

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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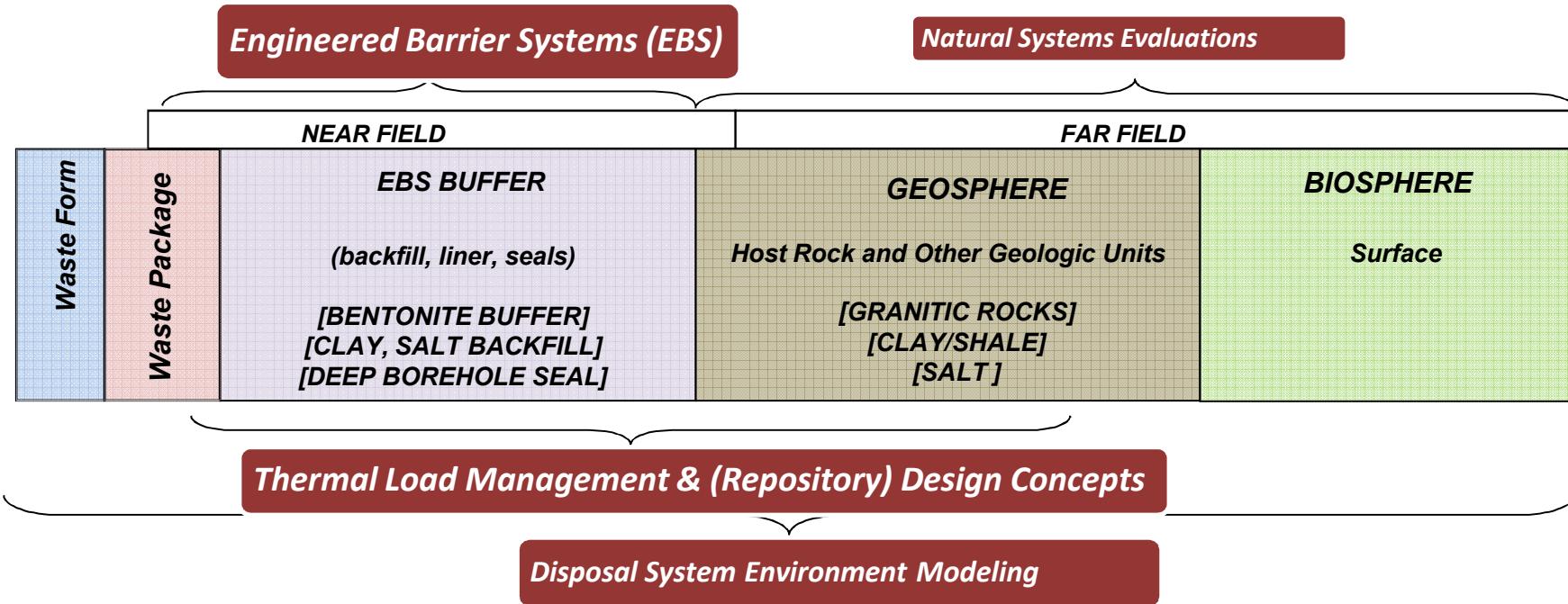


- FCAWG Task 3 - Spent Fuel Degradation and Durability over Geologic Time
- Used Fuel Disposition (UFD) Disposal Research Activities
- Used Fuel Degradation and Radionuclide Mobilization (UFD&RM) Activities
 - Overview
 - Fiscal Year 2011 Accomplishments
 - Fiscal Year 2012 Activities and Milestones
 - *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*

Used Fuel Disposition

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

- **ANL, PNNL, SNL**
 - Developed chemical-radiolysis model for evaluating the dissolution rate of used fuel
 - *enhanced the model for in-package chemical conditions (UO₂, 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)*

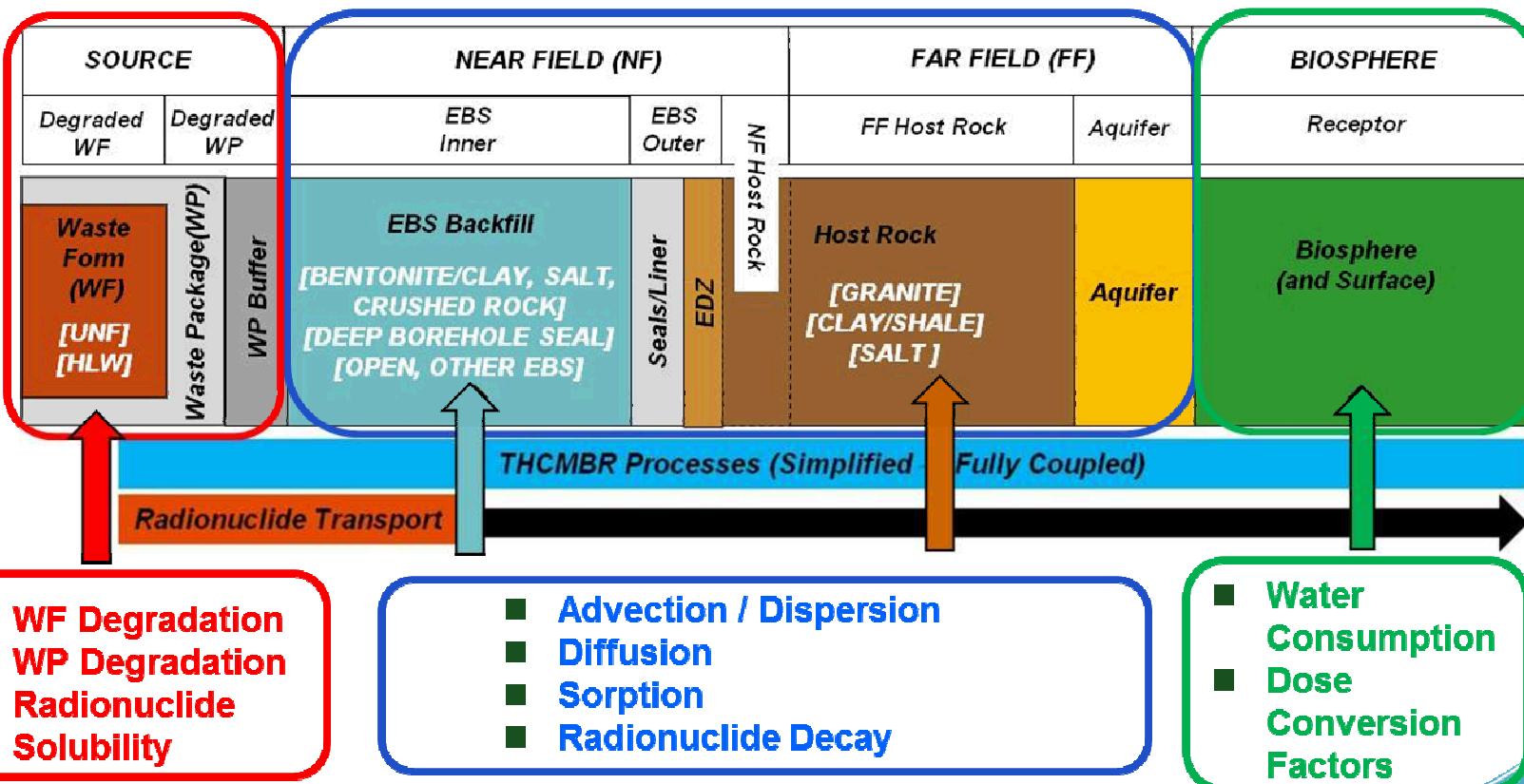
- **ANL tasks/milestones**

- 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)*

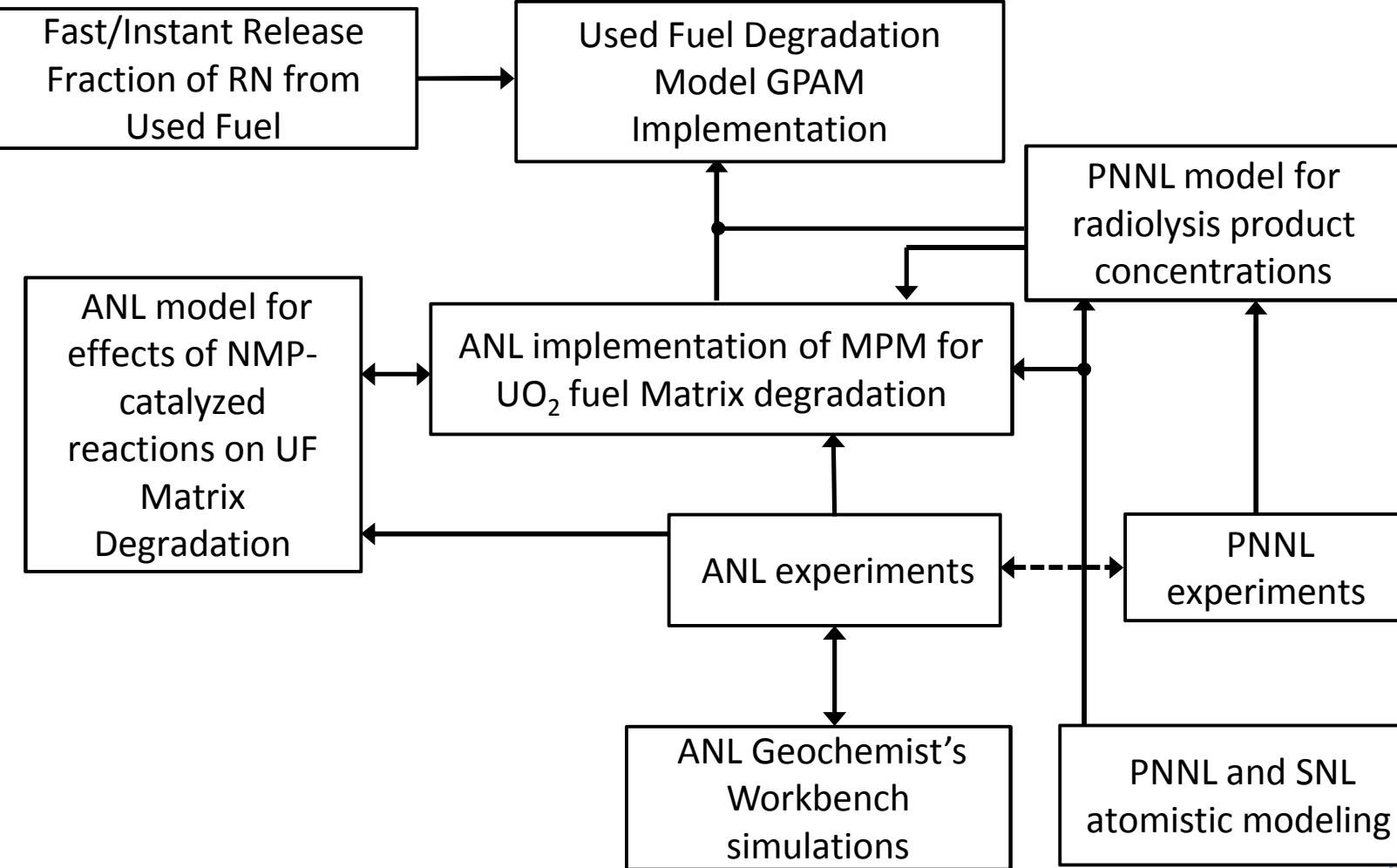
- SNL Team: David Sassani, Philippe Weck, Carlos Jove-Colon
- Developing strategy for model implementation into Generic Performance Assessment Model (GPAM)
- Constraining instant release fractions from used fuel;
 - Data and models from YMP: Triangular Distributions for ^{137}Cs ; ^{129}I ; ^{99}Tc ; ^{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 $\text{O}_2\text{-H}_2\text{O}\text{-H}_2\text{O}_2$ surface interactions with the UO_2 slab
 - Will extend to other U minerals, e.g., stuttite

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



GPAM – Conceptual Framework - UFD&RM Activities Context



- **Used Fuel Degradation and Radionuclide Mobilization Model Concepts**

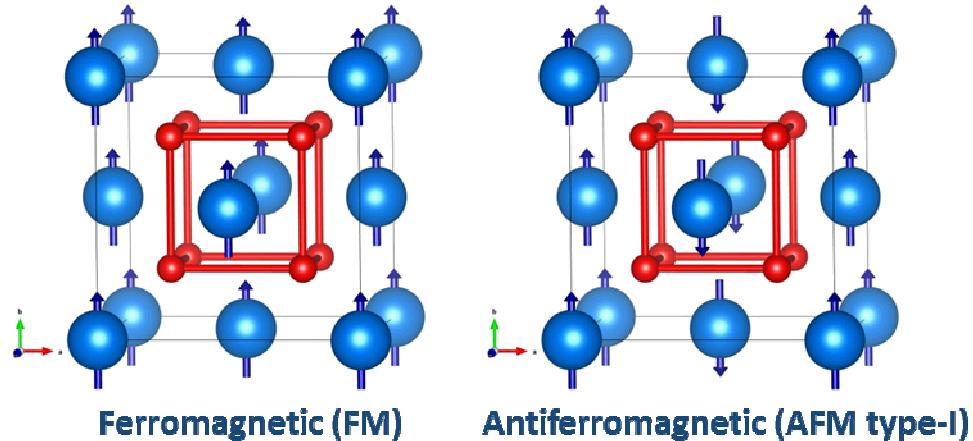
- The fast release fraction (or instant release) inventory that includes fission products located in
 - *The fuel gap*
 - *The plenum regions (fission gases)*
 - *The accessible grain boundaries/pellet fractures*
- The matrix degradation inventory that includes the matrix itself and fission products 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)

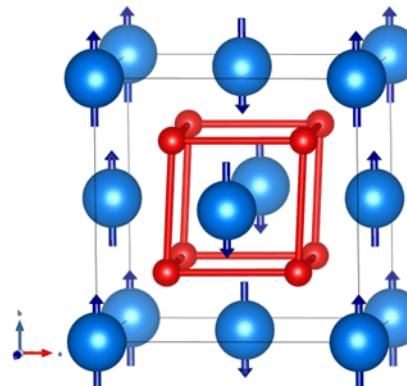
- GGA+ U study of *bulk* UO_2 : ordered and disordered oxygen lattice

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



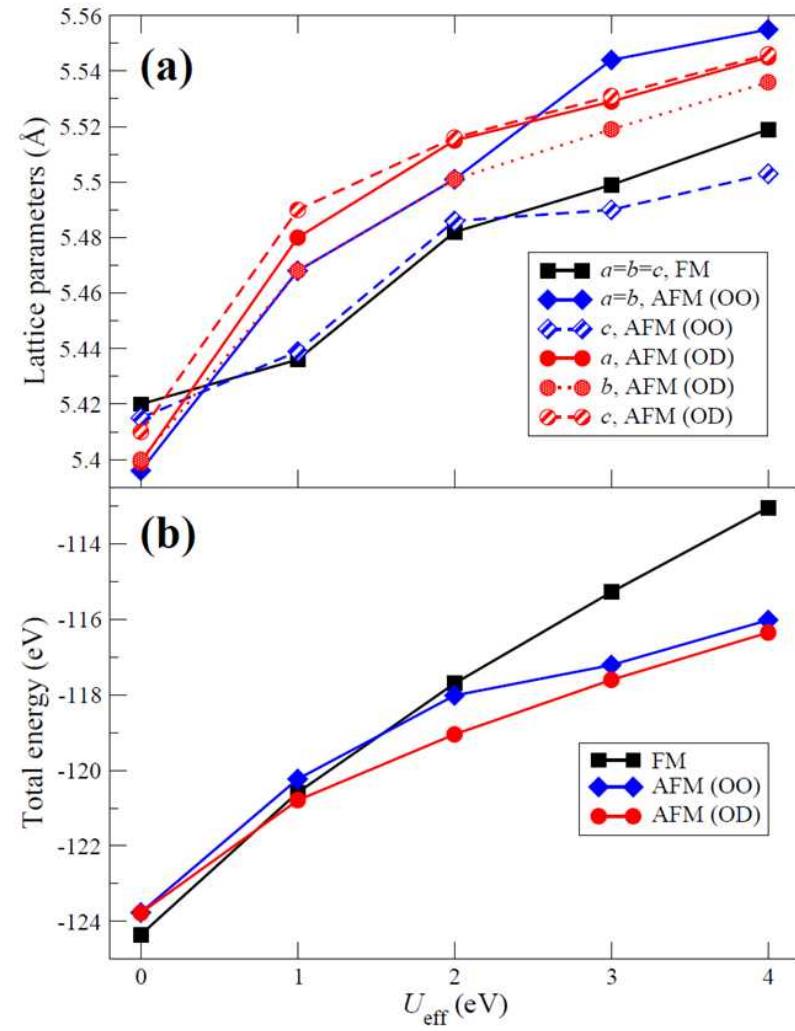
- Antiferromagnetic (AFM type-I) with oxygen sublattice distortion (OD) in the [111] direction:

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



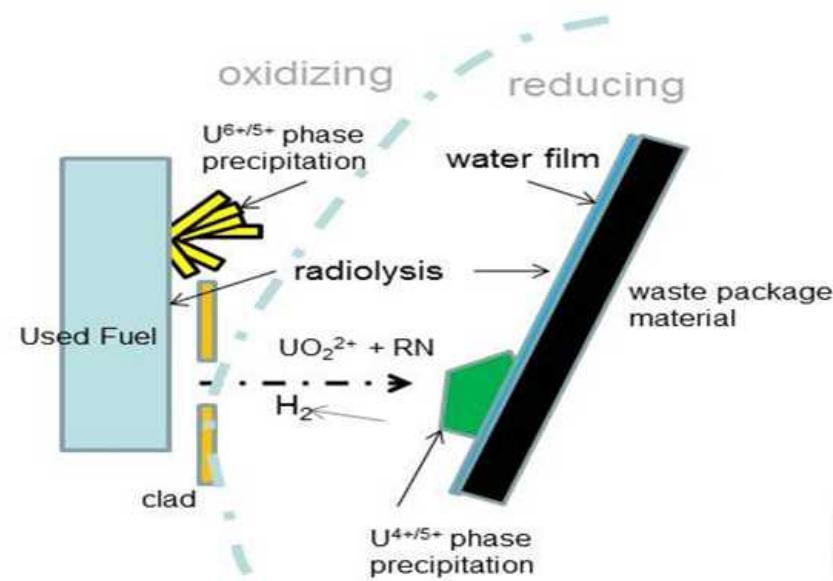
Molecular Modeling of UO_2 Surface Reactions (continued)

- **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



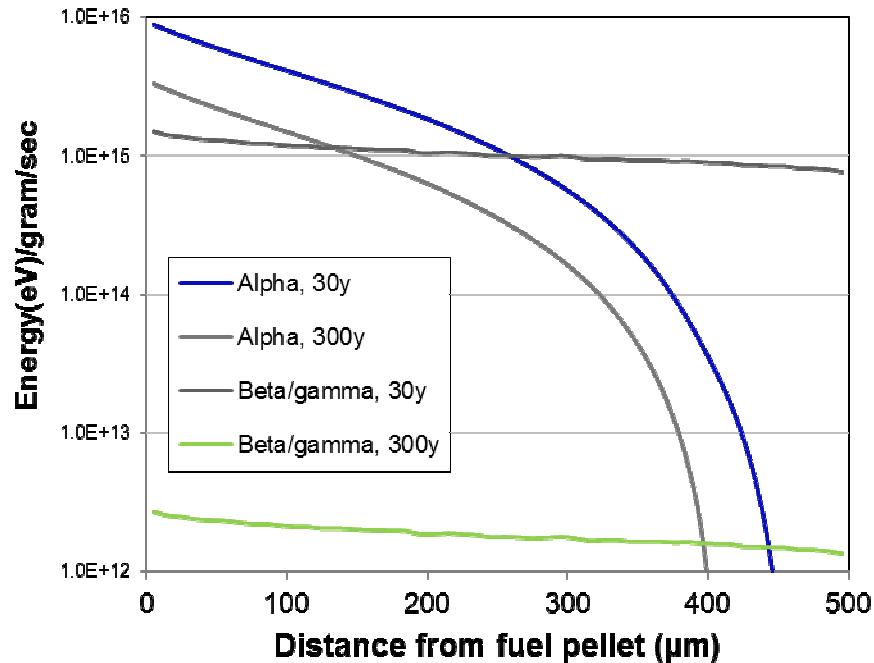
- **PNNL Team: Edgar Buck, Rick Wittman, Bruce McNamara, Frances Skomurski**
- **Implementation of Radiolysis Models for Used Fuel Degradation and Radionuclide Migration in a Degraded EBS Environment**
 - Development of a quality user interface for radiolysis model
- **Development of Simulant Fuels for 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 $\text{H}_2\text{-UO}_2\text{-H}_2\text{O}$ 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

- 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



Evaluation and Development of Radiolysis Models

Radiolysis Model Development

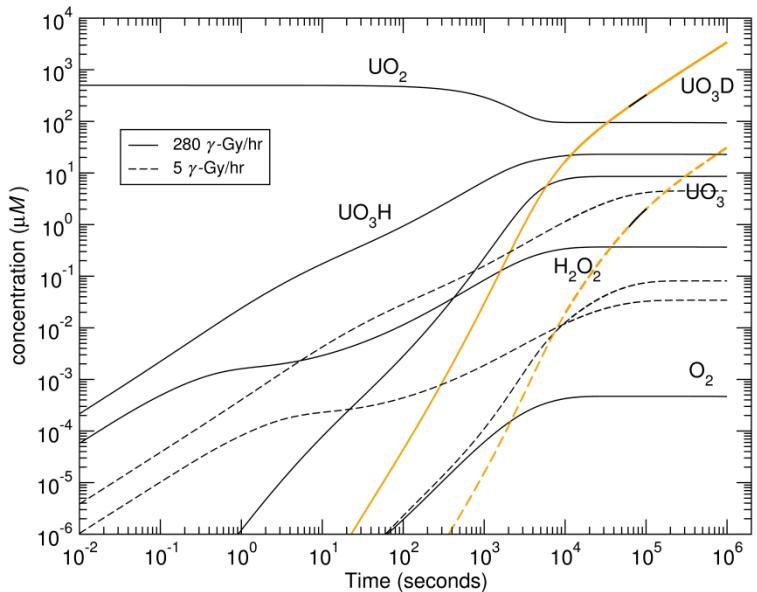


Figure 1

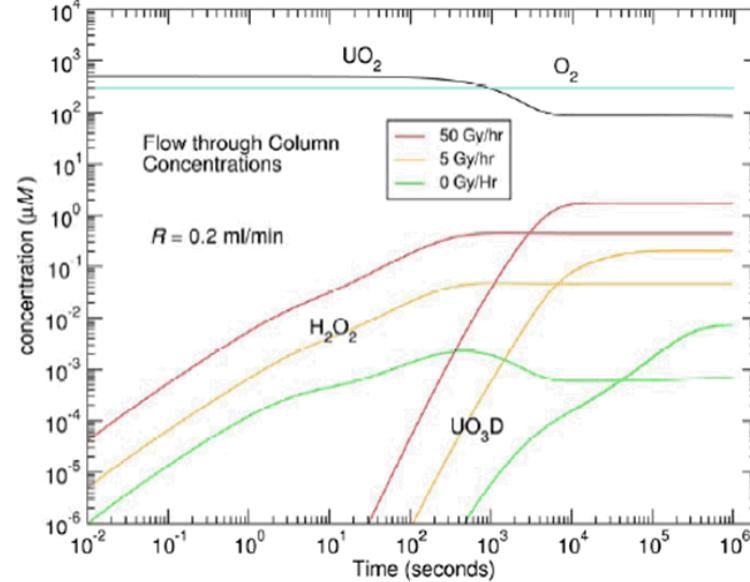


Figure 2

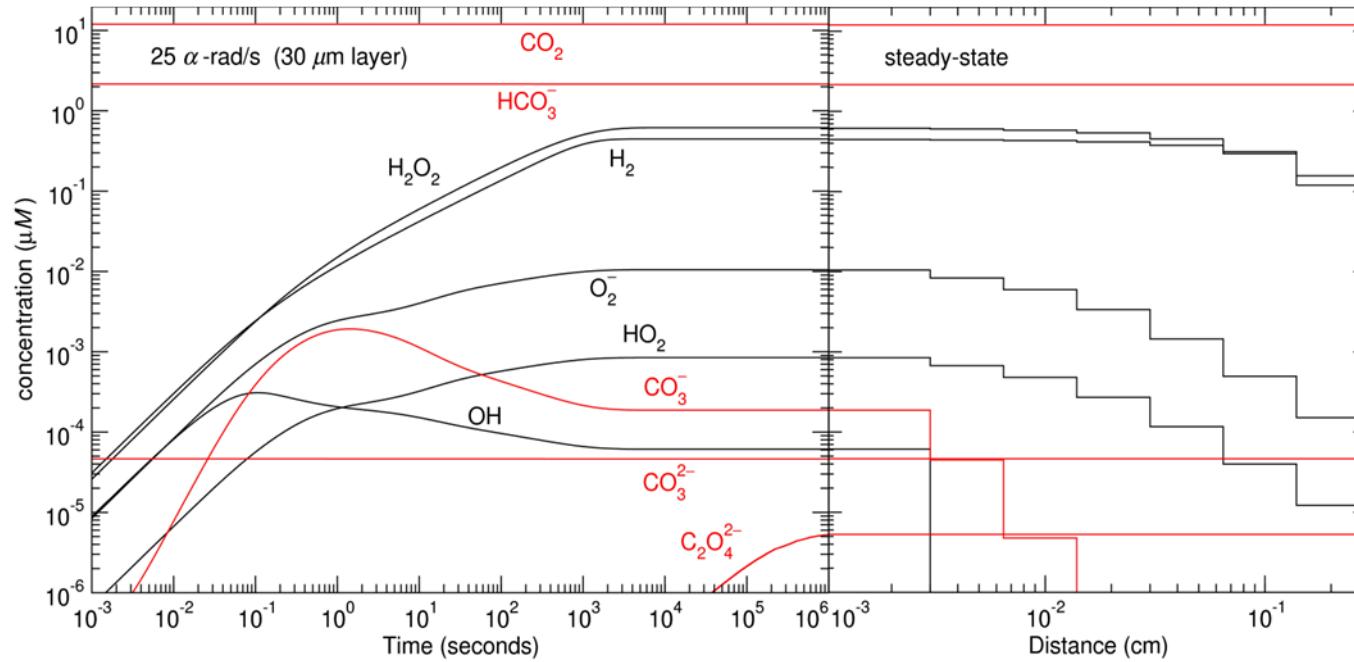
Figure 1. Shows the predicted dissolution rate with the radiolysis model.

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.

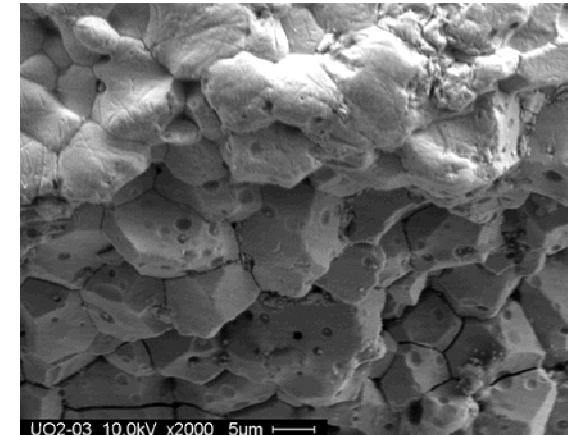
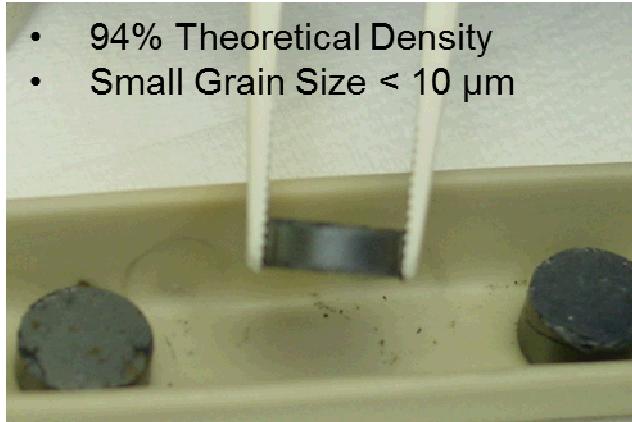
Carbonate System Study

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



Development of Simulant Fuels for Experimental Investigation

- Produce doped simulated fuels for experimental work

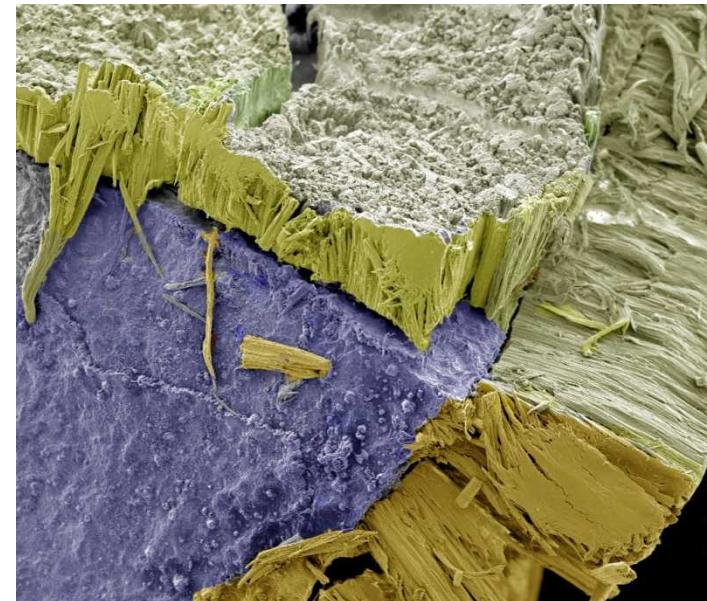


ID	MC	ME	RC	ZE	ZC	TM	TE	TR
OXIDE (WT%)	UO ₂ -MO-CE	UO ₂ -MO-EU	UO ₂ -RE-CE	UO ₂ -ZR-EU	UO ₂ -ZR-CE	UO ₂ -TH-MO	UO ₂ -TH-EU	UO ₂ -TH-RE
UO₂	93.89	90.74	92.28	88.59	91.59	82.19	79.06	80.80
ThO₂						15.07	14.50	14.81
ZrO₂				5.00	5.17			
MoO₃	2.78	2.69				2.74		
CeO₂	3.33		3.27		3.24			
ReO₂			4.45					4.38
Eu₂O₃		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

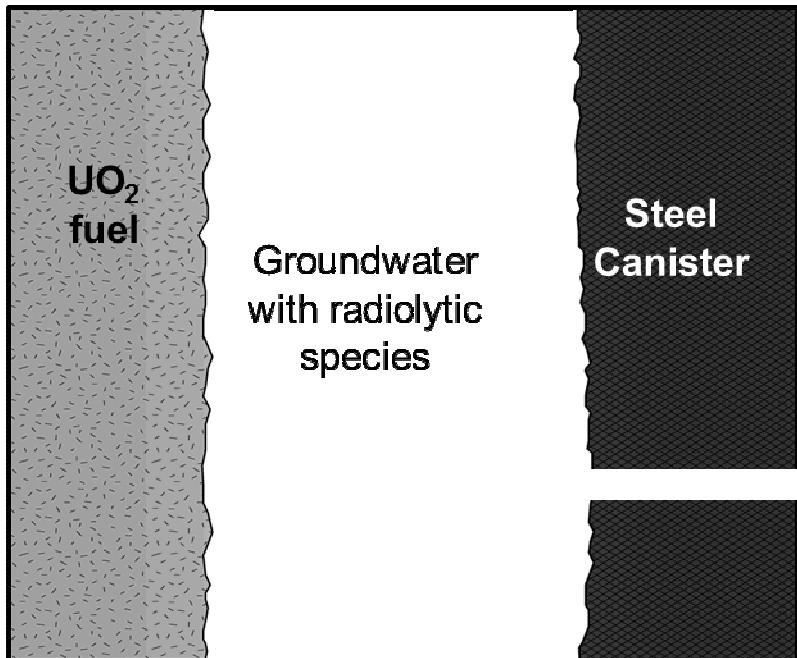
Studtite on UO_2



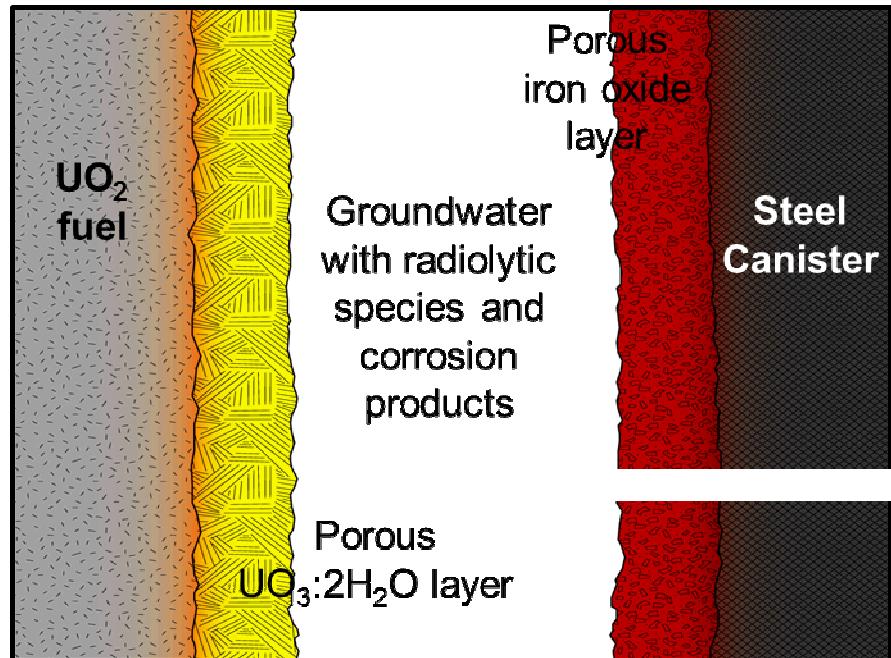
- **ANL Team: Jim Jerden, Terry Cruse, Kurt Frey, Jeff Fortner, Bill Ebert**
- **Implement used fuel matrix degradation rate model**
 - Based on the mixed potential model (MPM) of Shoesmith (2003, *Corrosion Sci. Sec.*)
- **Quantify catalytic effect of NMP on UO_2 oxidative dissolution rate by electrochemical 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.)



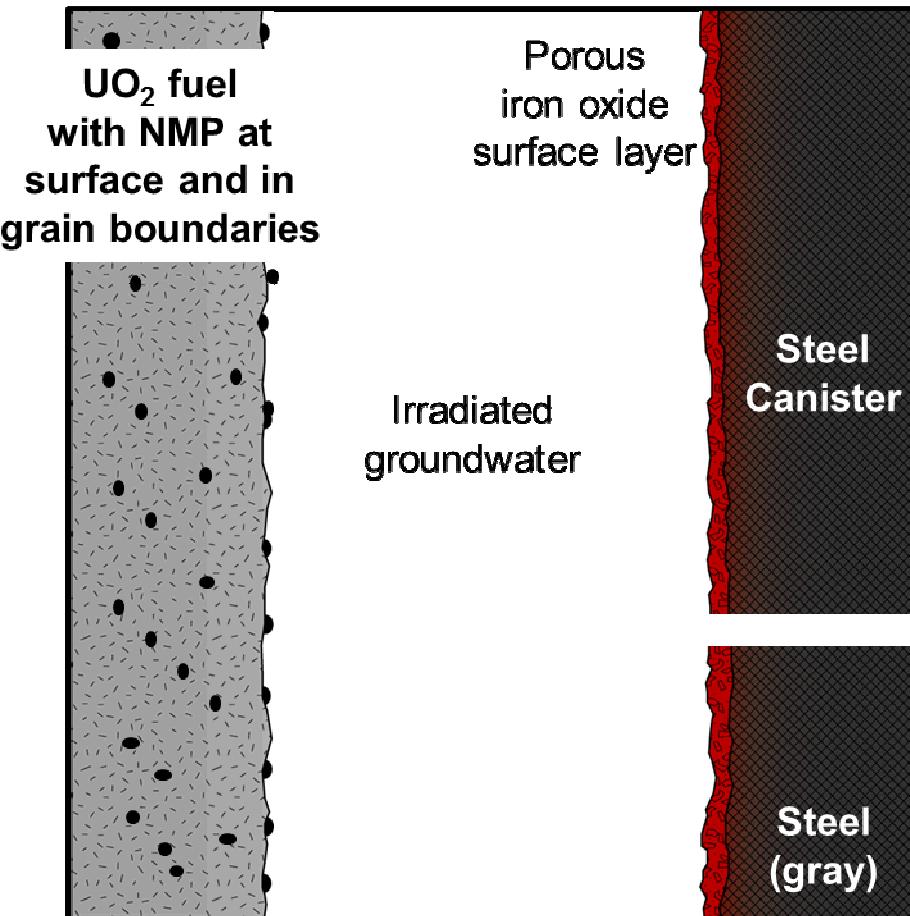
Initial Condition



Long-Time Condition
under oxidizing conditions

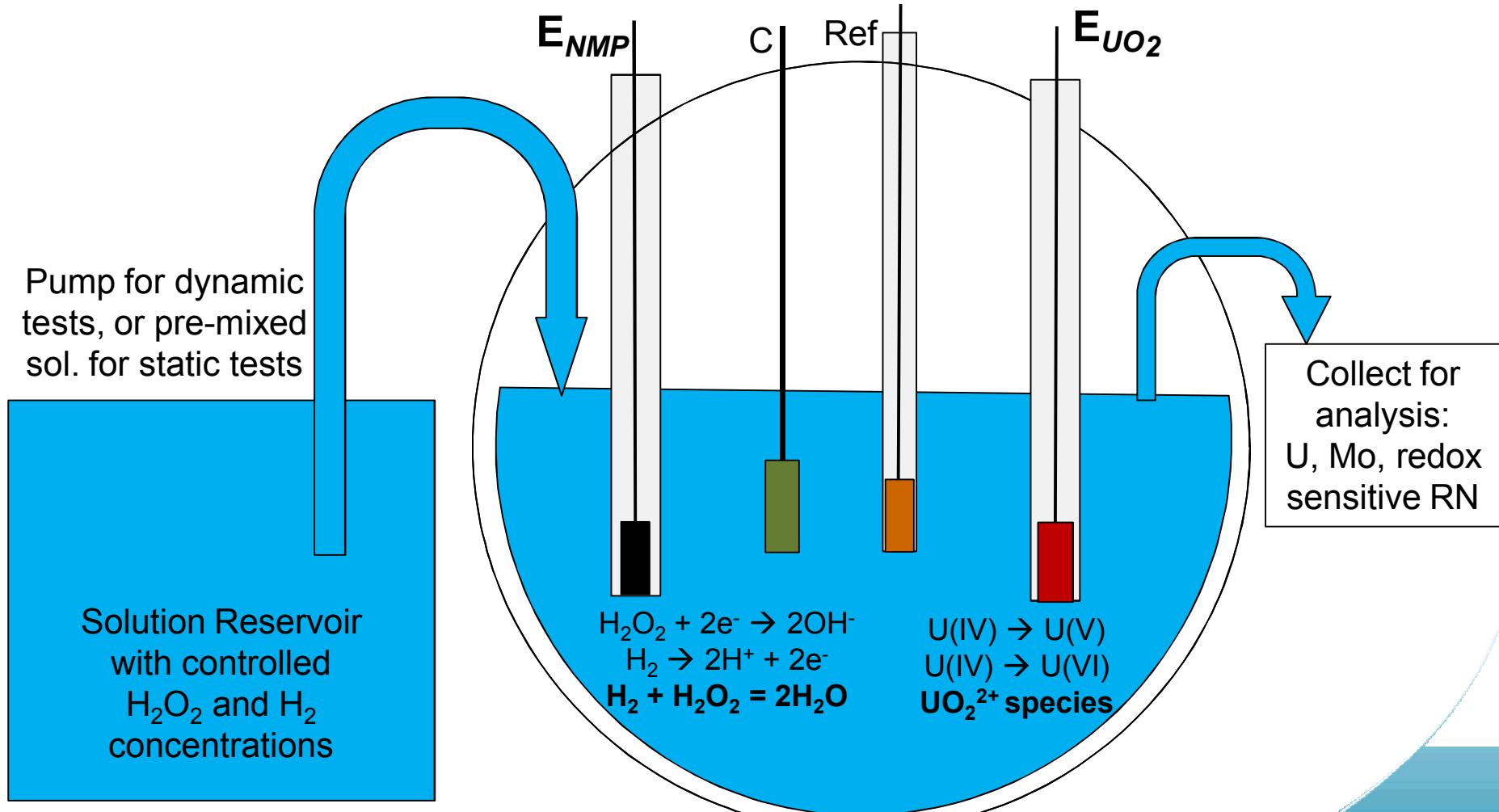
Extend MPM to Explicitly Account for Effects of NMP

- 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 UO₂
 - 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, H₂O₂ and H₂ concentrations, electrode surface areas, and imposed potentials
 - $H_2O_2 + 2e^- \rightarrow 2OH^-$ coupled with $H_2 \rightarrow 2H^+ + 2e^-$ (*catalyzed by NMP)
 - $H_2O_2 + 2e^- \rightarrow 2OH^-$ coupled with $UO_2 \rightarrow UO_2^{2+} + 2e^-$
 - Measure concentrations of U, Mo, Tc, etc. in solutions containing H₂O₂ and H₂ (separate tests with and without NMP alloys in system)
- Corrode surface of NMP under controlled conditions (*ex situ*)
 - Control potentials, T, pH, solution chemistry (H₂O₂, H₂, 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 UO₂ into solutions with dissolved H₂O₂ and H₂ 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*

- **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

- **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**

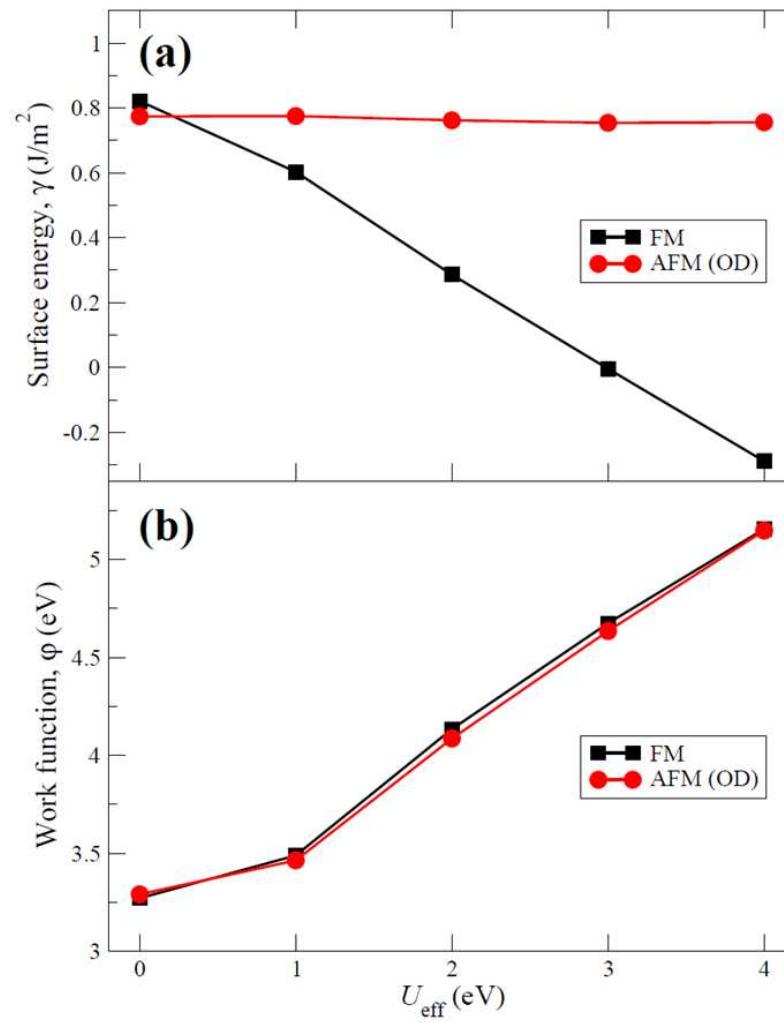
- Quantify the role of strong electron correlations in UO_2 bulk and in a $\text{UO}_2(111)$ slab model using the generalized gradient approximation corrected with an effective Hubbard parameter (GGA+U) to account for the strong on-site Coulomb repulsion between U 5f electrons (VASP code).
- Use perturbation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

- **Milestones**

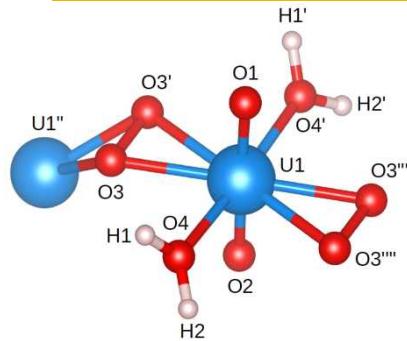
- M2FT-12SN0806062 “Integration of EBS Models with Generic Disposal System Models” (September 2012)

Molecular Modeling of UO_2 Surface Reactions (continued)

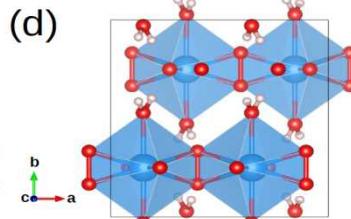
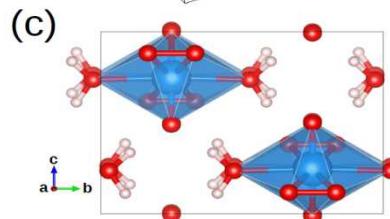
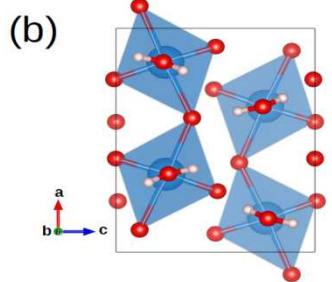
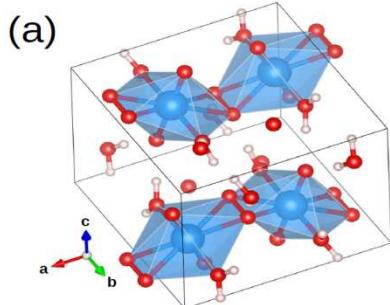
- Variation of the surface energy and work function of the relaxed $\text{UO}_2(111)$ surface
 - FM and AFM (OD) solutions
 - Only minor change for the $+U$ correction on the surface energy of the AFM structure
 - Use of $+U > 3$ eV leads to unphysical results for the FM solution.
 - Experimental estimate: $\gamma = 0.85 \text{ J/m}^2$ 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)



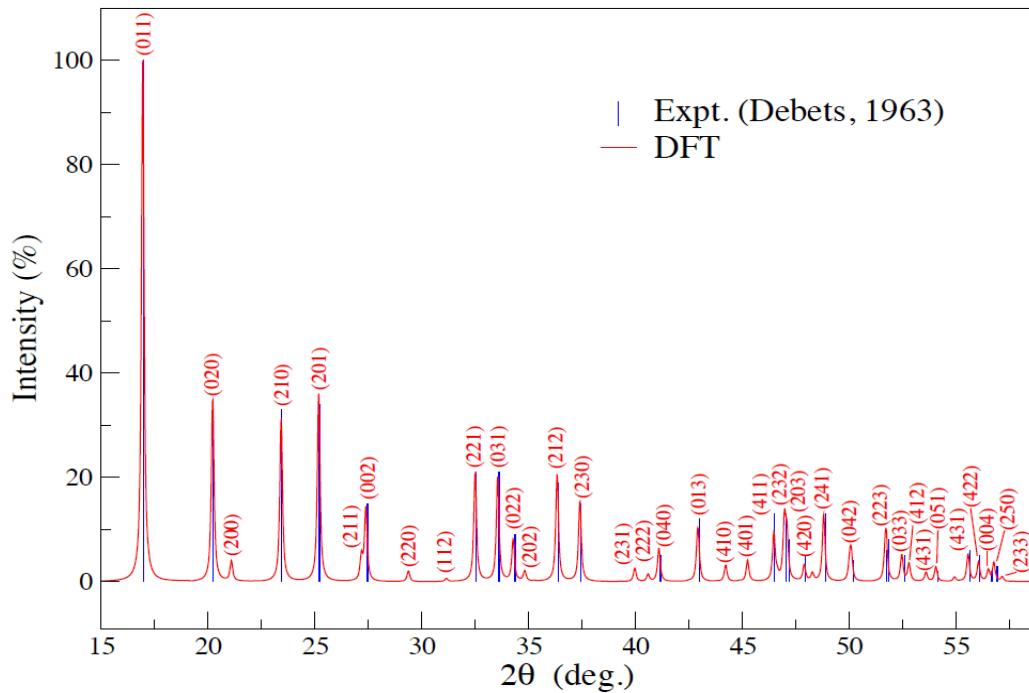
Structural properties of uranyl peroxide hydrates corrosion phases



Ball-and-stick representation of the $(UO_2)O(H_2O)$ complex composing metastudtite



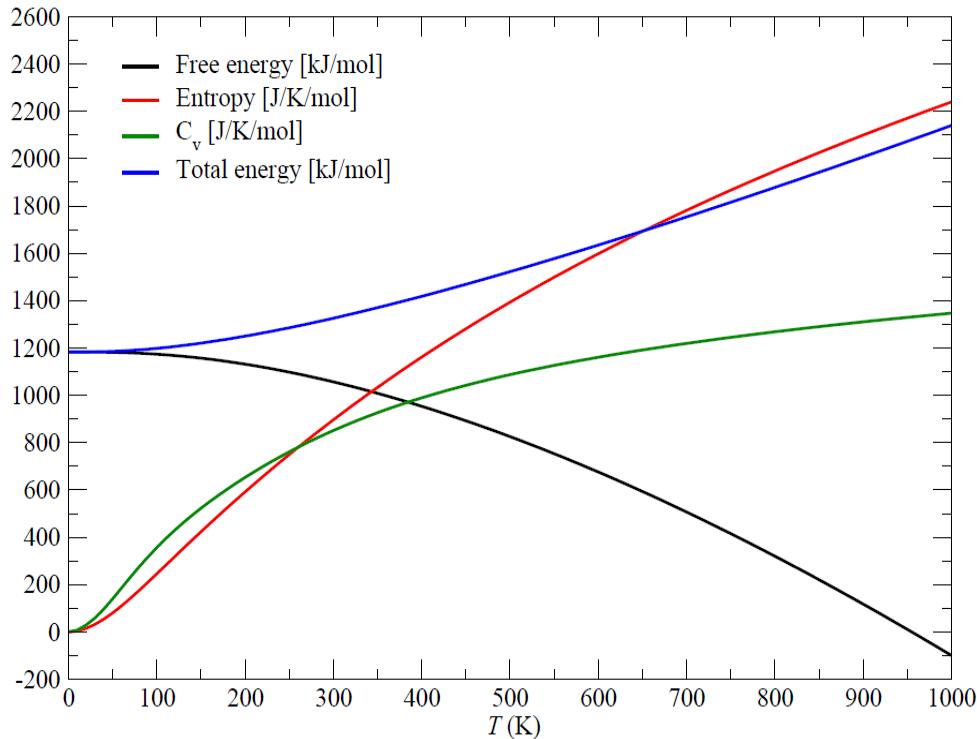
Crystal unit cell of metastudtite $(UO_2)O_2(H_2O)_2$ (space group $Pnma$, $Z = 4$) relaxed with DFT at the GGA/PW91 level of theory.



X-ray diffraction pattern of metastudtite. The experimental powder diffraction pattern for 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*).

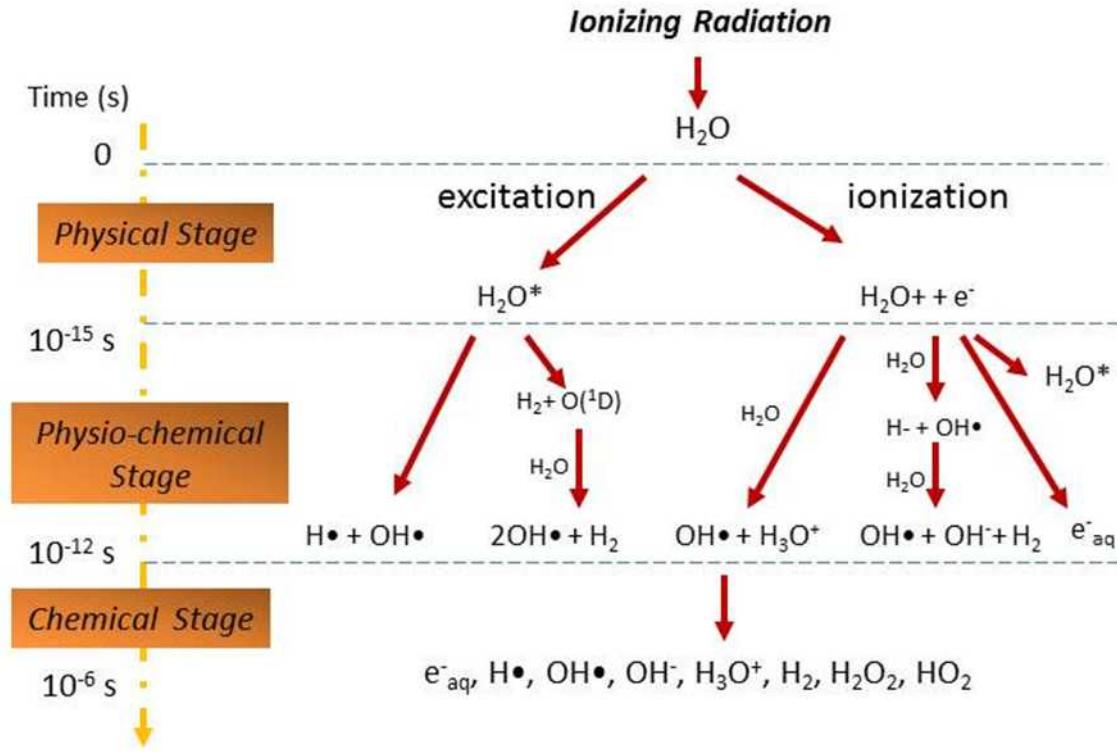
Thermal properties of uranyl peroxide hydrates corrosion phases: studtite



Evolution of the total energy and thermal properties of studtite ($UO_2O_2(H_2O)_4$ (space group $C2/c$, $Z = 4$) calculated from the structure relaxed with DFT at the GGA/PW91 level of theory.

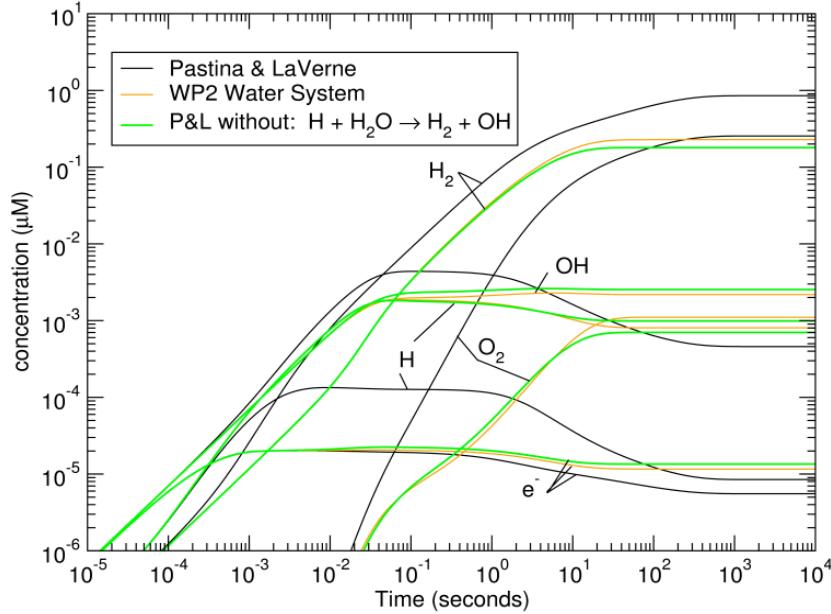
- **Thermal properties:**
 - Density functional perturbation theory (DF-PT) was used to calculate the phonon properties of the relaxed studtite structure
 - Thermal properties (free energy, entropy, heat capacity) were derived from phonon calculations.
- **Future work:**
 - Extend structural and thermal calculations carried out within the framework of DFT/DFPT to other phases that may be involved in the corrosion of UO_2 fuel (schoepite, metaschoepite, dehydrated schoepite, metastudtite,...)

Radiolysis Model Description

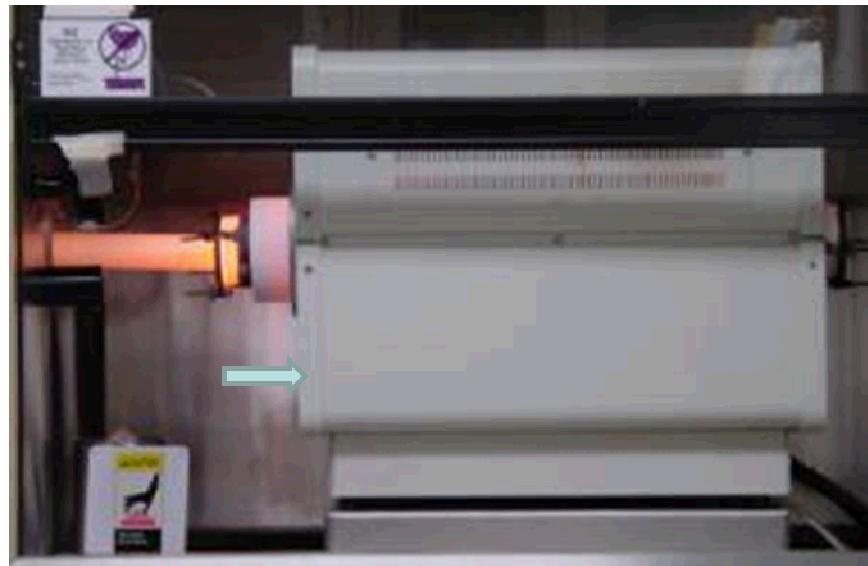
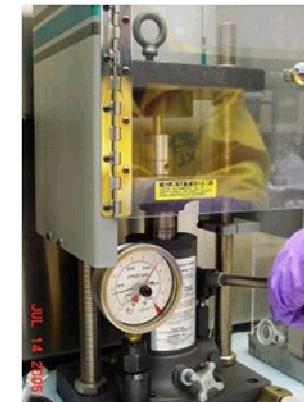


► Coupled Reaction Kinetics (146 reactions, 42 Species)

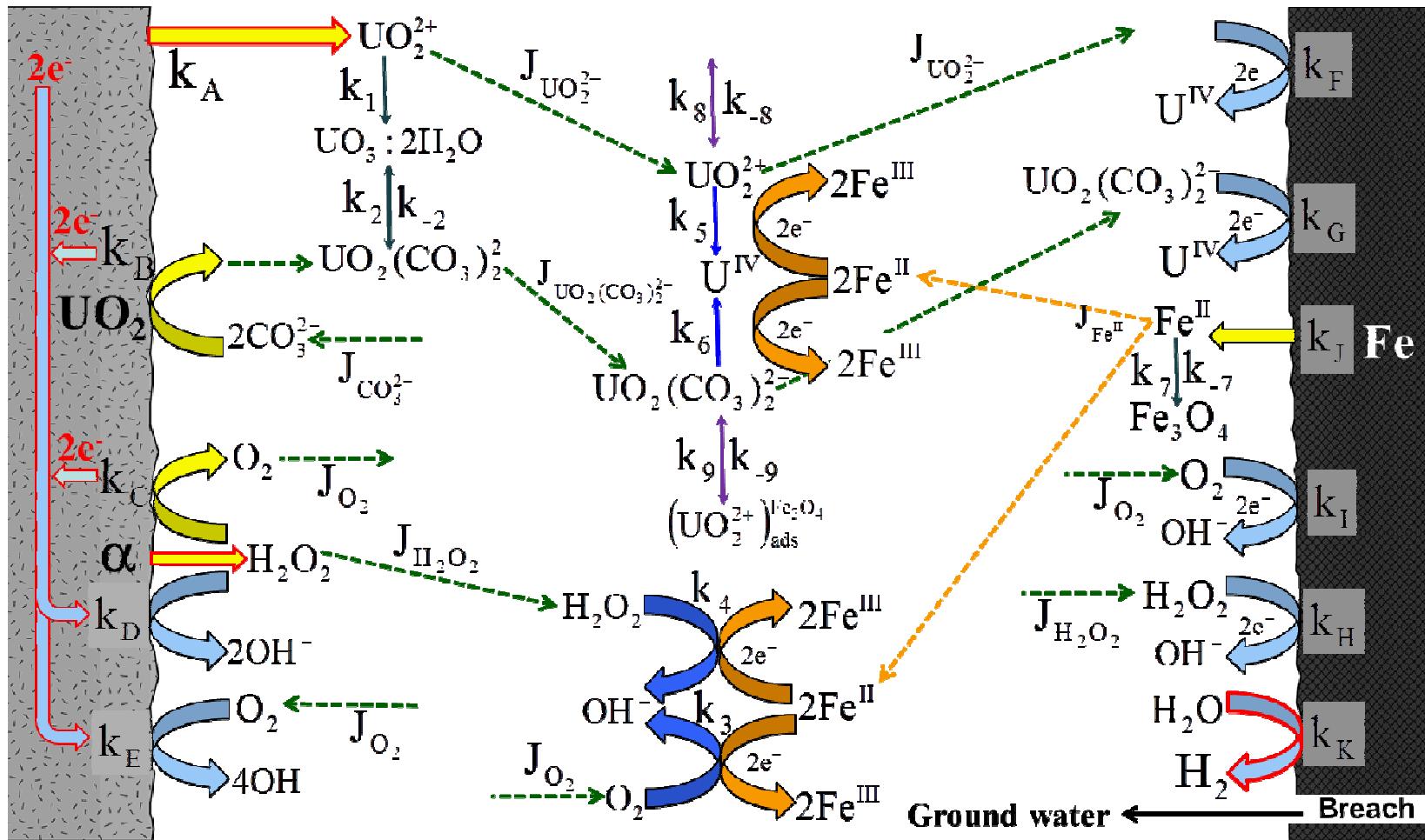
$$\frac{d[A_i]}{dt} = G_i \dot{D}[A_i] + \sum_{r=1}^{N_r} k_{ir} \prod_{j_r=1}^{n_r} [A_{j_r}]^{O_{jr}}$$



Fuel Fabrication – In the Laboratory



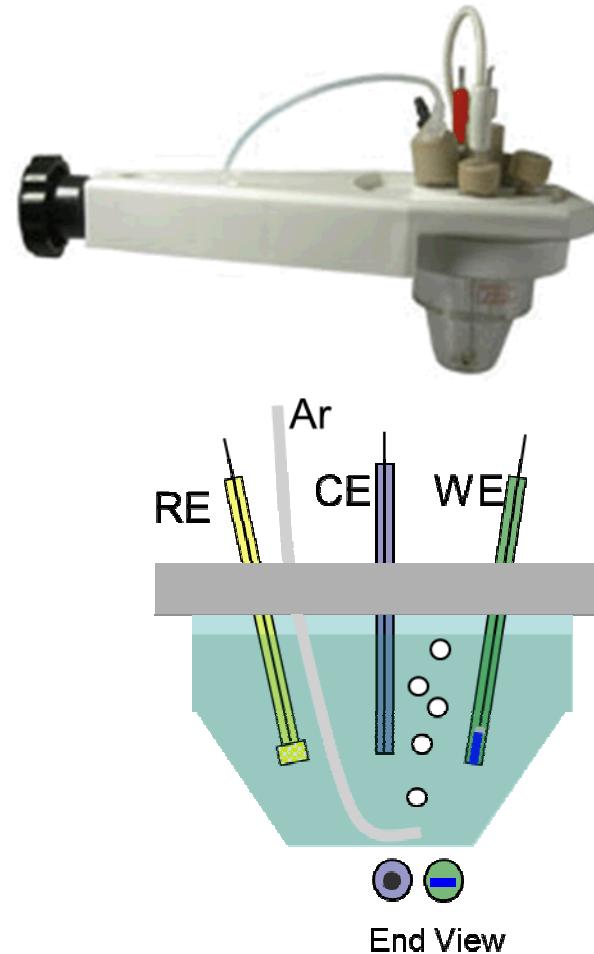
Reaction Scheme for MPM (anodic: yellow/orange, cathodic: blue)



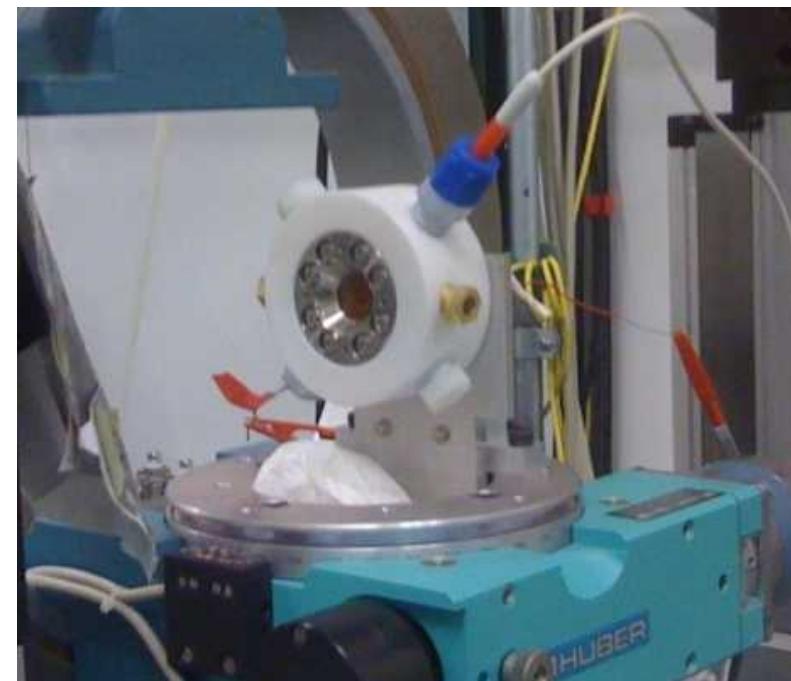
Shoesmith (2003) Corrosion Sci. Sec.

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



- Materials: Ru-Mo-Pd-Rh alloys & UO_2 electrodes: surrogates for NMP & used fuel matrix
- Multiple electrode electrochemical cell:
 - Separate potentiostats used to control & monitor electrodes made with alloy and UO_2 .
 - Tests run in static or flowing electrolytes with controlled H_2O_2 and H_2 concentrations.
- Spectroelectrochemistry
(Advanced Photon Source):
 - *In-situ* X-ray absorption spectroscopy of solution, NM and UO_2 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