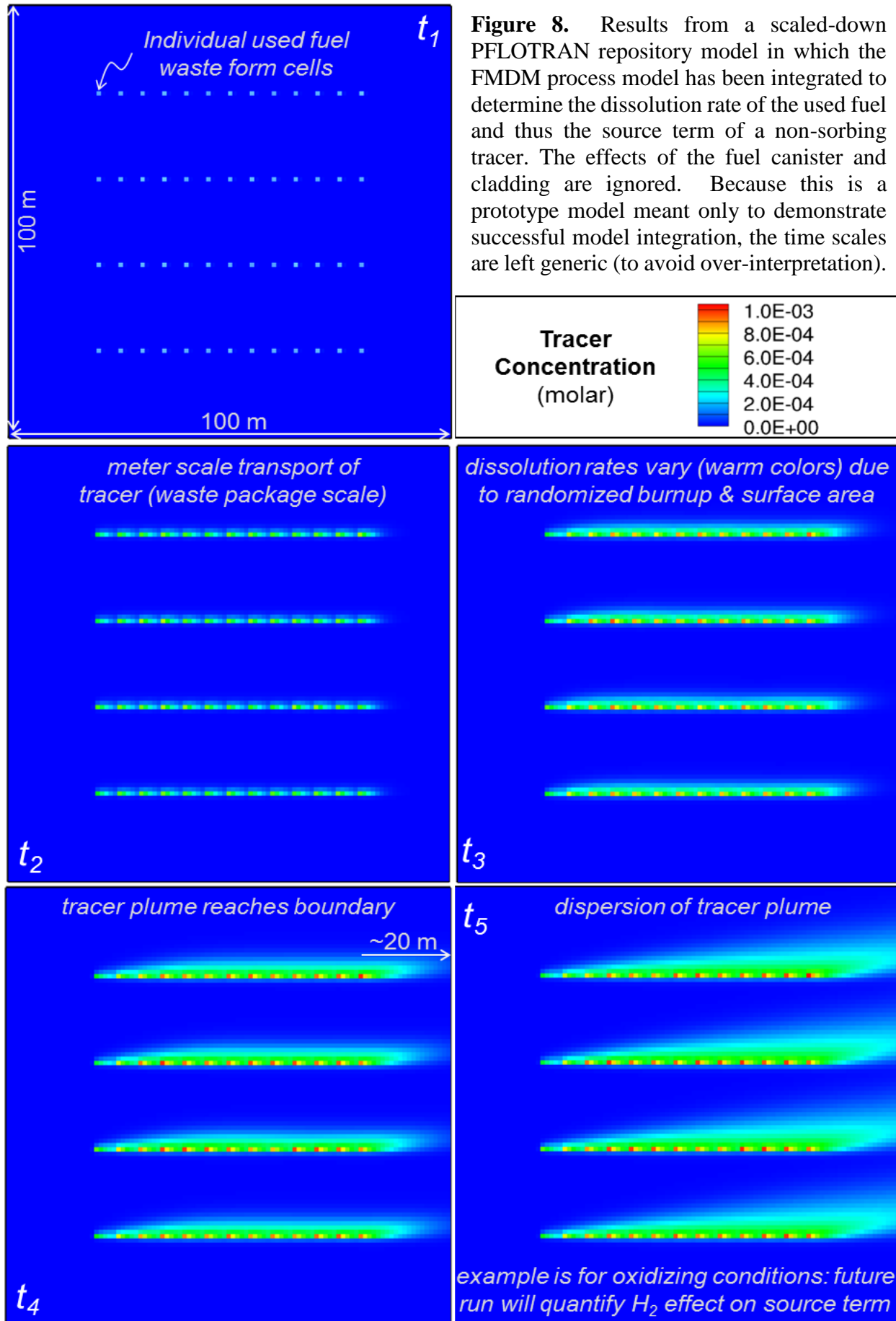


Figure 7. Schematic diagrams summarizing the workflow in the prototype PFLOTRAN – FMDM model (from Hammond, 2015).



The on-going model integration work is conceptually summarized in Figure 9, which shows the overall flows of information between the GDSA code (PFLOTRAN) and the FMDM. The FMDM box identifies what processes are currently included in the integrated model (v2.3), and the new processes that need to be added to bring the FMDM up to date with the recent scientific findings on the dissolution behavior of used nuclear fuel.

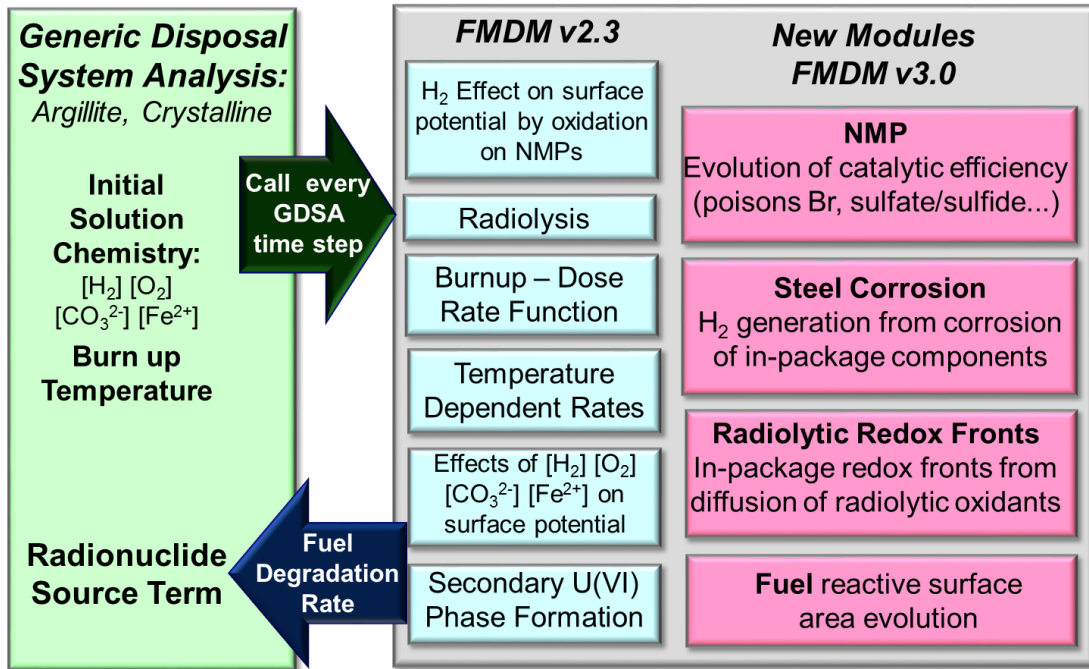


Figure 9. Conceptual summary of the flow of information between the GDSA PA model and the FMDM. Processes currently in the FMDM (v2.3) are shown in blue, while new processes that need to be added to bring the FMDM up to date with current scientific findings are shown in pink.

3. SCOPING WORK FOR THE DEVELOPMENT OF A CANISTER CORROSION MODEL

The quantification of the long-term corrosion behavior of steels in relevant environmental conditions is central to developing a science-based performance assessment for nuclear waste repositories. The mixed potential theory on which the FMDM is based is ideal for quantifying steel corrosion because it accounts for the fundamental electrochemical mechanisms. Scoping work has thus been initiated to investigate the extension of the FMDM to include the corrosion of a steel surface, which would be located at some distance x from the fuel/NMP surface in the one dimensional FMDM reaction/diffusion domain. That is, the steel corrosion model will have a one-dimensional reaction diffusion layout continuous with the existing FMDM.

As with the FMDM, the steel corrosion model will use mixed potential theory to determine the corrosion rate based on the kinetic balance of all relevant interfacial redox reactions. Homogeneous reactions and diffusion processes that determine the supply of reactants to the steel surface and alteration phase saturation indexes will be taken into account. There are several advantages to this approach of incorporating a steel corrosion model into the FMDM:

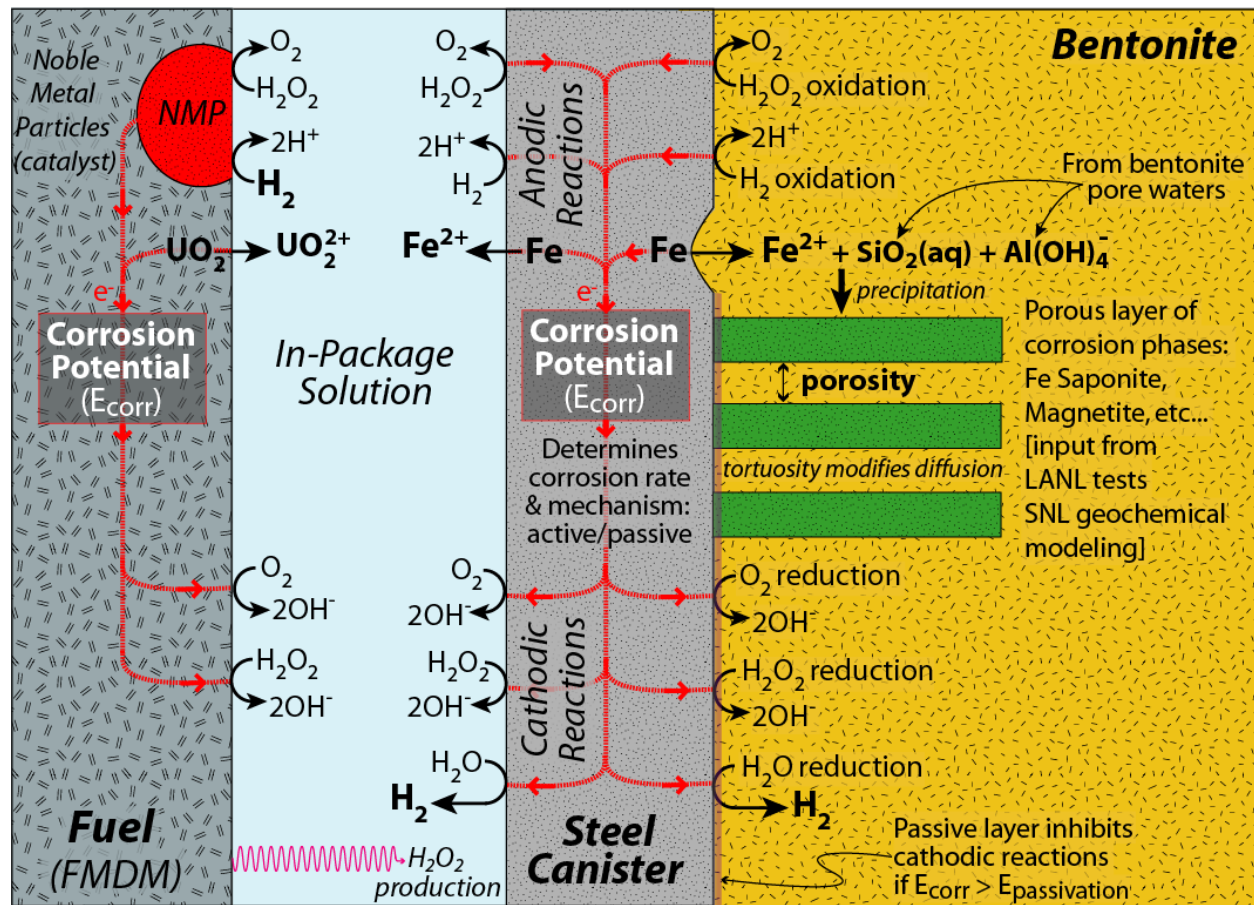
- It directly couples fuel degradation and steel corrosion. This is vital, as it has been shown that, even at sub millimolar concentrations, the H_2 produced from the anoxic corrosion of steel can decrease the fuel dissolution rate by over four orders of magnitude (Jerden et al., 2015).
- By directly coupling the fuel and steel degradation, this approach also allows for the quantification of redox fronts that develop within the waste container due to the diffusion of radiolytic oxidants away from the fuel surface and the reactions of these oxidants with the steel surface and the resulting aqueous Fe^{2+} and H_2 . This is also important because these redox fronts represent the Eh of the in package solutions in contact with the waste form and waste container internal components.
- This approach will allow the steel corrosion module to be readily implemented into the GDSA PA PFLOTRAN model, as it will be incorporated into the FMDM, a version of which has already been integrated with PA (see Section 2.3 above).

The original MPM developed as part of the Canadian repository program, on which the FMDM is based, contained a corroding steel surface (see King and Kolar, 2003). In fact, the earliest version of the FMDM included this corroding steel module, but it was removed so that the modeling efforts could focus on quantifying and optimizing the NMP catalyzed H_2 reactions at the fuel surface. By adding the full steel corrosion module, the extended FMDM could be used to quantify a number of processes that are essential for calculating both container life times and the kinetic interdependencies of fuel and steel corrosion. Specifically, the steel module of the envisioned extended FMDM (version 3.0) would quantify the following processes:

- Selection of passive or active corrosion mechanisms depending on the calculated corrosion potential.
- The generation of H_2 during anoxic corrosion, which has been shown to inhibit the dissolution of used fuel and can lead to alloy embrittlement.

- Production of radiolytic oxidants, which can determine whether a steel corrodes by aerobic or anaerobic processes.
- Interactions with porewaters to form iron silicate colloids and surface coatings such as Fe-saponite.
- Sorption of radionuclides to colloidal and fixed steel corrosion products. The model layout and context are shown in the figures at the end of this document.

The conceptual layout of the extended FMDM v3.0 is shown in Figure 10. The inputs from the PFLOTRAN PA model would be the same as those discussed in Section 2.0 above. However, the calculated steel dissolution rate (mass per area per time) would be added as an output to PFLOTRAN.



Width of irradiated zone depends on burn up, age of fuel

Figure 10. Conceptual layout for the extended FMDM version 3.0 that includes a module quantifying steel corrosion (only key interfacial reactions are shown).

As part of this scoping study the older version of the FMDM that contained the steel corrosion module was run for a number of cases to further investigate how the fuel and steel corrosion reactions would influence each other in the context of the model. Example results from these scoping runs are shown in Figure 11. The examples show how the diffusion of H_2O_2 away from the alpha radiation zone would set up redox fronts within the solution separating the corroding surfaces (Figure 11, top plot). Figure 11 also shows a how the concentration profile for H_2 is

predicted to evolve (Figure 11, bottom plot). The time labels for the profiles in Figure 11 are generic because this model is not fully developed and does not include some processes that will effect diffusion rates (e.g., porosity and tortuosity of corrosion layers). That is, the overall shape of the concentration profiles are believed to be accurate, but the absolute time evolution may not be. The overall shape of the concentration profiles, and how they change with time is instructive for understanding the inter-dependencies of the two corrosion processes.

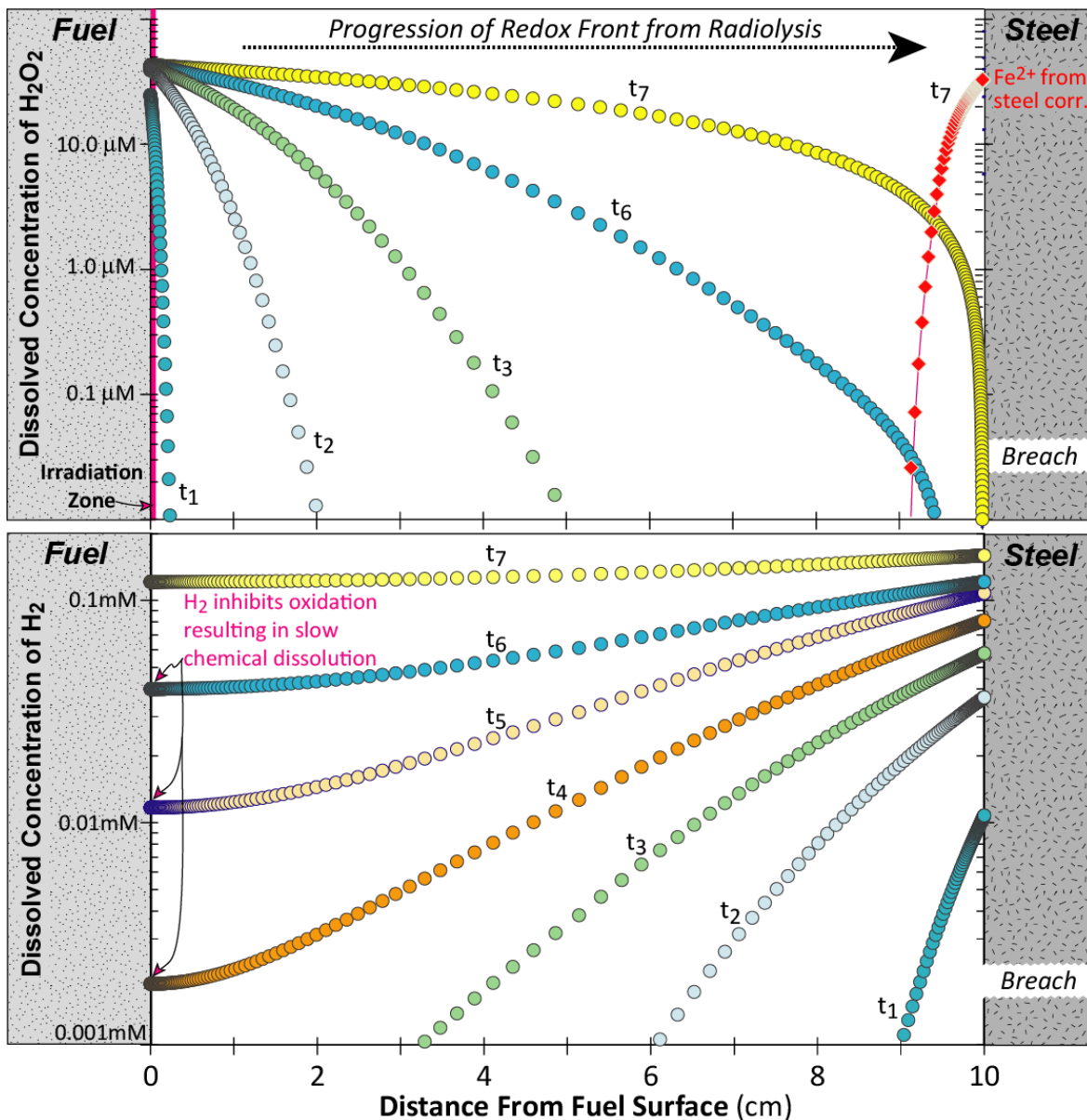


Figure 11. Results from an older version of the FMDM that included a corroding steel surface. The top plot shows how H₂O₂ diffusion away from the irradiation zone can set up redox fronts that evolve through time within the in-package solution. The bottom plot shows H₂ concentration profiles with time. Time labels are generic because this model does not include variables known to influence diffusion rates (porosity and tortuosity of corrosion layers). The overall shape of the concentration profiles are accurate, but the absolute time evolution is uncertain.

4. RESULTS FROM SCOPING EXPERIMENTS ON POISONING OF NOBLE METAL PARTICLES

In order to ensure that the process models for used fuel degradation and steel corrosion (sections 2.0 and 3.0 above) accurately represent reality within the relevant ranges of repository conditions, the model development efforts need to be coupled with a focused experimental program to quantify key parameters and provide data sets for validation. To this end, the radiological electrochemical testing facilities at Argonne are being used to investigate the interfacial and homogeneous reactions that dominate used fuel degradation.

As shown in Jerden et al., 2015, the catalysis of H₂ oxidation on the NMPs drives the used fuel dissolution rate down by as much as four orders of magnitude when dissolved H₂ concentrations reach approximately 0.1 mM. Because this NMP – H₂ catalysis process plays such a key role in determining the used fuel dissolution rates and its mechanism is not yet fully understood, it is the subject of on-going electrochemical experiments designed to directly inform the process modeling efforts (i.e., the extension of the FMDM to version 3.0).

The experimental set up consists of a 20 mL, three-electrode cell in which the experimental cover gas is continuously bubbled during the experiments (Figure 12). Multiple cells (experiments) are run simultaneously within an oven in a radiological laboratory. Multiple power supplies and potentiostats are available so that tests with two or more working electrodes (e.g., NMP and UO₂) can also be performed. The electrodes are characterized pre- and post-experiment by optical and Scanning Electron Microscopy (SEM). The solutions from selected tests are analyzed for electrode constituents (Ru, Mo, Pd, Rh, Tc, U, and other dopants such as REE) by Inductively coupled plasma mass spectrometry (ICP-MS).

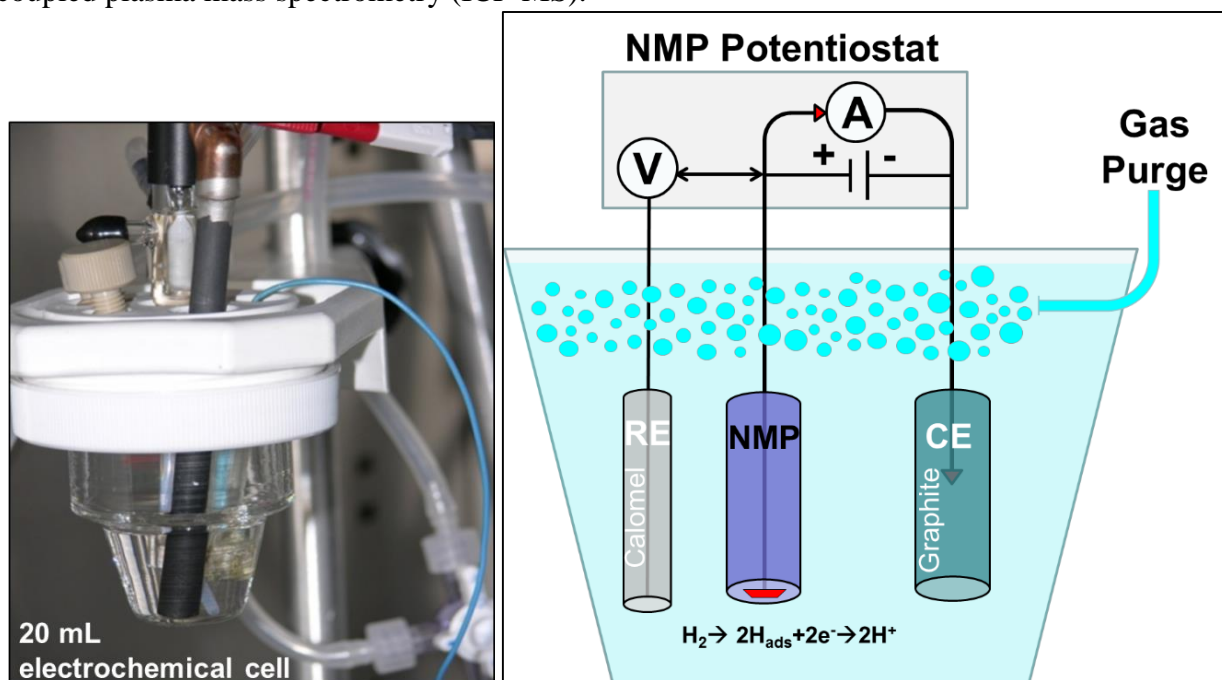


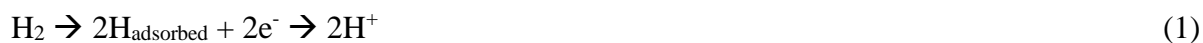
Figure 12. Photograph and schematic diagram of the type of cell used for the electrochemical experiments.

The scoping tests performed in FY 2015 focused on the H₂ reactions with a NMP electrode. The electrode was made in house (Argonne) from an alloy produced by Steve Frank at Idaho National Laboratory that closely matches the composition and homogeneity (single alloy phase) of the NMP found in used fuel. The NMP alloy used to make the electrode has a composition of Ru₅₆Mo₂₀Rh₁₁Pd₁₁Tc₂ and, based on SEM characterization, appears to be composed of a single phase with perhaps some minor amounts of TcO₂.

One of the most important experimental observations made regarding the role of H₂ in used fuel dissolution is that the presence of halides, particularly Br⁻, seems to counteract the H₂ effect (Metz et al., 2008). Although poorly understood, our new results (Figure 13) suggest that the NMP surface may be poisoned by halides thus reducing their catalytic efficiency (i.e., counteracting the protective H₂ effect). The poisoning and alteration of the NMP surfaces are not currently accounted for in the FMDM, because these processes are not well understood or quantified. However, due to the importance of the H₂ effect these processes are deemed high priorities for experimental investigations.

To investigate the reaction of H₂ on the NMP electrode scoping tests were performed in which the open circuit potential of the NMP electrode was measured for up to 80 hours in approximately 1 mM NaCl while cover gases of either air, Ar or 2% H₂ in Ar were bubbled through the solution. The possible poisoning effect of Br⁻ was also investigated by performing the 2% H₂ cover gas tests in solutions containing 1 mM NaBr. The pH for all tests remained relatively constant at around 7.0. Typical examples of the results are shown in Figure 13.

The results show a pronounced H₂ effect that causes a decrease in the potential of the NMP electrode from greater than 260 mV (vs. SHE) for the air cover gas tests down to less than 100 mV for tests performed with 2% H₂ in Ar as the cover gas. The observation that this large potential drop is not seen when the test is performed in pure Ar indicates that it is due to the H₂ oxidation on the NPM electrode. This shows that, under near neutral conditions, the NMP surface is hosting anodic reactions that can be generalized as:



As indicated by the green curve in Figure 13, the presence of 1 mM Br⁻ partially counteracts the H₂ effect, shifting the NMP surface potential up by approximately 60 mV. This shows that even over short time frames (minutes) the presence of Br⁻ has an effect on the NMP – H₂ reaction. This is a significant observation as it identifies a key chemical process that is not currently accounted for in the FMDM.

The implication is that, if repository ground waters contain sufficient Br⁻, the H₂ effect, which “protects” the used fuel from dissolution, will be counteracted due to the degradation of NMP catalytic efficiency. This implication was quantified by running the FMDM for a series of cases in which the NMP catalytic efficiency was decremented (Figure 14). The results highlight the importance of understanding poisoning or fouling processes that could counteract the NMP catalyzed H₂ effect. More experimental work is needed to quantify these key processes.

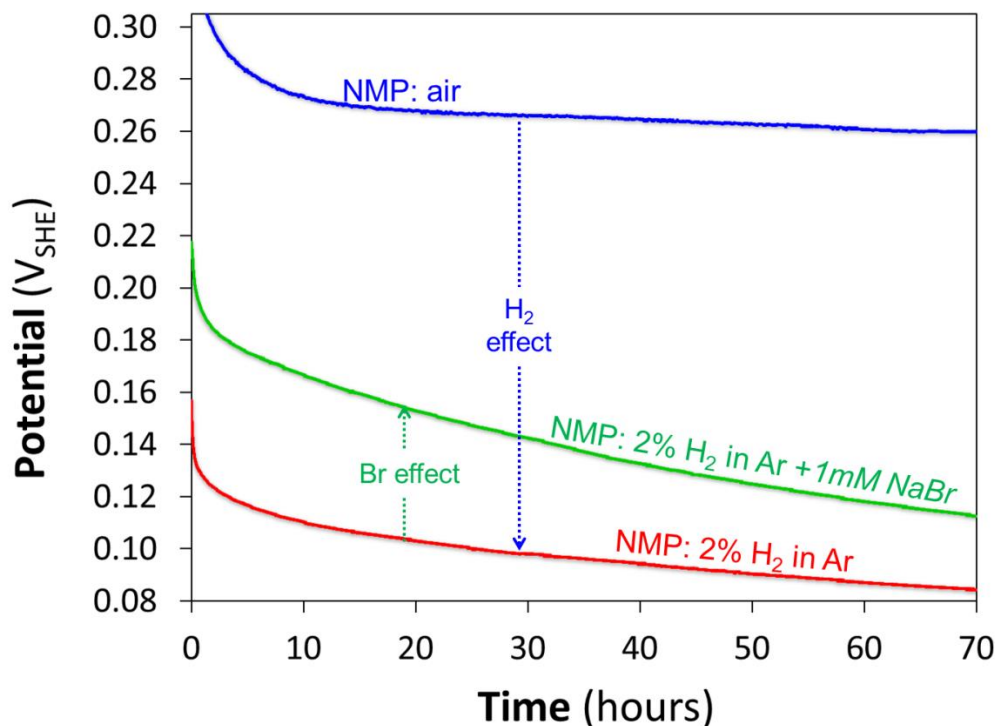


Figure 13. Results from scoping electrochemical tests showing the open circuit potential of the $\text{Ru}_{56}\text{Mo}_{20}\text{Rh}_{11}\text{Pd}_{11}\text{Tc}_2$ (NMP) electrode for three different tests. Note that the presence of Br partially counteracts the H_2 effect.

It is important to note that even after 70 hours, the open circuit potentials for the NMP have not reached a constant (steady state) value. This indicates that the surface of the electrode may need to be pre-conditioned in the solutions of interest for extended periods of time to achieve steady state with respect to all redox reactions. Future work will involve the thorough surface characterization of the NMP electrode by SEM before and after the experiments to identify any alteration or pitting that may affect the surface reactions.

Future work will also involve a series of electrochemical tests with simulated used fuel that consists of electrically coupled NMP in a UO_2 matrix. These tests will be used to generate a validation data set for the FMDM.

As mentioned above, to quantify the possible poisoning effect of the catalytic NMPs several sensitivity runs were performed with the FMDM v2.3 in which the poisoning process was simulated by decreasing the active NMP surface coverage while the H_2 concentration, burnup and temperature were held constant from run to run (Figure 14). For these sensitivity runs the fuel burnup was 60 GWd/MTU, the age of the fuel was assumed to be 30 years (out of reactor) and the temperature was held constant at 25°C.

The results show that for a solution containing 1 mM dissolved H_2 , the presence of 1% surface coverage of NMP leads a greater than 5 orders of magnitude decrease in the dissolution rate relative to the no NMP case. This H_2 effect is counteracted by decreasing the active surface area of the NMP. For example, decreasing the NMP surface coverage from 1% to 0.1% causes a factor of 50

increase in the predicted dissolution rate, while a decrease to 0.01% results in a dissolution rate increase of around 5 orders of magnitude. These FMDM sensitivity runs are quite preliminary as the mechanism and magnitude of the NMP poisoning process is not yet understood. These results do however underscore the need for continued experimental work to quantify processes that may have a significant effect (orders of magnitude) on the fuel degradation rate and thus radionuclide source term in the PA calculations.

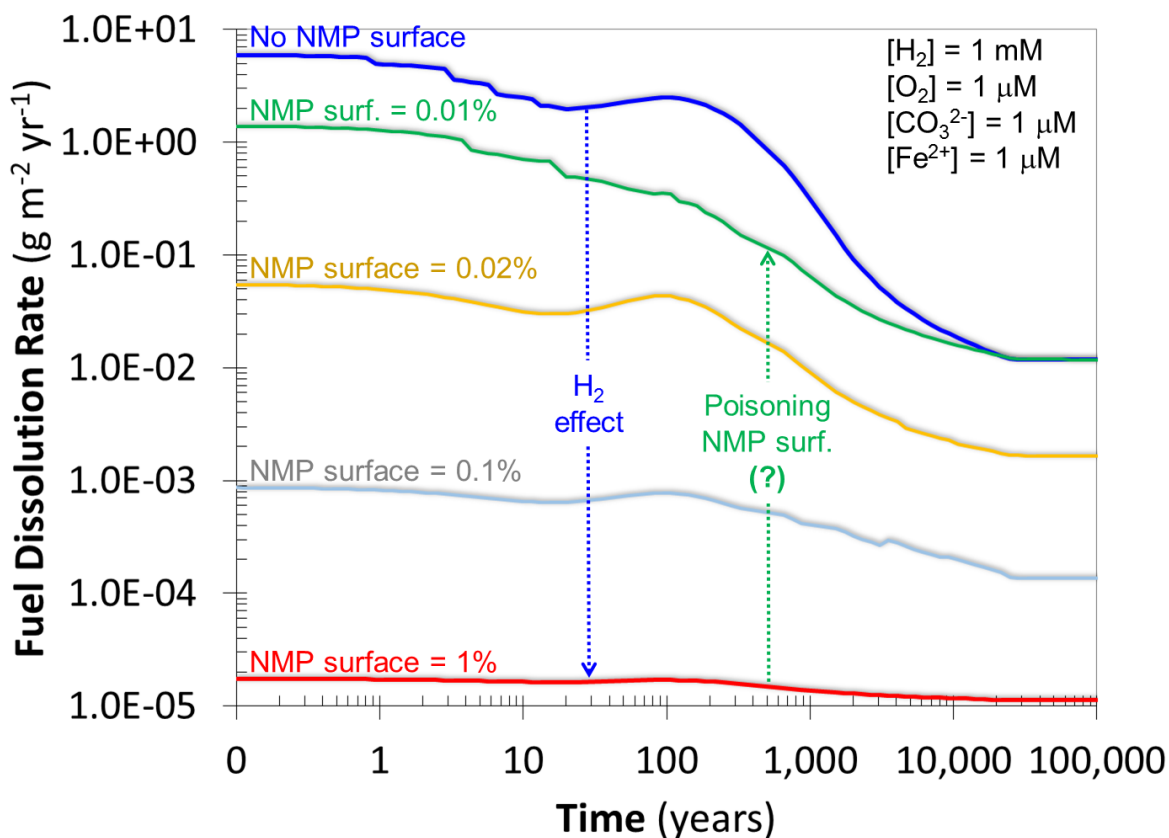


Figure 14. Results from the FMDM v2.3 showing the dramatic decrease in fuel dissolution rate caused by the oxidation of H₂ on the NMP and the possible effect of poisoning of the NMP surface (blocking the H₂ oxidation reaction). For these sensitivity runs the fuel burnup was 60 GWd/MTU, the age of the fuel was assumed to be 30 years (out of reactor) and the temperature was held constant at 25°C. The possible poisoning of the NMP surface was accounted for by decreasing the active surface area of the NMP.

5. CONCLUSIONS AND FUTURE WORK

The main accomplishments for Argonne’s FY2015 work on the Fuel Matrix Degradation Model (FMDM) development project are as follows:

- Completed a model validation study in which results from the state of the art FMDM were compared to experimental data from international geologic repository programs. This study was published in the Journal of Nuclear Materials: “A Multiphase Interfacial Model

for the Dissolution of Spent Nuclear Fuel” by J. Jerden, K. Frey and W. Ebert, Volume 462, July 2015, Pages 135-146.

- Completed conversion of the state of the art FMDM (version 2.3) to Fortran to facilitate integration with the Generic Disposal System Analysis (GDSA) repository Performance Assessment (PA) code PFLOTRAN.
- Worked with SNL scientists to complete and test a prototype integrated PFLOTRAN-FMDM repository model.
- Completed preliminary model runs focused on expanding the FMDM to account for corrosion of the used fuel steel canister.
- Completed scoping experiments investigating the possible poisoning of the Noble Metal Particles (NMP), which are known to catalyze the oxidation of H₂, thus shutting down the oxidative dissolution of used fuel.

The current version of the FMDM has proven effective for quantifying key processes affecting the rate of used fuel degradation; however, the implementation of FMDM within a performance assessment model requires further model development to account for steel corrosion and the possible poisoning of the NMP phase, which is responsible for the protective H₂ effect. Focused experiments are also needed quantify key parameter values and provide data sets for model validation. In order to take advantage of the work that has been done so far on the FMDM, a number of needs have been identified:

- Take next step in integration of FMDM with PFLOTRAN: demonstrate sensitivity of the Argillite PA model to key variables in the FMDM such as burnup, surface area and the dissolved concentrations of H₂, O₂, carbonate and ferrous iron.
- Extend the FMDM to account for the corrosion of the steel waste canister. This will quantify feedbacks between H₂ production at the corroding steel surface and the dissolution rate of the used fuel.
- Perform focused electrochemical experiments to determine the effect of halides and other possible poisons on the catalytic efficiency of the NMP. These tests will quantify processes that may counteract the protective H₂ effect.

Several specific priorities that have come out of the FMDM – PFLOTRAN integration work are as follows:

- Increase flexibility of coupling
- Ability to customize FMDM discretization from PFLOTRAN side
- Incorporate transient surface area
- Update to FMDM v3.0
- Optimized FMDM serial performance
- Integration into simulation of a repository with many waste packages
- Add increasingly mechanistic geochemistry

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