

ROK – US Joint Fuel Cycle Study, Fuel Cycle Alternatives Working Group: Task 3 - Spent Fuel Degradation and Durability over Geologic Time

David C. Sassani
Sandia National Laboratories
Department 6225, Advanced Systems Analysis

UFD Fuel Cycle Alternative Working Group (FCAWG)
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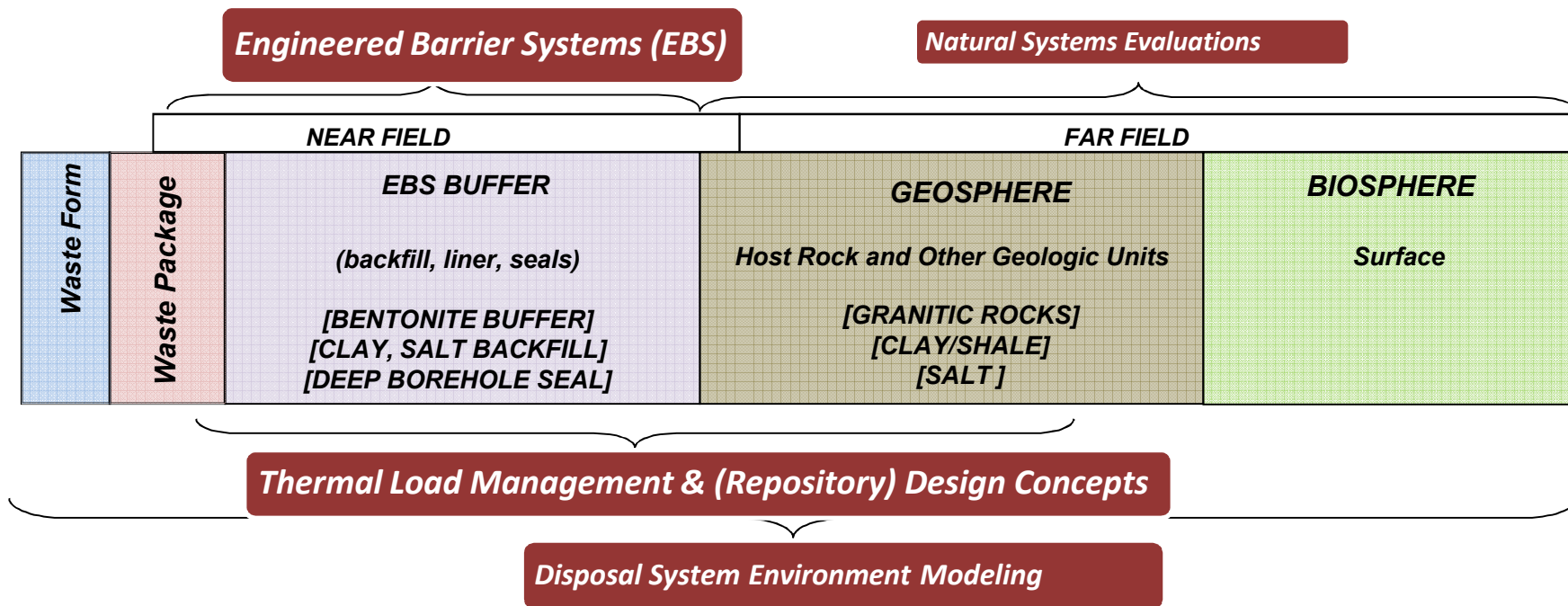


Presentation Outline

- **FCAWG Task 3 - Spent Fuel Degradation and Durability over Geologic Time**
- **Used Fuel Disposition (UFD) Disposal Research Activities**
- **Used Fuel Degradation and Radionuclide Mobilization (UFD&RM) Activities**
 - Overview
 - Fiscal Year 2011 Accomplishments
 - Fiscal Year 2012 Activities and Milestones
 - *Modeling and Experimental Work at Collaborating National Laboratories*
 - Sandia National Laboratories (SNL)
 - Pacific Northwest National Laboratory (PNNL)
 - Argonne National Laboratory (ANL)
- **Summary and Discussion**
 - UFD&RM Activities Summary
 - Focus and discussion areas for Task #3

- **Purpose – collaborative evaluation of constraints on**
 - UO_2 (i.e., used/spent fuel) degradation rates in granite repository conditions including
 - *Fission gas release*
 - *Cladding failure effects*
 - *Dissolution behavior*
- **U.S. Reports for Task 3**
 - **November 2012**
 - **Second report –**
 - *Currently scheduled for October 2013*
 - *Possible reschedule for April 2014 based on interactions/discussions of ROK-US POC*
- **Interactions to date (Task 3 POC - US UFD; KAERI; KMRC)**
 - Exchange of email discussing relevant work being done within UFD and ROK programs
 - Distribution of SNL FY2011 Milestone Report on Used Fuel Degradation and Radionuclide Mobilization (FCR&D-USED-2011-000403; SAND2011-7289P)
 - **Telecom (May 1, 2012 U.S. date)**
 - *Discussion of current focus within the UFD program and within ROK programs*
 - *Identification of possible areas of mutual benefit for Task 3 focus*
 - **This calendar year**
 - **Out years**

UFD Disposal Research Activities



SUPPORT, ANALYSIS & EXPERIMENTAL ACTIVITIES

*Engineered Materials Performance
Features, Events & Processes
Low Level Waste Disposition Issues
Inventory Projections*

*(corrosion, degradation studies)
(how R&D is organized and prioritized)
(part of total nuclear waste consideration)
(LLW/HLW, used fuel, open → closed fuel cycles)*

- **Collaborative Effort – ANL, PNNL, SNL**
- **Purpose**
 - Investigating the long-term behavior of used fuel as a waste form
 - *Developing a comprehensive understanding of the current technical bases for disposing of used fuel*
 - *Evaluating range of disposal environments*
 - *Identifying the opportunities for long-term research and development*
 - Integrate with Waste Form Campaign for other waste forms
- **Approach**
 - Process Modeling
 - *Implementation of Radiolysis Model (PNNL)*
 - *Implementation of the Mixed Potential Model (MPM) for Matrix degradation (ANL)*
 - *Molecular scale modeling of UO_2 , alteration products, and surface reactions (SNL)*
 - *Molecular scale modeling of epsilon phase (noble metal particles) and surface reactions (PNNL)*
 - Experimental Studies
 - *Electrochemical cell studies to quantify the effects of noble metal particles (catalytic/cathodic) on matrix degradation (ANL)*
 - *Generation of radiolytic species and studies of used fuel degradation at future conditions (PNNL)*
 - Integration and UFD&RM Model Implementation into GPAM
 - *Constraints on the Fast/Instant Release fractions (SNL)*
 - *Integration of the process models into GPAM (SNL, ANL, PNNL)*
 - **GPAM staff working up new platform for implementation**

UFD&RM Fiscal Year 2011 (FY11) Activities Accomplishments

- **ANL, PNNL, SNL**

- **Developed chemical-radiolysis model for evaluating the dissolution rate of used fuel**
 - *enhanced the model for in-package chemical conditions (UO_2 , Cl, Carbonate)*
 - *investigated model parameters sensitivities to delineate effective uncertainty reduction*
 - *validated model through comparisons with literature (e.g., the AECL model)*
- **Evaluated flow-through testing data to identify data sets relevant to fuel dissolution in a radiolytic field**
 - *obtained and evaluated MOX material as sufficient surrogate for testing used fuel dissolution with alpha-radiation*
 - *developed compositions for synthetic used fuel preparation*
- **Conducted Literature review/gap analysis on UOX and MOX degradation rates and models**
 - *identified key gaps for modeling and testing work*
- **Developed electrochemical studies of fuel matrix and radionuclide oxidation and dissolution**
 - *conducted shakedown testing of micro-electrochemical cell*
- **Produced draft 3-5 year plan of UFD&RM activities**
- **ANL Level 4 Milestone Report Completed 7/15/2011**
- **PNNL Level 4 Milestone Report Completed 7/15/2011**
- **SNL Level 3 Milestone Report Completed 10/07/2011 (SAND2011-7289P)**
 - *integrates input from the Level 4 milestone reports*

- **For FY12 UFD&RM activities integrated within the Engineered Barrier System (EBS) Evaluation work**
 - **Work Package Generic EBS Evaluation**
 - *Carlos Jove-Colon, SNL Work Package Manager*
 - *Bill Spezialetti, DOE Technical Lead*
- **SNL tasks/milestone**
 - **Integrate ANL, PNL, and SNL activities to synthesize model and experimental results into overall model for Used Fuel Degradation and Radionuclide Mobilization**
 - **Facilitate coupling the radiolysis model with the baseline model for used fuel matrix degradation rate**
 - **Constrain fast/instantaneous release fraction for the UFD&RM model**
 - *Participate as Associate Group in EC FIRST-nuclides collaborative project*
 - **Implement the UFD&RM model into the Generic Disposal System Models (GDSM)**
 - *Generic Performance Assessment Model (GPAM) implementation*
 - **Currently contains simplified source-term models in four GDSM**
 - *First external EBS model implementation into the GPAM*
 - **Milestone:**
 - *Report on Integration of EBS Models with Generic Disposal System Models (09/07/2012 – M2)*

- **PNNL tasks/milestones**

- Evaluation of Radiolysis Models to Used Fuel Degradation and Radionuclide Migration in a Degraded EBS Environment
- Experimental Investigation of Used Fuel Degradation at Future Conditions (radiation levels)
- Milestones
 - *Testing plan (12/02/2011 - M4)*
 - *Modeling Results (7/21/2012 - M3)*
 - *Experimental Results (8/24/2012 - M3)*

- **ANL tasks/milestones**

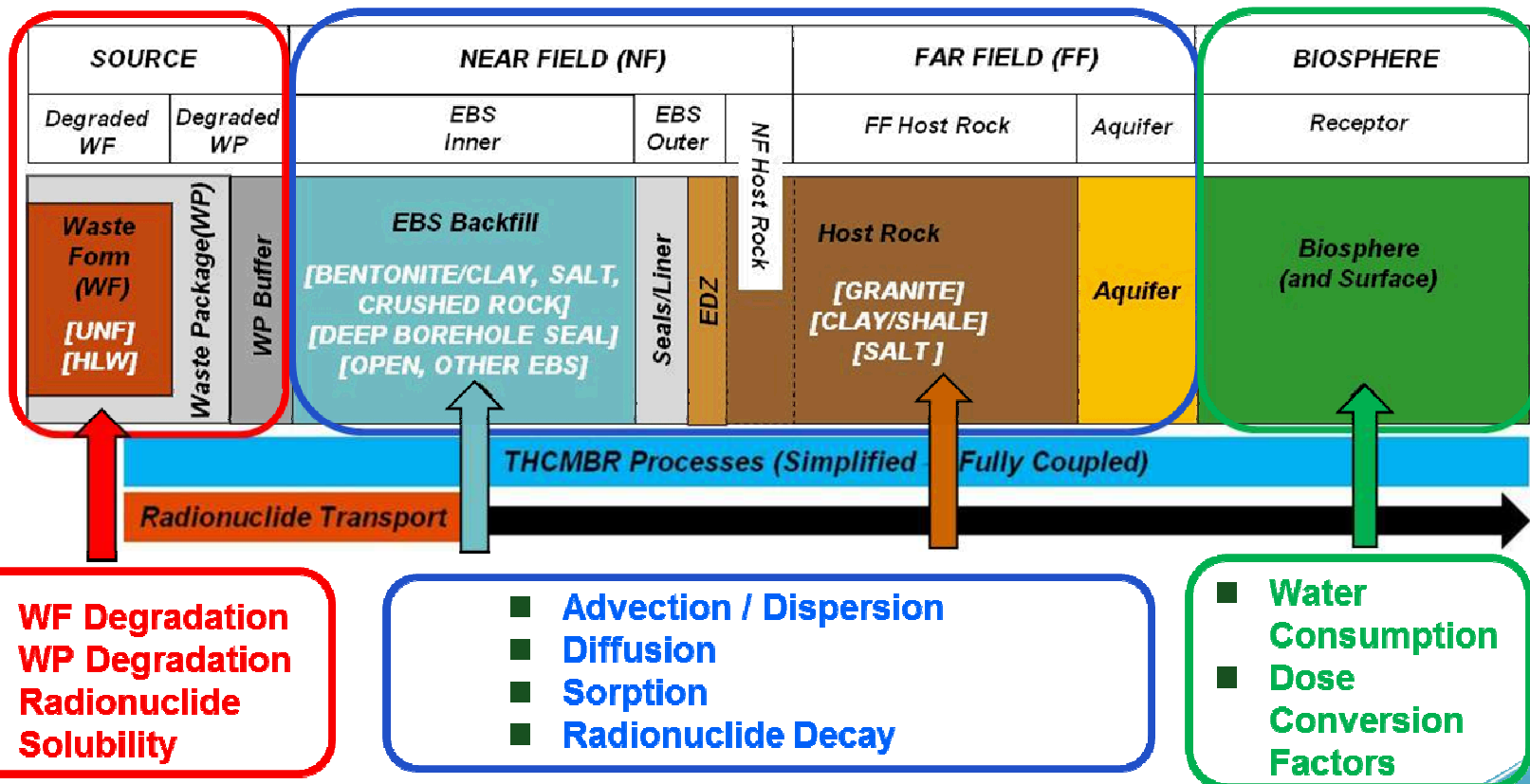
- Implement a used fuel matrix degradation rate model that accounts for key redox reactions (H_2 , radiolytic oxidants) and chemical speciation
- Experimentally investigate and quantify effect of Ru-Mo-Pd-Rh “noble metal particles” (NMP ~epsilon phase in used fuel) as catalysts for the destruction (scavenging) of oxidants (H_2 oxidation) for enhancement to the baseline matrix degradation rate model
- Milestones
 - *Experimental plan for electrochemical corrosion studies (1/6/2012 - M4)*
 - *Report results of electrochemical experiments (9/21/2012 - M3)*
 - *Waste form degradation model status report (8/9/2012 - M3)*

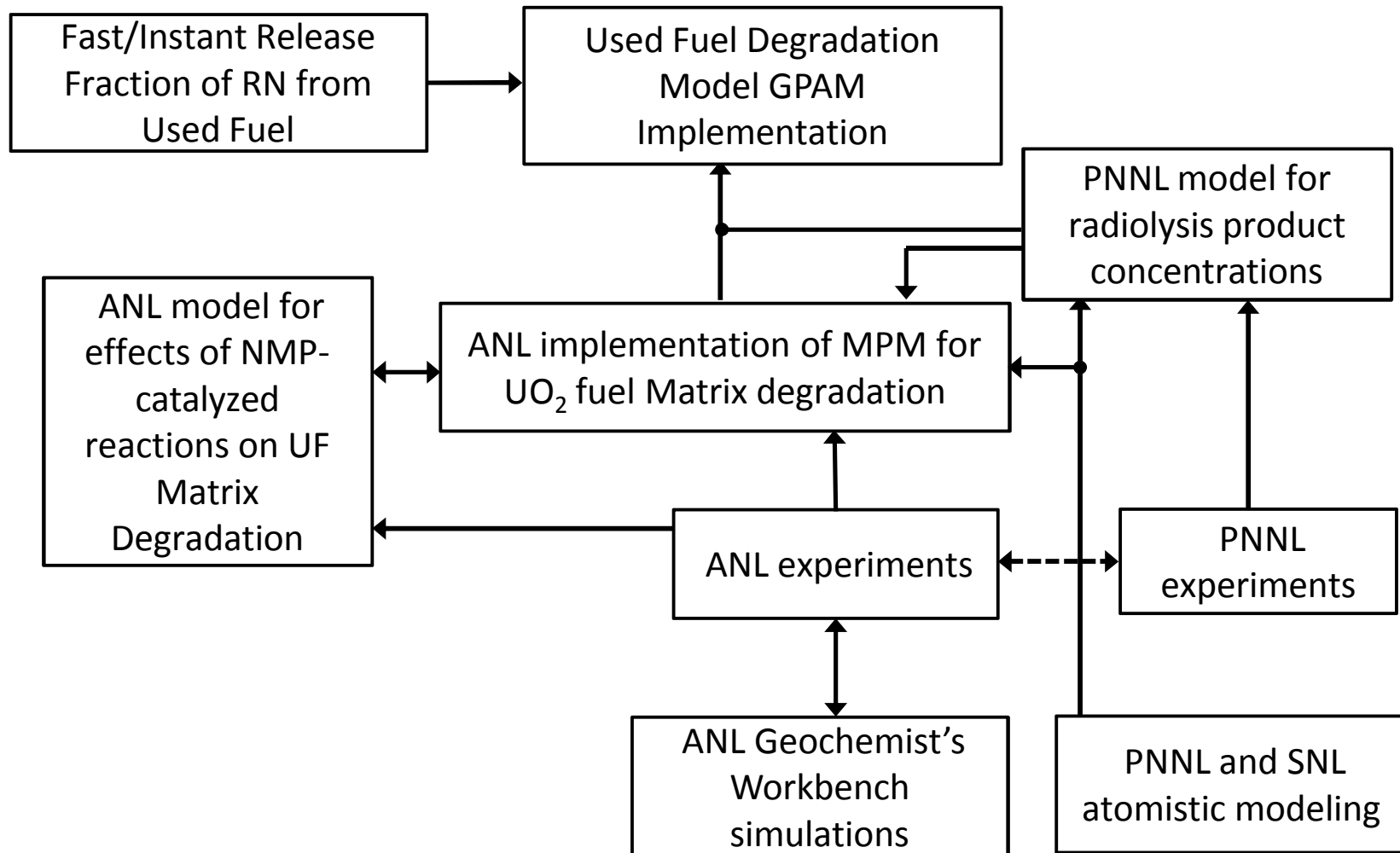
- SNL Team: David Sassani, Philippe Weck, Carlos Jove-Colon
- Developing strategy for model implementation into Generic Performance Assessment Model (GPAM)
- Constraining instant release fractions from used fuel;
 - Data and models from YMP: Triangular Distributions for ^{137}Cs ; ^{129}I ; ^{99}Tc ; ^{90}Sr (^{14}C from hardware) - these are conservative
 - Evaluating European data now for relevant application in reduced systems
- Molecular-scale modeling of UO_2 surface reactions
 - The first principle calculations for the optimized bulk UO_2 structural solution have been carried out
 - *For uranium systems, strong electron-electron Coulomb interaction are being taken into account in these calculations (using a Hubbard term)*
 - Being performed for ferromagnetic solution (as in previous FS work; Skomurski et al., 2008) and for the antiferromagnetic solution
 - *The calculations will progress to O_2 - H_2O - H_2O_2 surface interactions with the UO_2 slab*
 - *Will extend to other U minerals, e.g., studtite*

Used Fuel Disposition

GPAM – Conceptual Framework

- Can accommodate a range of processes and process model fidelities (from EBS and Natural Systems evaluations and FEP screening)
 - Simplified process abstractions or relationships with reduced dimensionality
 - Highly coupled partial differential equations for THCMBR in full 3D





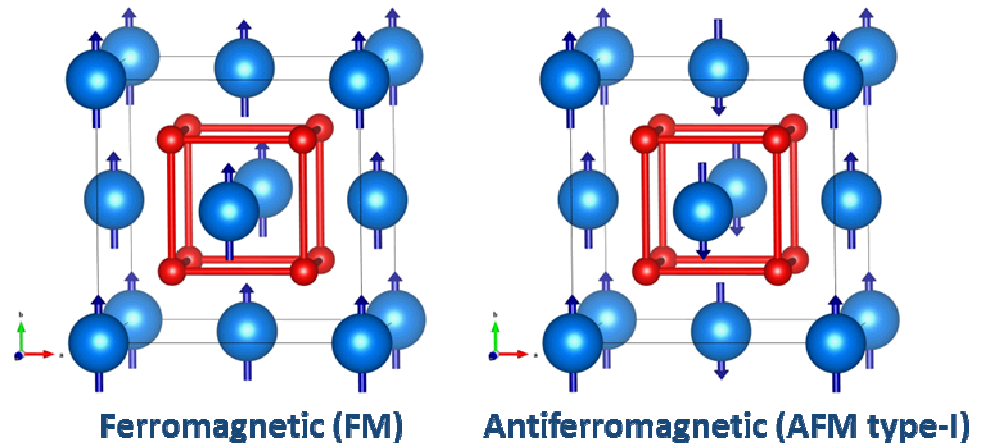
- **Used Fuel Degradation and Radionuclide Mobilization Model Concepts**
 - The fast release fraction (or instant release) inventory that includes fission products located in
 - *The fuel gap*
 - *The plenum regions (fission gases)*
 - *The accessible grain boundaries/pellet fractures*
 - The matrix degradation inventory that includes the matrix itself and fission products located in
 - *The inaccessible grain boundaries/pellet fractures*
 - *The matrix as solid solution or dissolved within the grain structure*
 - *The noble metal particles (which undergo their own degradation rate once exposed)*
 - Focus on the major rate limiting processes (e.g., radiolysis, matrix degradation, noble metal particle degradation)
 - Future – couple with physical degradation of cladding and mechanical evolution of degrading fuel

- Investigate role of strong electron correlations in the surface properties of UO_2
 - Previous quantum-mechanical (Skomurski et al, 2008, *J. Nucl. Mater.*)
 - *Low-index surface slab models from bulk UO_2 with a ferromagnetic ground state*
 - experiment shows that UO_2 is antiferromagnetic
 - neglected strong electron correlations
 - *strong electron correlations in UO_2 may affect the corrosion/dissolution process*
 - Currently investigating the possible role of strong electron correlations in the properties and reactivity of the $\text{UO}_2(111)$ surface
 - *using density functional theory within the generalized-gradient approximation (DFT, GGA+U/PW91)*
 - *corrected with an effective Hubbard parameter to account for the strong on-site Coulomb repulsion between U 5f electrons (Dudarev's approach).*

Molecular Modeling of UO_2 Surface Reactions (continued)

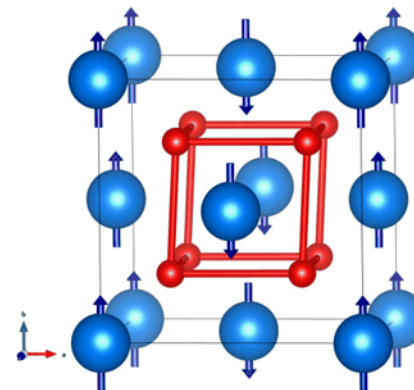
- GGA+ U study of *bulk* UO_2 : ordered and disordered oxygen lattice

- Fluorite-type structure (CaF_2 , Fm-3m space group) with ordered oxygen (OO) sublattice:



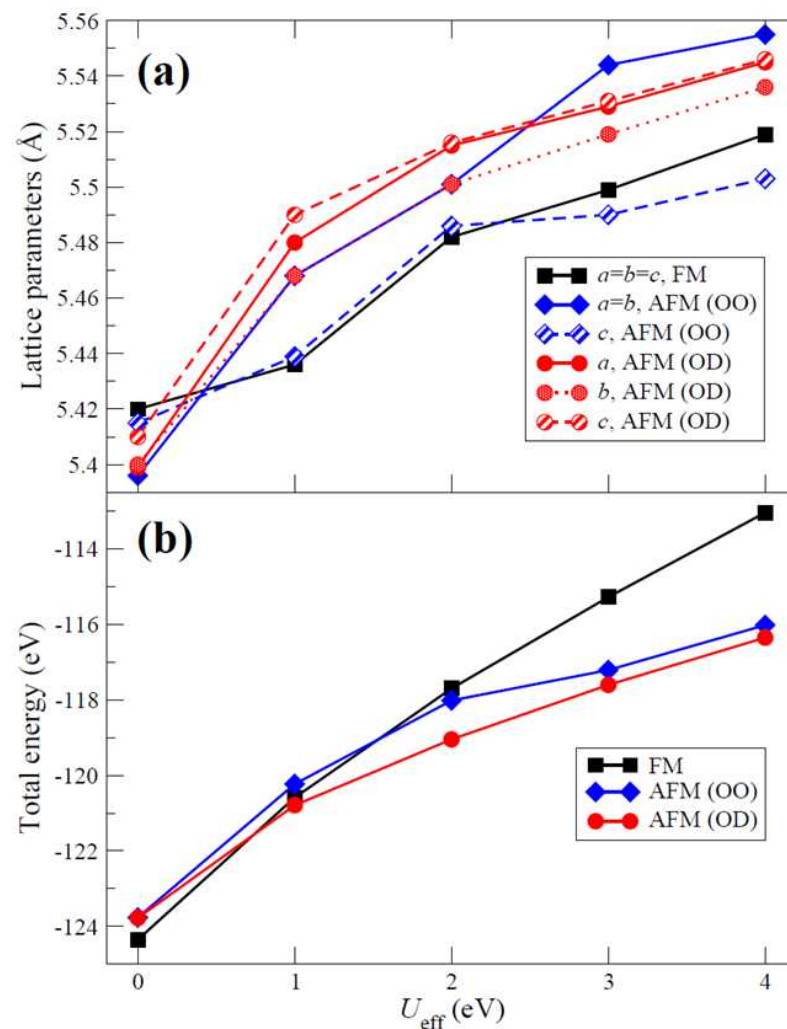
- Antiferromagnetic (AFM type-I) with oxygen sublattice distortion (OD) in the [111] direction:

- (Thompson et al., Phys. Rev. B, 84 (2011), 134111)



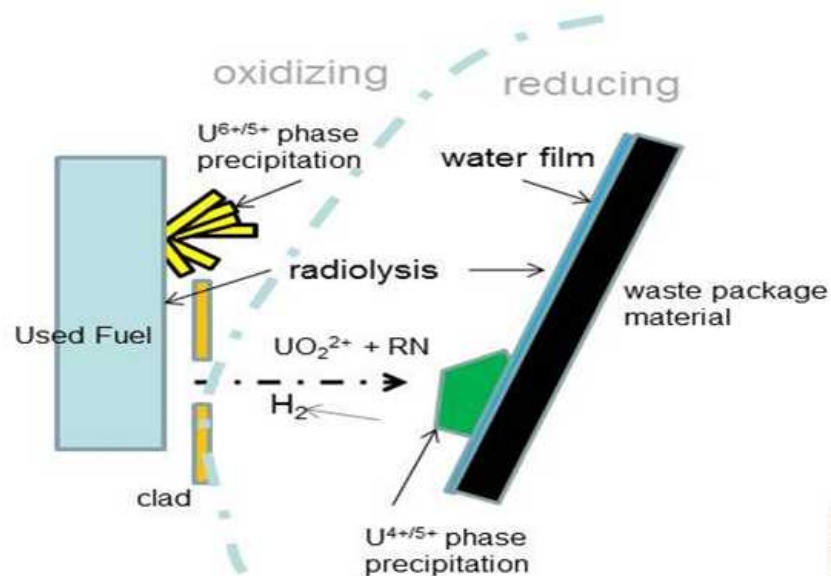
Molecular Modeling of UO_2 Surface Reactions (continued)

- GGA+ U study of *bulk* UO_2 : ordered and disordered oxygen lattice results
 - The FM solution is energetically favorable for standard DFT ($U = 0$ eV)
 - The AFM solution with oxygen distortion is preferable for $U = 4$ eV (i.e., the value suggested from the analysis of core-level X-ray photoemission spectra of UO_2).
- Evaluate properties of the relaxed surface
- Evaluate surface reactions
 - O_2 , H_2O , H_2O_2



- **PNNL Team: Edgar Buck, Rick Wittman, Bruce McNamara, Frances Skomurski**
- **Implementation of Radiolysis Models for Used Fuel Degradation and Radionuclide Migration in a Degraded EBS Environment**
 - Development of a quality user interface for radiolysis model
- **Development of Simulant Fuels for Experimental Investigation of Used Fuel Degradation at Future Conditions**
 - Experimental investigation of radiolysis on Simulated Fuels and MOX materials.
 - Test plan completed in December, 2011

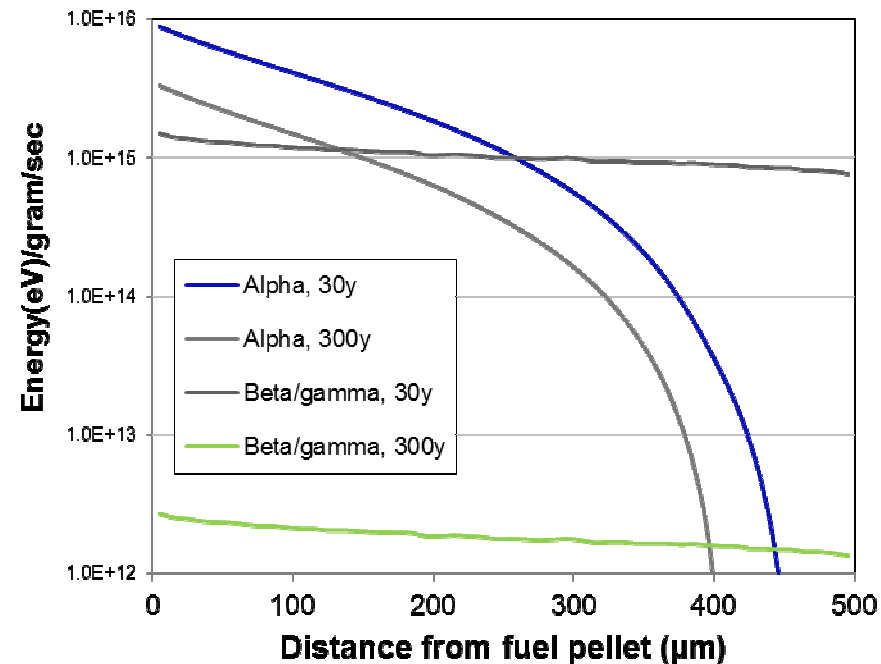
- Assuming fuel will be placed in a 'reducing environment' for long term storage/disposal
- Radiolysis (alpha) will be the only long term driver for creating very localized oxidizing conditions
 - UO_2 will oxidize to $\text{UO}_{2.67}$ which is 1000x more soluble.
 - Even if soluble U is precipitated at reducing fronts (e.g., Fe^{2+} redox processes, soluble radionuclides may migrate
 - However, groundwater corrosion of canister materials could produce H_2
- Behavior of the H_2 - UO_2 - H_2O system will be critical to limiting used fuel corrosion and the solubilizing of important radionuclides.
- Determining the conditions at which the waste package environment might no longer be reducing will be important.



Schematic of processes in the EBS being investigated in this task

Radiolysis Model Concepts

- The dose to the surface of used fuel is dominated by long-lived alpha even at relatively short times out of reactor
- Focused mainly on radiolysis modeling and testing
 - Useable program enables modeling of a three state system with UO_2 , water and an atmosphere.
 - Reducing environments were examined
- The combined effects of engineered barrier system degradation and waste form degradation were considered
- Future systems of interest:
 - Carbonate; Chloride



Radiolysis Model Development

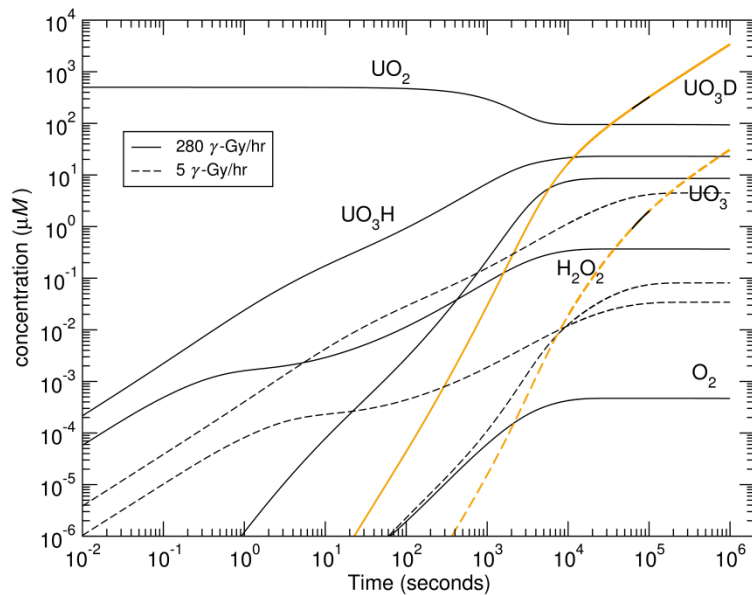


Figure 1

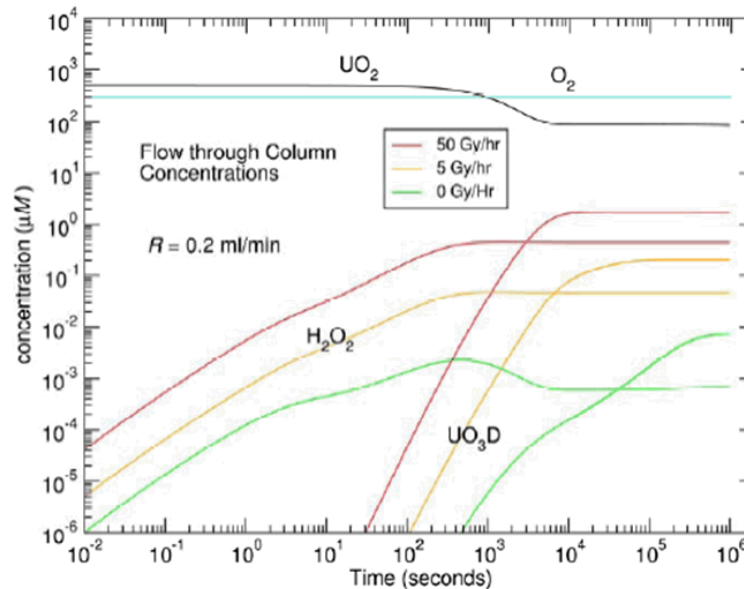


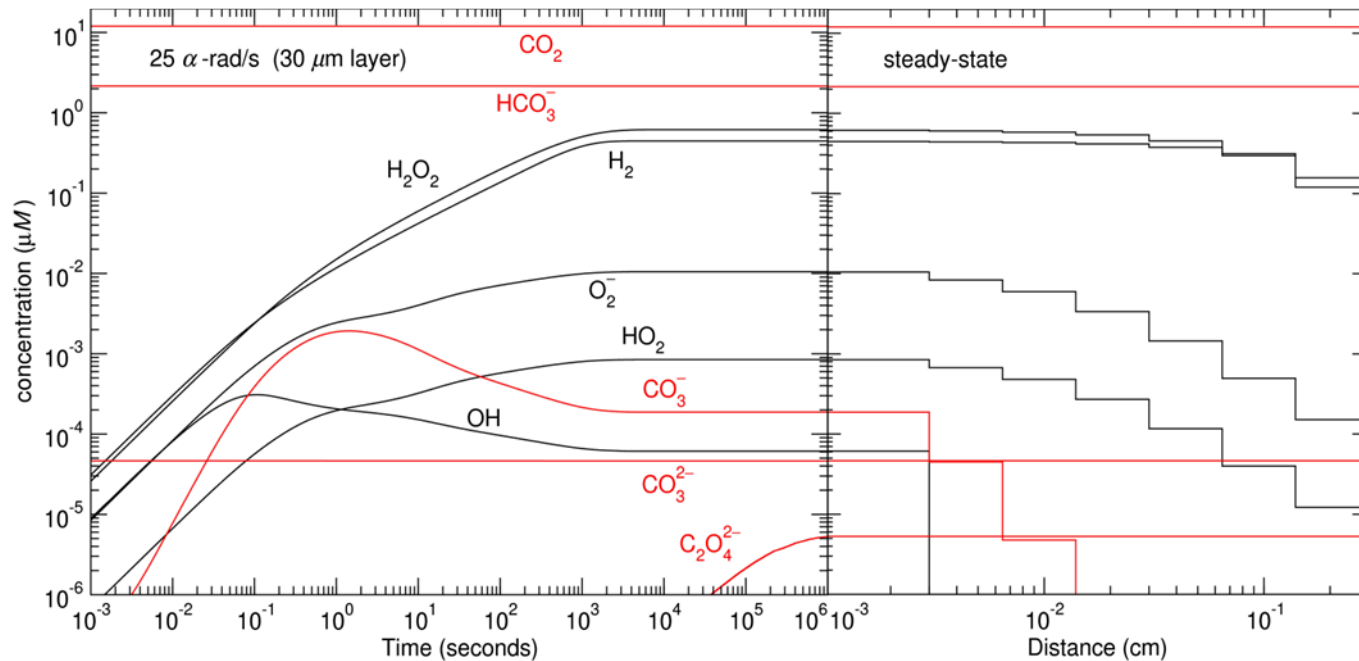
Figure 2

Figure 1. Shows the predicted dissolution rate with the radiolysis model.
Figure 2. Predicted dissolution UO_2 rate and H_2O_2 production at a range of doses

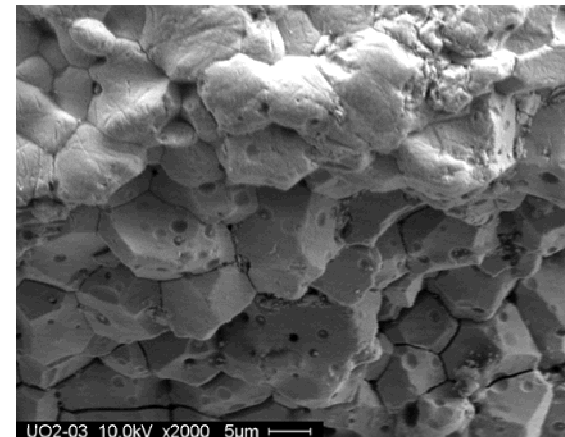
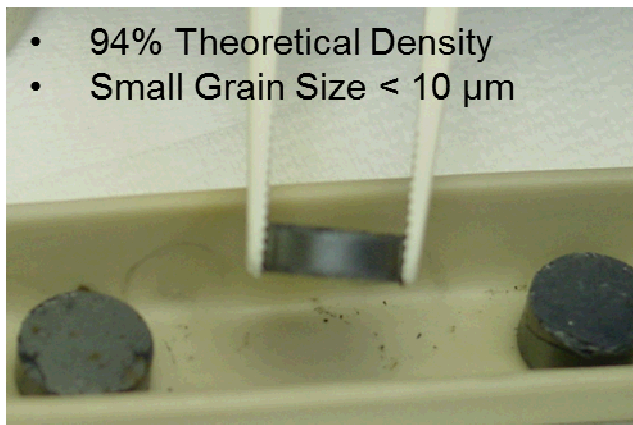
- Working on model complexity and interfacing with geochemical software.

Carbonate System Study

- Role of CO_2 in the system - OH^\bullet can generate CO_3^- , which is also a strong oxidant.
- Formation of oxalate in a U-Oxide system may be more important.



- Produce doped simulated fuels for experimental work

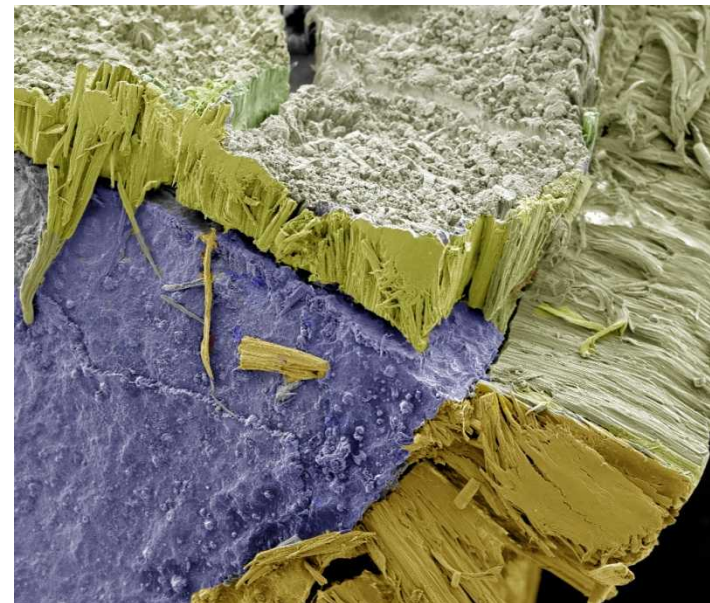


ID	MC	ME	RC	ZE	ZC	TM	TE	TR
OXIDE (WT%)	UO ₂ -MO-CE	UO ₂ -MO-EU	UO ₂ -RE-CE	UO ₂ -ZR-EU	UO ₂ -ZR-CE	UO ₂ -TH-MO	UO ₂ -TH-EU	UO ₂ -TH-RE
UO ₂	93.89	90.74	92.28	88.59	91.59	82.19	79.06	80.80
ThO ₂						15.07	14.50	14.81
ZrO ₂				5.00	5.17			
MoO ₃	2.78	2.69				2.74		
CeO ₂	3.33		3.27		3.24			
ReO ₂			4.45					4.38
Eu ₂ O ₃		6.57%		6.41			6.44	

Investigation of Radiolysis Driven Fuel Oxidation

- New methods for producing SimFuels (RADFUELS)
- Using MOX as a simulant for tests
- Irradiation facilities for model validation experiments
- Collaboration with ANL with specimens

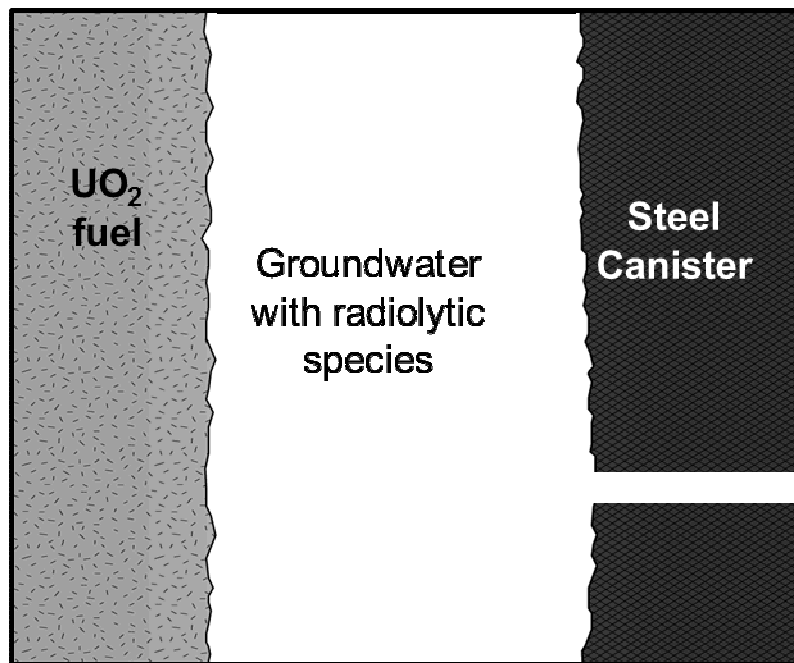
Studtite on UO_2



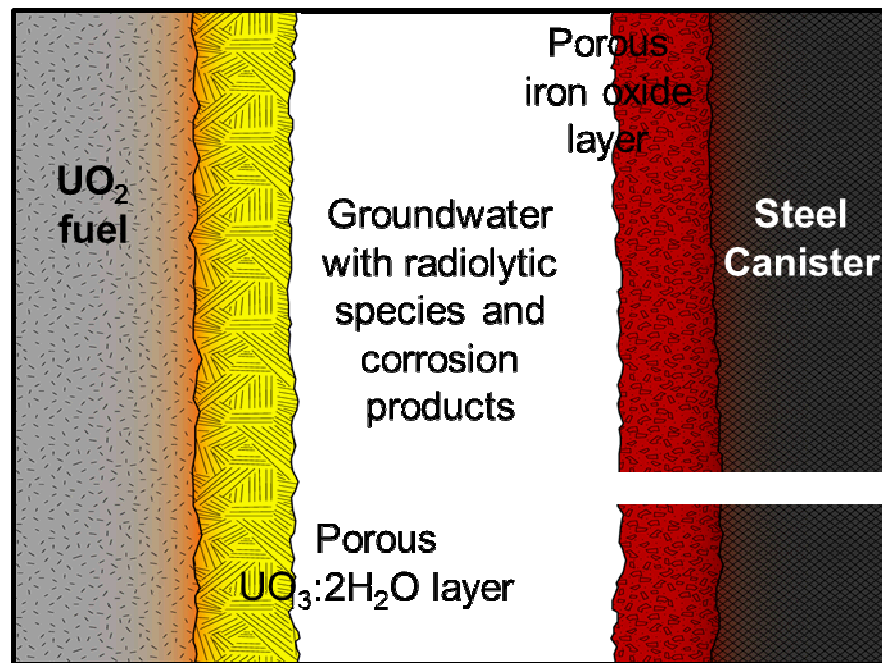
- ANL Team: Jim Jerden, Terry Cruse, Kurt Frey, Jeff Fortner, Bill Ebert
- Implement used fuel matrix degradation rate model
 - Based on the mixed potential model (MPM) of Shoesmith (2003, *Corrosion Sci. Sec.*)
- Quantify catalytic effect of NMP on UO_2 oxidative dissolution rate by electrochemical experiments
 - Coupled with detailed characterization of solids and solutions by microscopic and spectroscopic techniques
 - Test plan completed January 2012
- Quantify effects of NMP corrosion, alteration, and poisoning on catalytic efficiency
- Develop module for effect of NMP on UO_2 oxidative dissolution rate that can be included in used fuel matrix degradation rate model

Mixed Potential Model (MPM) Concept for Used Fuel Degradation

- Simplified representation of breached canister system used in MPM for oxidizing conditions (Shoesmith (2003) Corrosion Sci. Sec.)



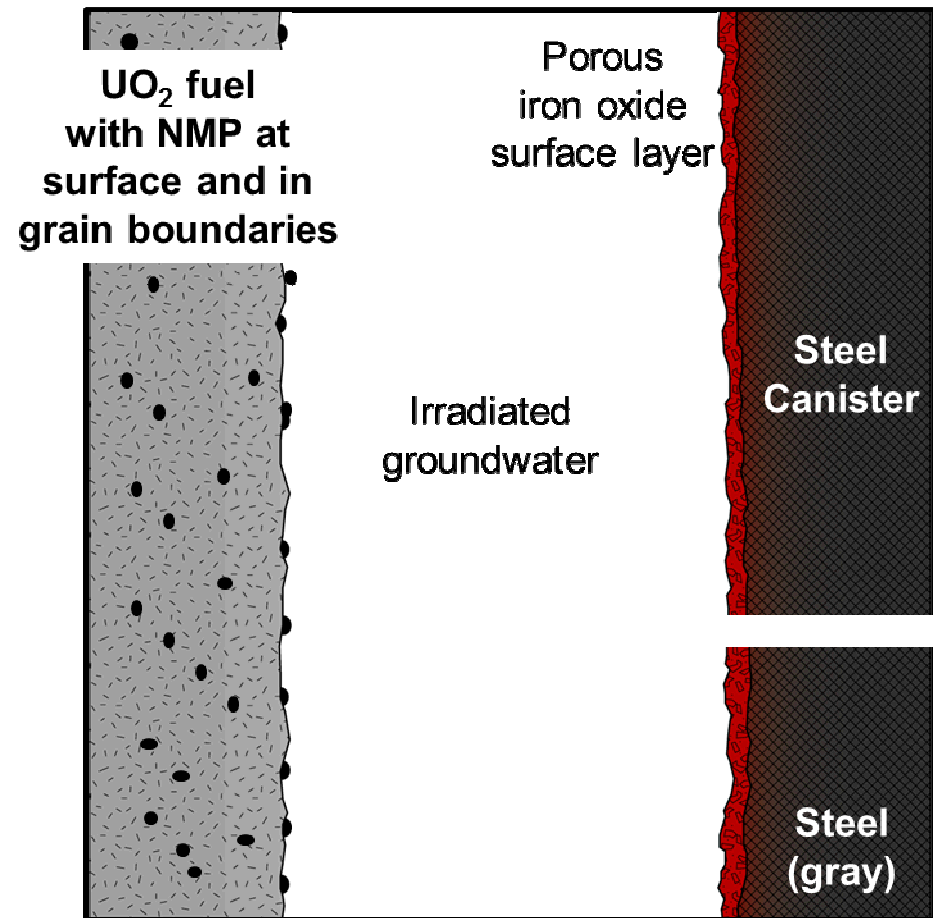
Initial Condition



**Long-Time Condition
under oxidizing conditions**

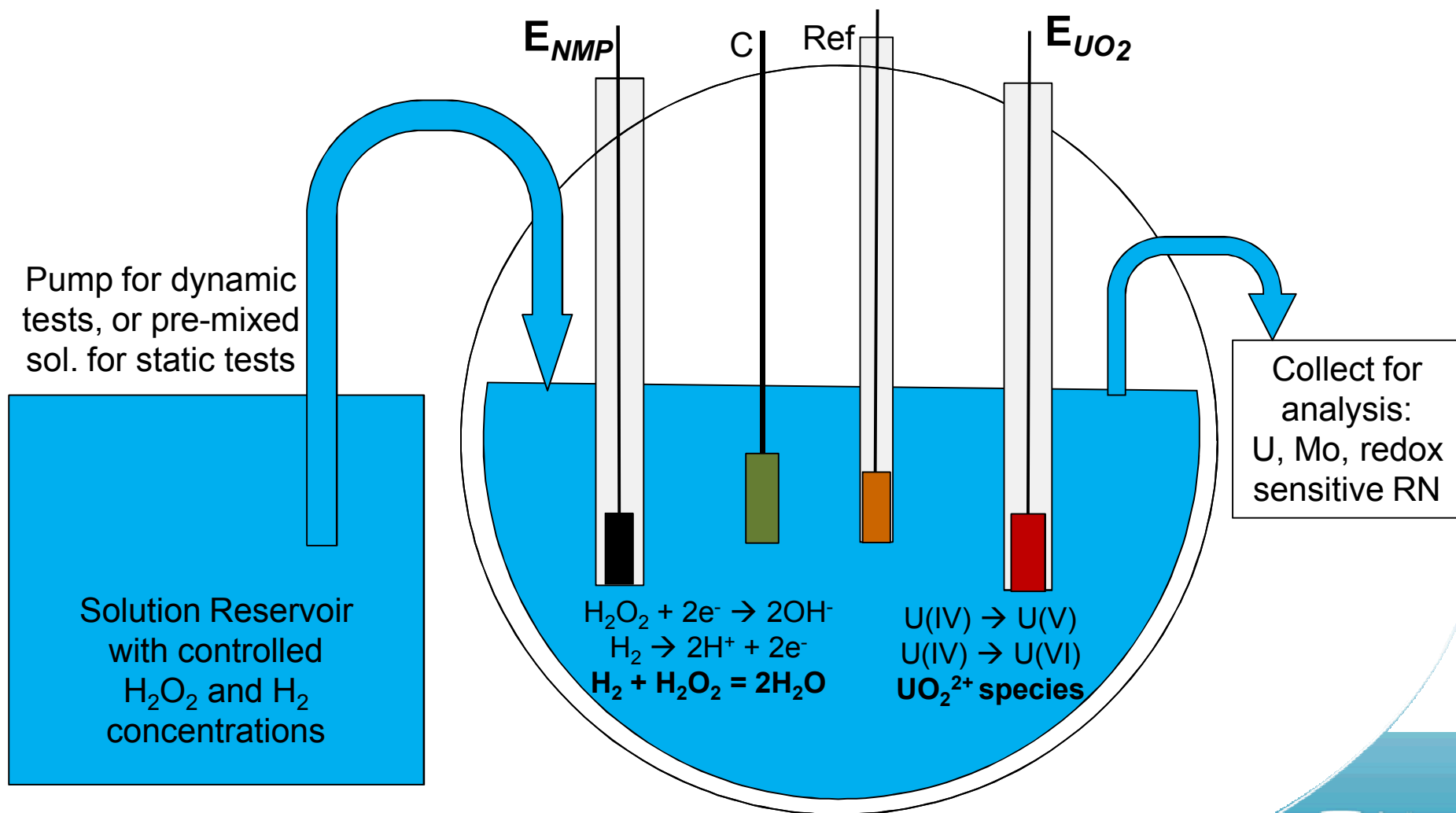
Extend MPM to Explicitly Account for Effects of NMP

- Incorporate the catalytic effect of noble metal particles (NMP) into MPM
- Account for corrosion or poisoning of NMP catalytic properties (experimental focus)



- Fabricate electrodes with surrogate alloys representing NMP and UO_2
 - Use separate electrodes to control potentials and isolate reactions
- Measure catalytic behavior of NMP alloys prior to corrosion
 - kinetics of competing redox reactions at various T, pH, H_2O_2 and H_2 concentrations, electrode surface areas, and imposed potentials
$$\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- \text{ coupled with } \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \text{ (*catalyzed by NMP)}$$
$$\text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- \text{ coupled with } \text{UO}_2 \rightarrow \text{UO}_2^{2+} + 2\text{e}^-$$
 - Measure concentrations of U, Mo, Tc, etc. in solutions containing H_2O_2 and H_2 (separate tests with and without NMP alloys in system)
- Corrode surface of NMP under controlled conditions (*ex situ*)
 - Control potentials, T, pH, solution chemistry (H_2O_2 , H_2 , NaCl, NaBr, NaI, S, Se, etc.)
 - Characterize electrode surface electrochemically, with SEM, XAS, etc.
- Measure catalytic efficiency of corroded NMP alloys
 - kinetics of redox reactions at various pH, solution chemistries
 - Measure dissolution of UO_2 into solutions with dissolved H_2O_2 and H_2 in system with corroded NMP alloy

Electrochemical Experiment to Measure Effect of Metal Particles on UO_2 Dissolution



- **Directly measure total U in solution at end of test**
 - ICP-MS
- **Measure current through UO_2 electrode during test**
 - Is dissolution rate sufficiently sensitive to H_2O_2 concentration?
- **Use floating UO_2 electrode potential**
 - Will it react with H_2O_2 at a particular rate at a fixed potential?
- **Electrically couple UO_2 and NMP alloy electrodes**
 - Is dissolution rate sufficiently sensitive to H_2O_2 concentration?
- **Using separate electrodes provides flexibility in electrochemical measurements**

- **Experimental work is being initiated**
 - Based on gap analysis and for validation and testing models
 - Developed test plans and testing matrix (ANL and PNNL) - completed
 - Begin executing testing matrix (ANL and PNNL)
- **Development of used fuel degradation model**
 - Constraints on fast/instant release fractions of radionuclides
 - Molecular modeling of UO_2 surface reactions
 - Implementation of baseline matrix degradation rate model
 - Implement radiolysis model in more user oriented fashion
 - Include/couple radiolysis model with baseline matrix degradation rate model
 - Develop targeted enhancements for baseline matrix degradation rate model
 - *role of H_2*
 - *epsilon phase catalytic properties*

UFD&RM FY12 Activities Summary (continued)

- **Implement UFD model within Generic Repository System models**
 - Develop specific scenarios for system analyses
 - *create detailed integration with GPAM (Generic repository models)*
 - Implement used fuel degradation model into GPAM
 - Initiate analyses for highest priority scenarios
- **Further integration with Waste Form Campaign**
 - As additional waste form degradation models develop (e.g., glass waste form degradation model), define strategy for implementation into GPAM

Focus and discussion areas for Task #3

- **First U.S. report – November, 2012**
 - Used fuel degradation in a repository environment (granite initial system)
 - *Fast/instant release fractions for radionuclides*
 - *Matrix degradation rate*
 - Radiolysis model
 - Implementation into generic performance assessment model (GPAM)
 - Relevance to storage evaluations
- **Second U.S. report - areas of possible emphasis/discussion**
 - Cladding model(s) integration with used fuel degradation
 - Other potential waste forms
 - Schedule

BACKUP MATERIALS

- **Objectives**

- Investigate the role of strong electron correlations in UO_2 bulk and surface properties.
- Study the structural properties of uranyl peroxide hydrates corrosion phases; determine the crystal structure of metastudtite using density functional theory (DFT).
- Calculate the thermal properties of uranyl peroxide hydrates from first-principles.

- **Approach**

- Quantify the role of strong electron correlations in UO_2 bulk and in a $\text{UO}_2(111)$ slab model using the generalized gradient approximation corrected with an effective Hubbard parameter (GGA+ U) to account for the strong on-site Coloumb repulsion between U 5f electrons (VASP code).
- Use perturbation theory (PT) to calculate the phonon properties of uranyl peroxide hydrates structures relaxed with DFT and derive their thermal properties.

- **Milestones**

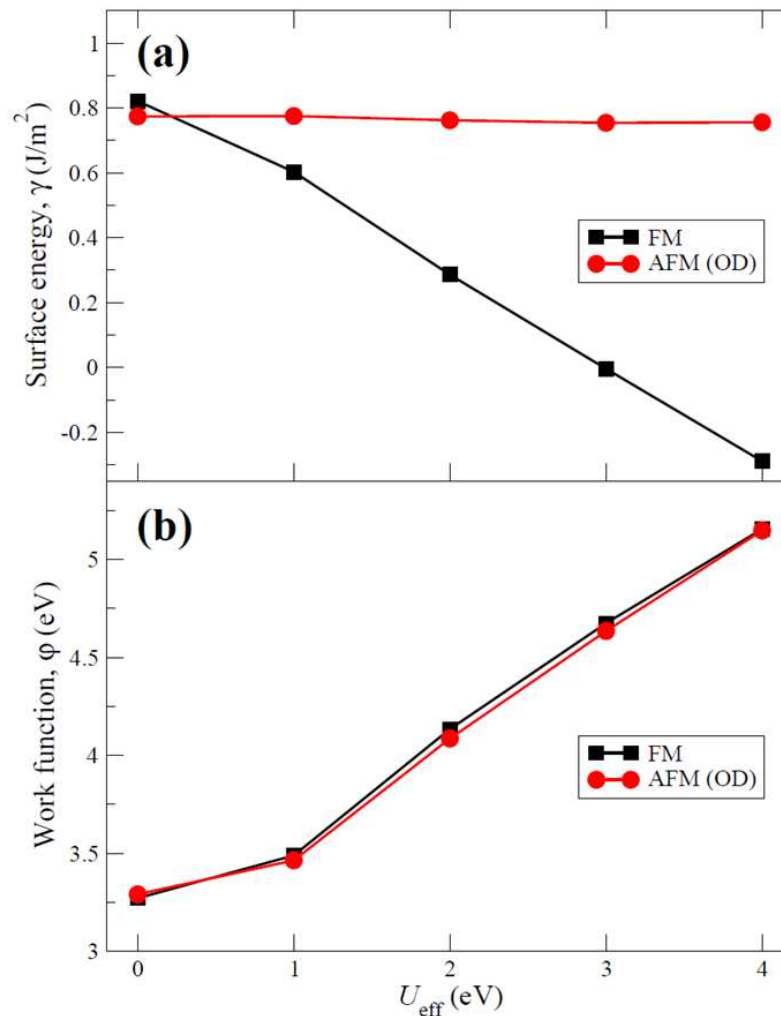
- M2FT-12SN0806062 “Integration of EBS Models with Generic Disposal System Models” (September 2012)

Molecular Modeling of UO_2 Surface Reactions (continued)

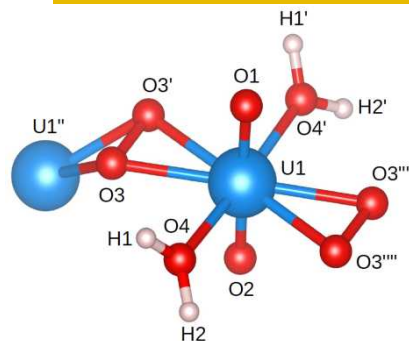
- Variation of the surface energy and work function of the relaxed $\text{UO}_2(111)$ surface

- FM and AFM (OD) solutions

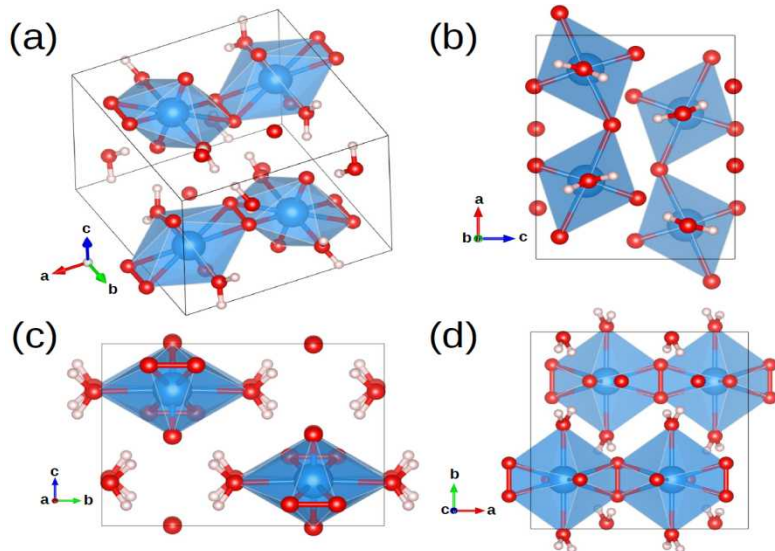
- Only minor change for the $+U$ correction on the surface energy of the AFM structure
- Use of $+U > 3$ eV leads to unphysical results for the FM solution.
 - Experimental estimate: $\gamma = 0.85 \text{ J/m}^2$ with up to $\pm 70\%$ uncertainty (Hall et al., 1987, J. Nucl. Mater.)
- Nearly-linear variation of the work function with $+U$
 - Experimental estimate: $\Phi = 3.5 \pm 0.5 \text{ eV}$ (Page et al., 1974, Combustion and Flame)



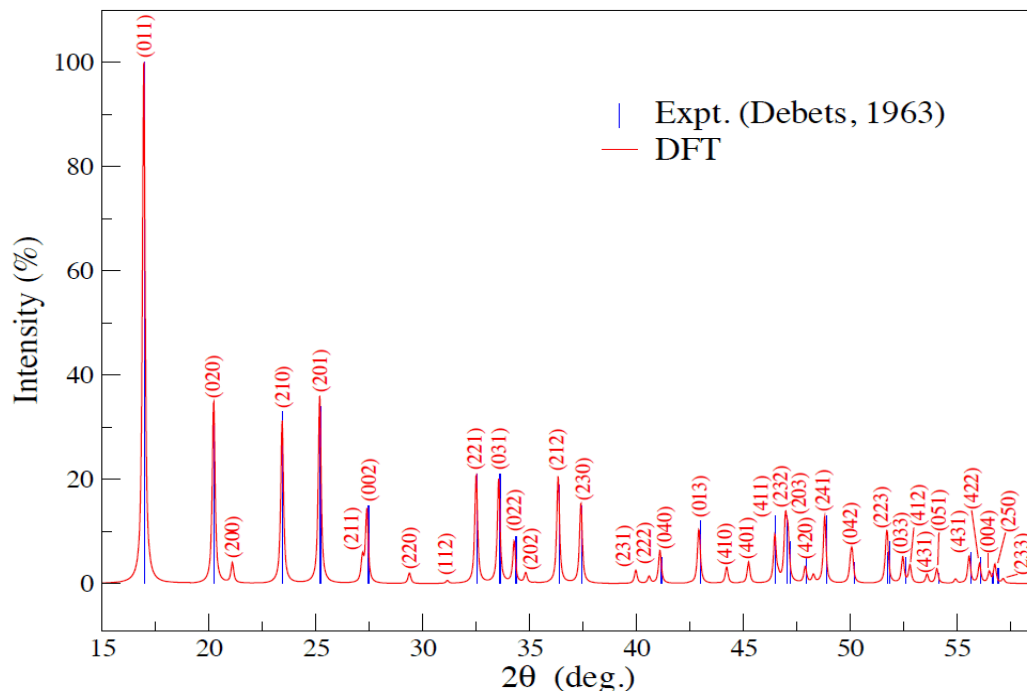
Structural properties of uranyl peroxide hydrates corrosion phases



Ball-and-stick representation of the $(\text{UO}_2)\text{O}(\text{H}_2\text{O})$ complex composing metastudtite



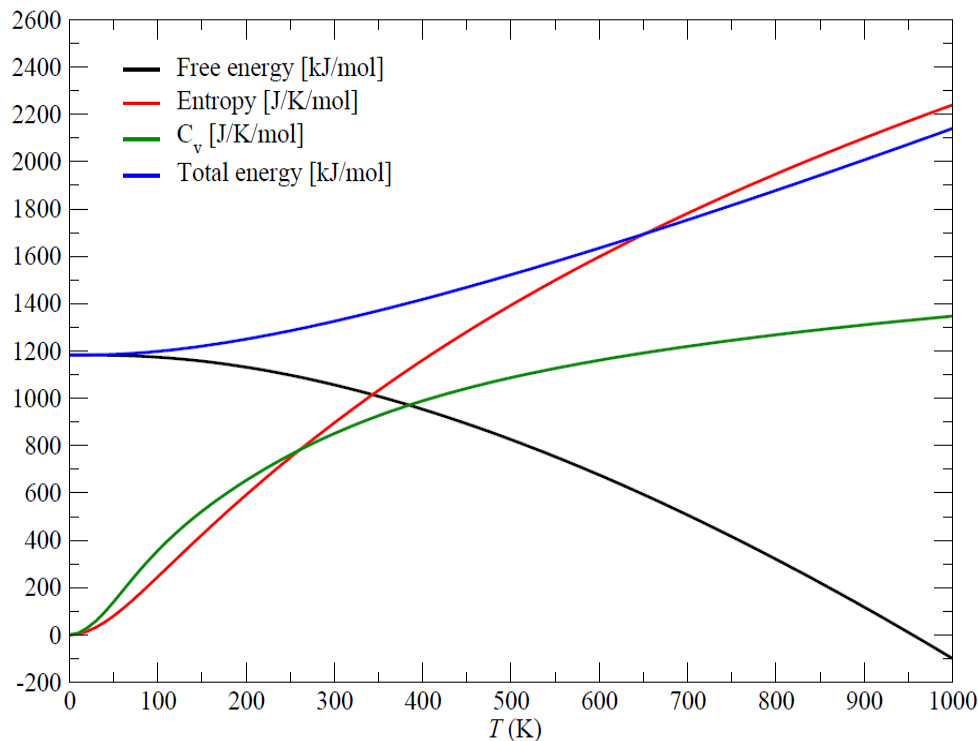
Crystal unit cell of metastudtite $(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2$ (space group $Pnma$, $Z = 4$) relaxed with DFT at the GGA/PW91 level of theory.



X-ray diffraction pattern of metastudtite. The experimental powder diffraction pattern for $\text{Cu K}\alpha_1$ radiation (Debets, 1963) is represented by blue lines. The diffraction pattern simulated from the orthorhombic structure (space group $Pnma$, $Z = 4$) reported in the present study is shown in red.

(Manuscript submitted to Dalton Transactions).

Thermal properties of uranyl peroxide hydrates corrosion phases: studtite



Evolution of the total energy and thermal properties of studtite (UO₂)O₂(H₂O)₄ (space group C2/c, Z = 4) calculated from the structure relaxed with DFT at the GGA/PW91 level of theory.

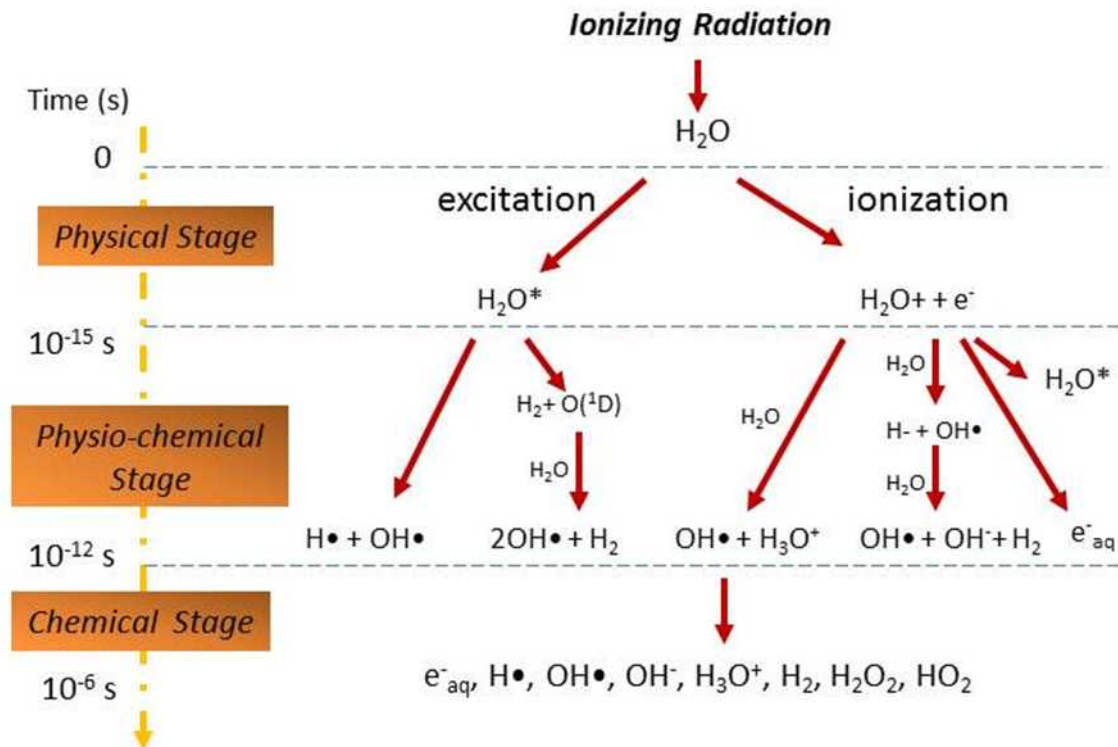
- **Thermal properties:**

- Density functional perturbation theory (DF-PT) was used to calculate the phonon properties of the relaxed studtite structure
- Thermal properties (free energy, entropy, heat capacity) were derived from phonon calculations.

- **Future work:**

- Extend structural and thermal calculations carried out within the framework of DFT/DFPT to other phases that may be involved in the corrosion of UO₂ fuel (schoepite, metaschoepite, dehydrated schoepite, metastudtite,...)

Radiolysis Model Description

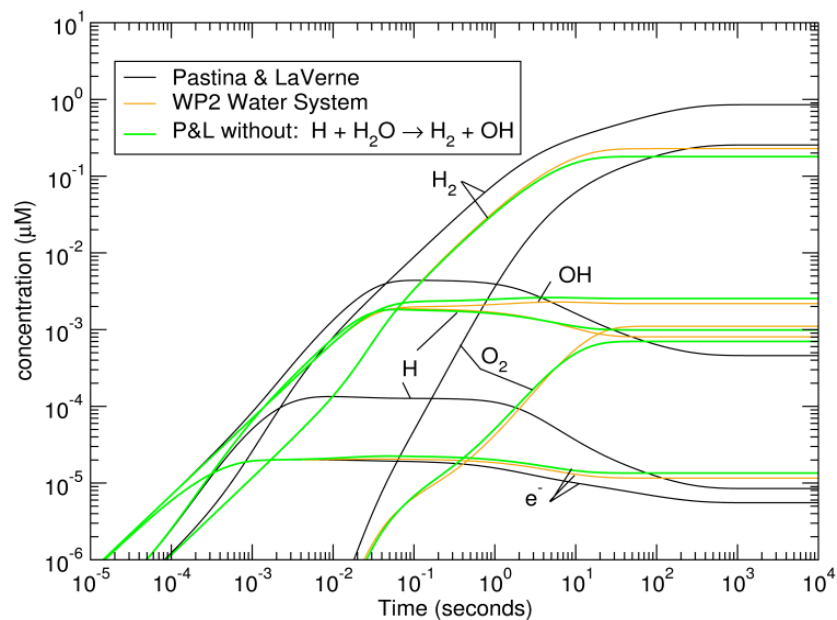


► **Coupled Reaction Kinetics
(146 reactions, 42 Species)**

$$\frac{d[A_i]}{dt} = G_i \dot{D} [A_i] + \sum_{r=1}^{N_r} k_{ir} \prod_{j_r=1}^{n_r} [A_{j_r}]^{O_{j_r}}$$

Used Fuel Disposition

PNNL Radiolysis Model



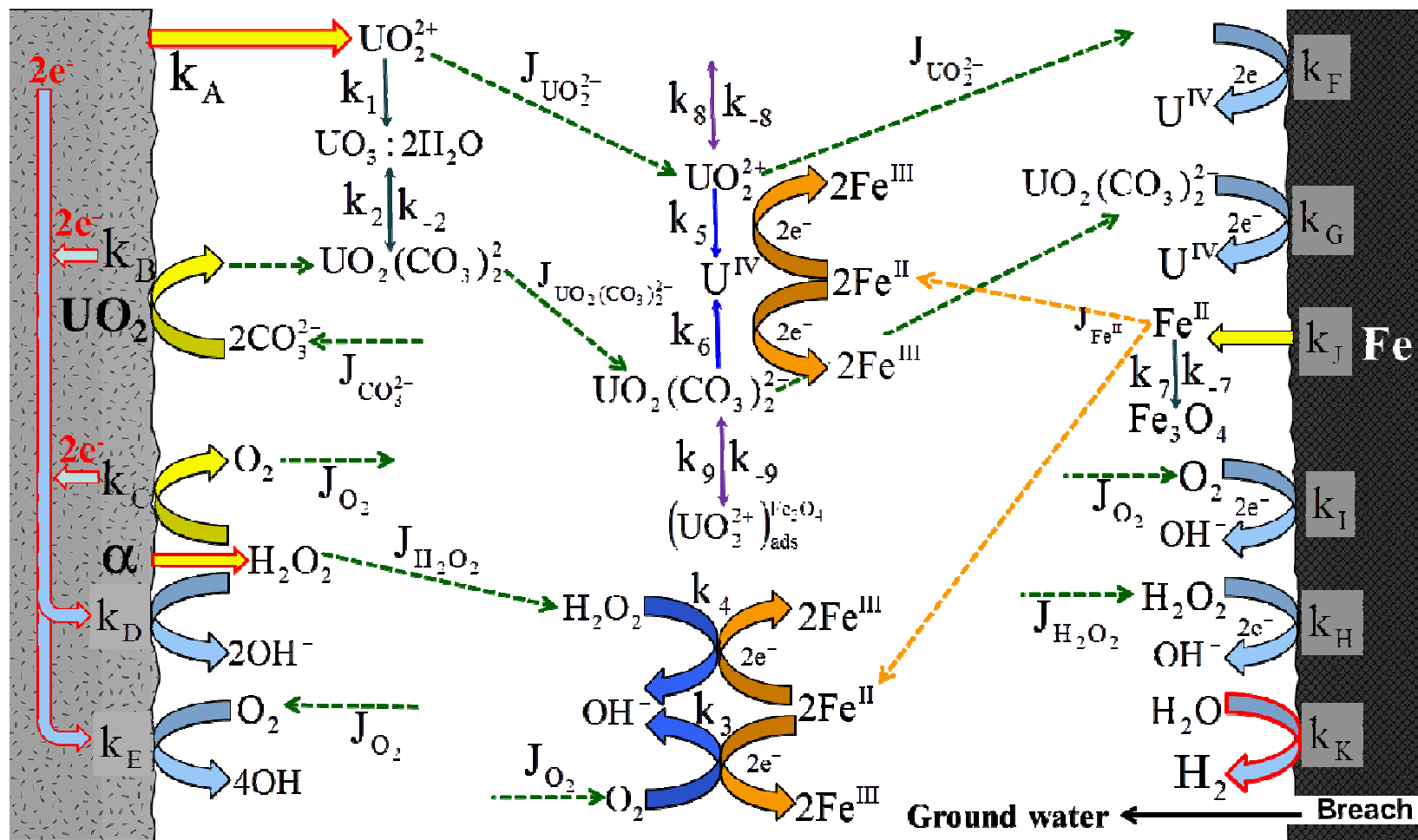
Used Fuel Disposition

Fuel Fabrication – In the Laboratory



Used
Fuel
Disposition

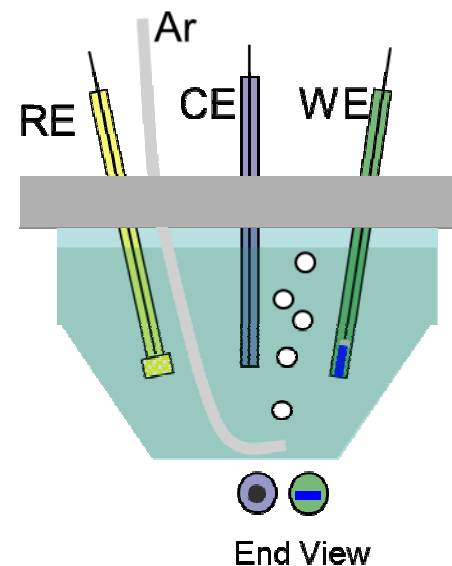
Reaction Scheme for MPM (anodic: yellow/orange, cathodic: blue)



Shoesmith (2003) Corrosion Sci. Sec.

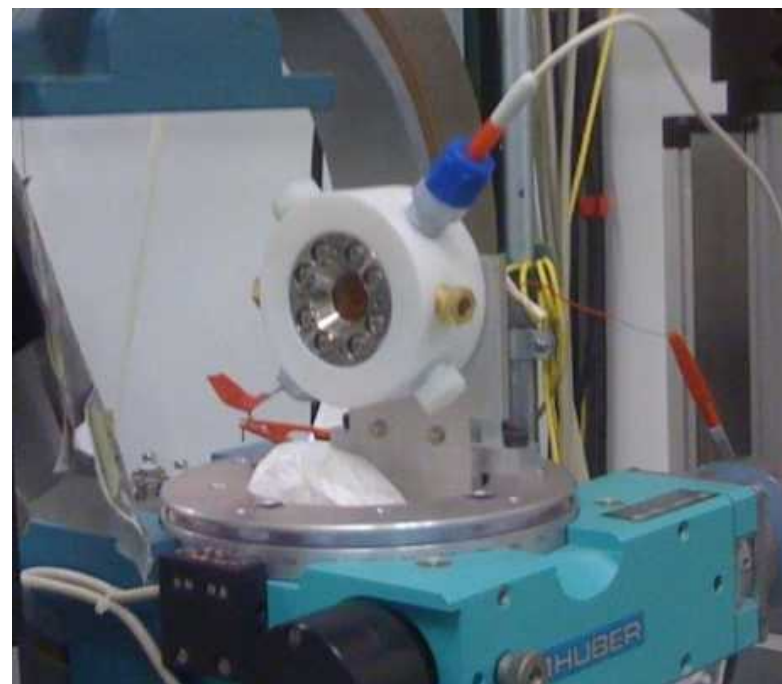
ANL Experimental Setup

- **Reference Electrode (RE):** Ag/AgCl
3M NaCl/saturated Ag/Cl
- **Counter Electrode (CE):** 2 mm
Diameter Pt Disk
- **Microcell**
 - Solution Volume: ~20 mL
 - Can de-air (Ar gas feed)
 - Use cover gas
 - Jacketed for temperature control via
flowing water



ANL Electrochemical Experiments: Capabilities for Radioactive Samples

- **Materials: Ru-Mo-Pd-Rh alloys & UO₂ electrodes: surrogates for NMP & used fuel matrix**
- **Multiple electrode electrochemical cell:**
 - Separate potentiostats used to control & monitor electrodes made with alloy and UO₂.
 - Tests run in static or flowing electrolytes with controlled H₂O₂ and H₂ concentrations.
- **Spectroelectrochemistry (Advanced Photon Source):**
 - *In-situ* X-ray absorption spectroscopy of solution, NM and UO₂ electrode surfaces under controlled redox conditions.
 - determine oxidation states & coordination environments of key radionuclides.
- **Full system characterization**
 - Electrochemistry
 - SEM, TEM, XRD, XAS surface analyses
 - Solution analyses: ICP-MS, LC...



Electrochemical cell for *in situ* XAS