

# Used Fuel Disposition Campaign

## Task 1: Screening Tools for Repository Decisions

**Palmer Vaughn: *Sandia National Laboratories (SNL)***

***ROK – US Joint Fuel Cycle Study***

***UFD Fuel Cycle Alternative Working Group (FCAWG)***

***March 11-13, 2013***

## Task 1: Staffing

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### ■ Duration: October 2011 – June 2014

### ■ Leads:

- Haeryong JUNG                      KRMC                      [nohul@krmc.or.kr](mailto:nohul@krmc.or.kr)
- Jeongtae Jeong                      KAERI                      [jtjeong@kaeri.re.kr](mailto:jtjeong@kaeri.re.kr)
- Palmer Vaughn                      SNL                      [pvaughn@sandia.gov](mailto:pvaughn@sandia.gov)

### ■ SNL Team:

- Geoff Freeze                      Disposal System Modeling                      SNL                      [gafreez@sandia.gov](mailto:gafreez@sandia.gov)
- Shaoping Chu                      Generic Granite Modeling                      LANL                      [spchu@lanl.gov](mailto:spchu@lanl.gov)
- Paul Mariner                      Source Term, Biosphere Modeling                      SNL                      [pmarine@sandia.gov](mailto:pmarine@sandia.gov)

## Task 1: Goals and Purpose

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- **Develop and apply capability for the analysis of potential disposal sites for used nuclear fuel.**
  - The Korean Radioactive Waste Management Corporation (KRMC) has launched an R&D program for potential site investigation and selection .
    - *Develop a tool for the analysis of potential disposal sites for used nuclear fuel.*
    - *First stage of this program: Implementation plan for developing preliminary safety assessments of the potential disposal sites.*
    - *Second stage KRMC and KAERI: Develop a general performance assessment program (TSPA) for disposal site selection of used nuclear fuel. The TSPA program development includes exposure dose assessment both deterministically and probabilistically for operating scenarios including normal operations, well intrusions, earthquakes, and the early failure of waste packages.*
  - US DOE/UFDC is reevaluating disposal options for the fate of nuclear fuels. A number of potential repository host rock types, waste forms, and engineered barrier system concepts are proposed for investigation.
    - *GDSM is developing generic performance assessment models for disposal in Granite, Salt, Clay, and Deep Borehole to support technical and programmatic decisions.*
    - *Develop disposal system model in a flexible fashion to meet the evolving needs of the DOE NE/UFDC mission by providing the capability to produce risk information throughout the potential future phases of the mission and that facilitates incorporating new knowledge as it becomes available and necessary.*
    - *First iteration simplified probabilistic disposal system models have been developed.*

## Task 1: Deliverables

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- **12/15/2012: A draft report “Gap Analysis: Data and Modeling Needs for Korean Reference Geologic Media Site Selection Performance Assessment Modeling.”** Document results of collaboration with ROK staff. Conceptual models, numerical implementation, and data needs relevant to Korean reference geologic media modeling will be identified. Current data availability and gaps to support the modeling will be documented, including waste form, engineered barriers, inventory, and characterization of the natural system. **Delayed due to budget and reprioritization of DOE/UFD GDSM/ADSM activities. Proposed target date of 08/30/2013.**
- **6/30/2014 : Report titled “Comparative Analysis of GPAM and ROK TSPA Safety Assessment of a Potential ROK Granite Repository.”** Utilize the data and conceptual models resulting from the collaboration and implement in the GPAM and the ROK TSPA. Document description of the models and results of the safety assessment, and provide logical explanations for any differences in results. **Proposed revised target date of 3/1/2014.**

## Task 1: Supporting Efforts

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- **Develop a mutual understanding of disposal system modeling needs relevant to disposal of Used Nuclear Fuel in ROK granite. **In process.****
  - FEPs,
  - System Conceptualization,
  - Numerical Implementation,
  - Supporting Data.
- **Identify gaps in models and supporting data. **In process.****
- **Perform comparative safety assessment using currently available models and data and evaluate results. (e.g. ROK TSPA and DOE UFD GPAM). **Proposed timeframe: December 2013.****
- **Make recommendations for future efforts. **TBD****

## **■ Initial technical contact December 2011**

- Sent UFD FEPs Report, GDSM FY11 milestone report
- Request info from RPK on current state of safety assessment model, FEPs analysis, system model requirements, conceptualizations, data, and sub-model components .

## **■ Technical exchange 2012**

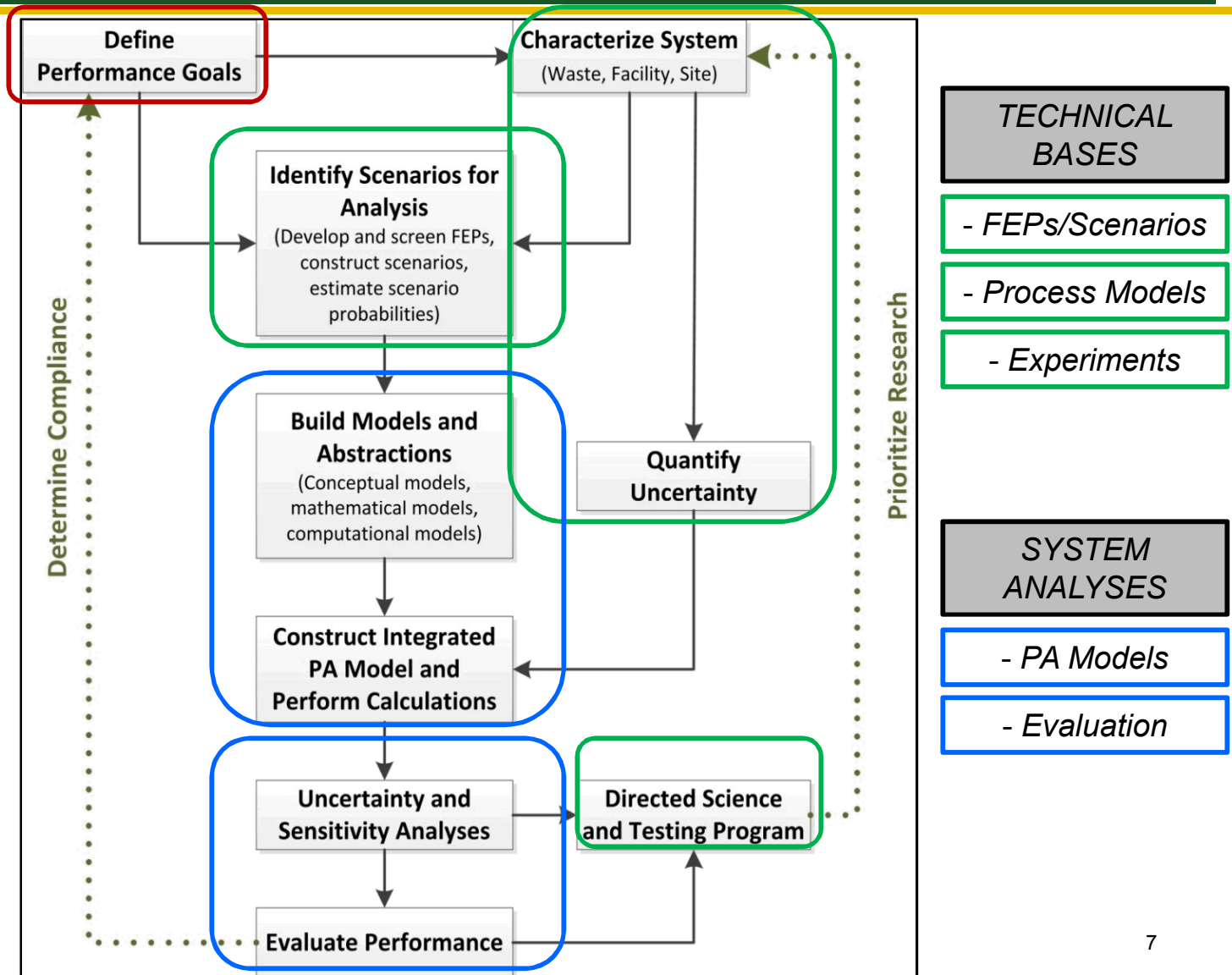
- Sent UFD Generic Granite Model. A GoldSim “player” file that permits running of the GDS Granite model; an Excel spreadsheet of data, descriptions, and usage, and an word document of system model overview,
- Requested ROK critique and suggestions to better reflect ROK specific needs in the GPAM model.

## **■ Technical exchange 2013**

- Received ROK mark-up of Excel spreadsheet.
- SNL is reviewing for understanding and to identify and resolve potential gaps in information required to make a GDS Granite model run.
- SNL sent a series of questions and requested further clarification on some points.

# Used Fuel Disposition

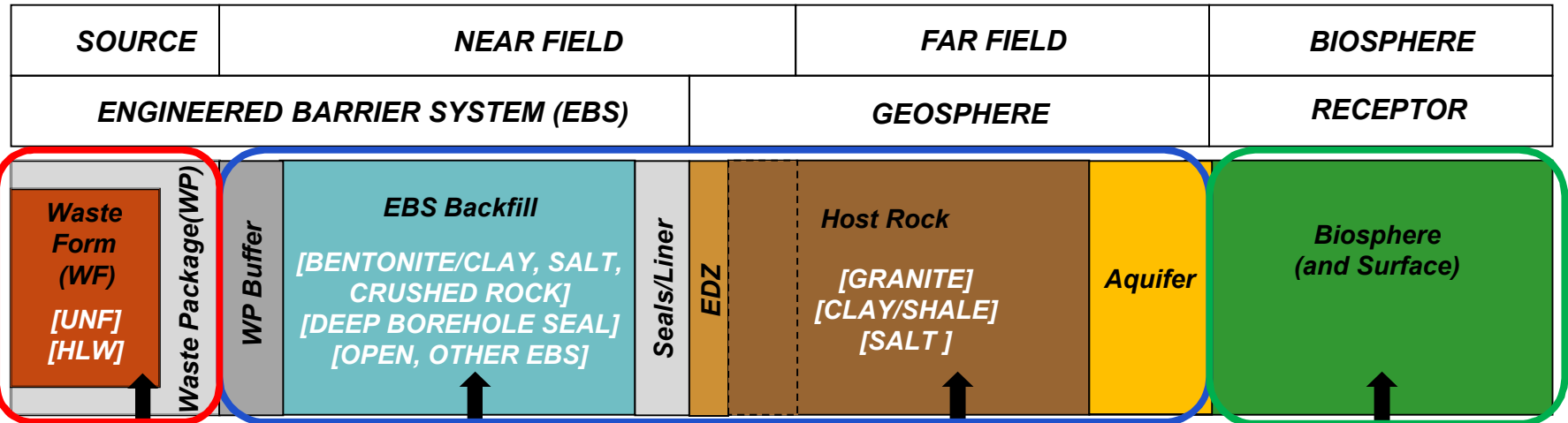
## PA Methodology – Overview



# Used Fuel Disposition

## GPAM: Conceptualization

- Conceptual Model and supporting “high-level” FEPs
- Not all Model Domains need to be utilized (e.g., "active") in a specific model application



THCMBR Processes (Simplified – Fully Coupled)

Radionuclide Transport

- WF Degradation
- WP Degradation
- Radionuclide Solubility

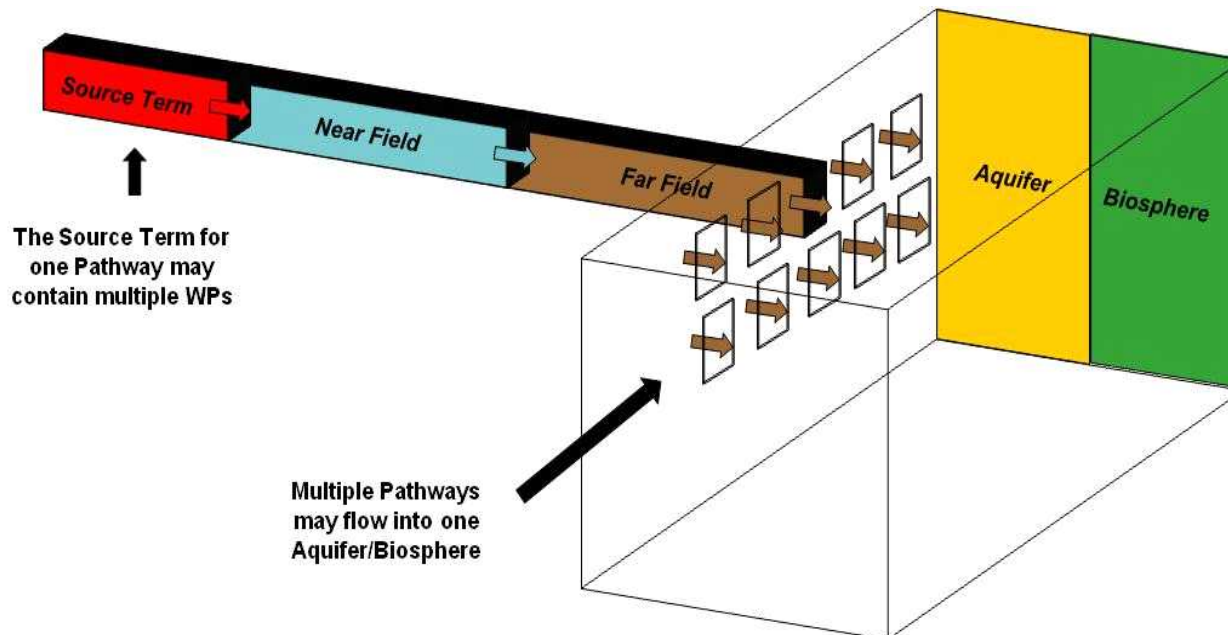
- Advection / Dispersion
- Diffusion
- Sorption
- Radionuclide Decay

- Water Consumption
- Dose Conversion Factors

## GPAM: Conceptualization

A GPAM Disposal System may be conceptualized to contain multiple identical Pathways that all feed into the Aquifer and Biosphere

A GPAM Disposal System may also be conceptualized to contain a fast pathway that bypasses some of the Model Domains.



■ **Major components:**

- The near field (waste form, waste package, the EBS, and bentonite buffer).
- The far field (Advection, diffusion, 5km to Biosphere).
- Stylized Aquifer and water well.
- Reference biosphere (IAEA ERB 1B model).

■ **Assumptions**

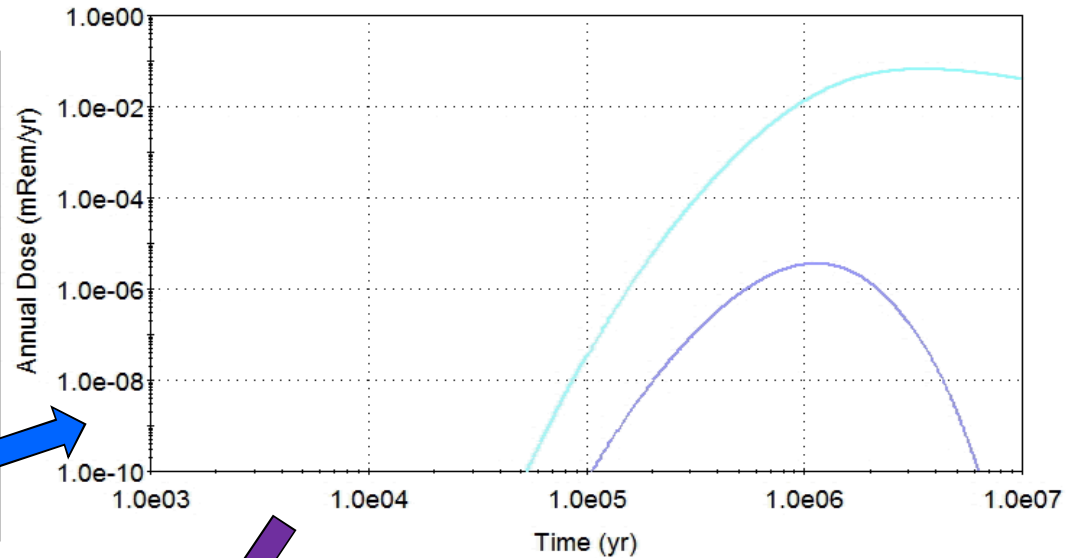
- Undisturbed scenario only.
- Isothermal conditions.
- Waste package failure occurs at the time of emplacement.
- Specified Fraction of WP that release to fractures. (Matrix F&T is negligible).
- Constant waste form degradation rate is used, no gap release.
- Flow is at steady state and fixed.
- Transport is calculate in 1-D using the GoldSim series of pipes as the pathway. (Dissolved species, decay and ingrowth, reversible linear sorption, solubility limits).

# Used Fuel Disposition

# GoldSim Granite Safety Case Model – FY 2012 Deterministic Nominal Scenario

## Inputs

- Inventory ~ 70,000 MTHM
- WF degr =  $2 \times 10^{-5}$  yr<sup>-1</sup>
- WP degr = instant
- EBS bentonite = diffusive transport with sorption
- FF fractured granite = advective transport (5 km) with sorption and matrix diffusion



## Important Processes

- WF degradation / WP degradation
- Slow transport through EBS bentonite buffer
  - Diffusion-dominated
  - Sorption
  - No defects
- Minimal direct connection from EBS to FF fractures
  - Only 1% failed WPs connect to FF fractures
- Delay in FF granite
  - Sorption, matrix diffusion, 5 km length

## Potential March Meeting Objectives: Task 1

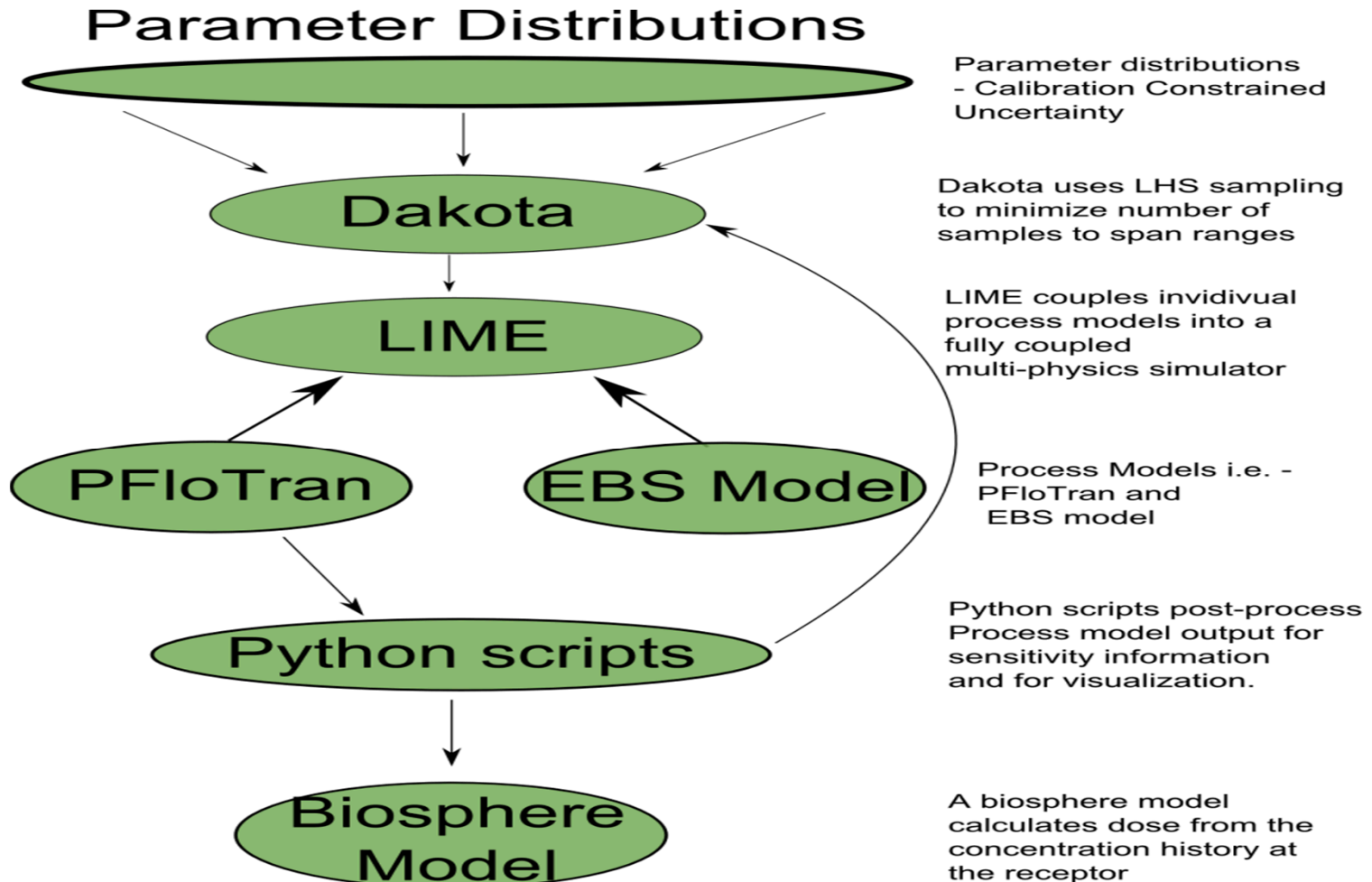
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- **Discuss details of ROK Granite model and existing capabilities of DOE Simplified GDS GoldSim Granite Model.**
  - Address outstanding questions
  - Identify and discuss “new” questions.
- **Identify and discuss potential gaps between ROK needs and GDS Granite model capabilities and discuss work around.**
- **Define or refine activities and schedule supporting Task 1 for 2013/2014.**
- **Recommendations for future efforts.**

- **In FY12 GoldSim was determined not to be adequate for the future of DOE generic disposal system modeling.**
- **Simplified GoldSim implementations are being maintained and used until new capability is developed.**
- **DOE current approach is based on using an advanced PA model framework to implement and couple existing grid-based numerical models describing the source term release and the migration of radionuclides to the accessible environment.**
- **Provides the ability to model repository processes in a more fundamental fashion and provides more flexibility in sub-model component model options.**
- **Utilizes Sandia high-performance computing (HPC) capabilities and platforms.**

- **LIME (Lightweight Integrating Multi-physics Environment) framework**
  - Numerically Couples Multi-Physics Codes
    - *Source Term Model* – waste form degradation, waste package degradation, solubility limits
    - *PFLOTRAN (THC)* – radionuclide flow and transport through EBS and NBS
    - *Biosphere Model* – conversion of dissolved radionuclide concentrations to receptor dose
- **PFLOTRAN capabilities**
  - Multi-physics
    - *Flow*
    - *Transport*
    - *Radionuclide Chemistry/Behavior*
    - *Thermal*
  - High-Performance Computing (HPC)
    - *Built on PETSc – parallel solver library*
    - *Massively Parallel*
    - *Structured and Unstructured Grids*
    - *Scalable from Laptop to Supercomputer*
  - Open Source
    - *Freely available*
    - *Cross-platform*
  - Extremely modular design for easy integration of new capabilities

# Used Fuel Disposition



*Fuel Cycle Technologies – Used Fuel Disposition*

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

***David Sassani***

Sandia National Laboratories

Department 6222, Advanced Systems Analysis

*UFD Fuel Cycle Alternative Working Group (FCAWG)*

March 2013



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- **FCAWG Task 3 - Spent Fuel Degradation and Durability over Geologic Time**
  - Description
  - Status Update
- **Used Fuel Degradation and Radionuclide Mobilization (UFD&RM) Activities**
  - Overview
  - Integration Summary
  - Generic Performance Assessment Model (GPAM) Concepts
  - Engineered Barrier System (EBS) Interface
  - UFD&RM Model Structure
- **Summary and Discussion**
  - UFD&RM Activities Accomplishments/Summary
  - Focus and discussion areas for Task #3

- **Purpose – collaborative evaluation of constraints on**
  - $\text{UO}_2$  (i.e., used/spent fuel) degradation rates in granite repository conditions including
    - *Instant release radionuclides (fission gas and other fission products, e.g., Cs, I, Sr, Cl, Tc)*
    - *Cladding failure effects*
    - *Oxidative and chemical dissolution behavior*
- **U.S. Deliverables for Task 3**
  - November 2012 – UFD Milestone Report (complete)
  - Second report –
    - *Rescheduled for April 2014 based on interactions/discussions of ROK-US POC (June 2012)*
- **Interactions Prior to June 2012 Meeting (Task 3 POC - US & ROK)**
  - Exchange of email discussing relevant work being done within UFD, KAERI, and KRMC
  - 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*
      - **Storage environments (radiolysis)**
      - **Integration with cladding degradation models**
      - **Strategy for integration with Performance Assessment**

## *Spent fuel degradation, long term durability over geologic time (FY 2012 – FY 2017)*

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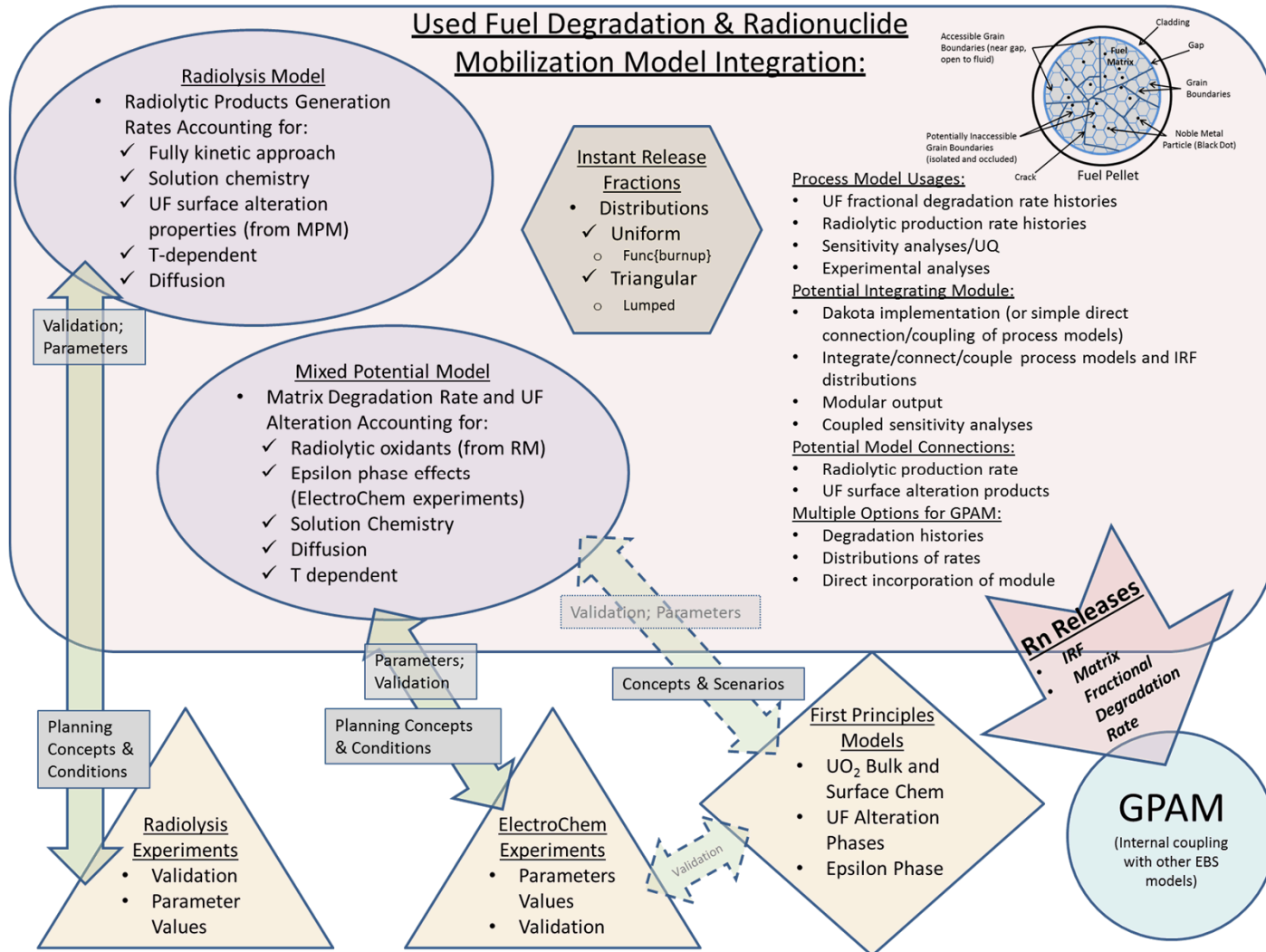
### • **June 2012 Meeting (Task 3 POC - US & ROK)**

- Sassani discussed collaboration to date including exchange of reports and telecom on May 1, 2012
- Discussed US UFD SNF degradation activities from FY11 through FY12, including work at SNL, PNNL and ANL
- SNL SNF degradation initial models are specific to granitic environment – additional chemical environments will be included in out years
- Siting aspects of large PA models and storage evaluation relevance appears to be the two initial areas of interest and collaboration with ROK – US models will be directly integrated with relevant storage related models in out years
- ROK will review US materials for now, but ROK has no funding to work in this area
- Some potential  $UO_2$  experimental work in ROK was not funded at this point – there may be relevant data generated within the EC FIRST- nuclides collaborative project.
- Fulfilled (11/13/2012) U.S. deliverable (due on 11/16/2012) by supplying via email a copy of our recent UFD Report Titled “Integration of EBS Models with Generic Disposal System Models” SAND- SAND2012-7762 P (FCRD-UFD-2012-000277)
- Report provides current process model implementations and strategy for integrating models into GPAM

- **Collaborative Effort – ANL, PNNL, SNL**
  - **Work Package Generic EBS Evaluation**
    - *Carlos Jove-Colon, SNL Work Package Manager*
    - *Bill Spezialetti, DOE Technical Lead*
- **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/expansion of Radiolysis Model (PNNL)*
    - *Implementation/expansion 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)*
  - **Integrating UFD&RM Models into GPAM**
    - *Constraints on the Fast/Instant Release fractions (SNL)*
    - *Integration of the process models into GPAM (SNL, ANL, PNNL)*
      - **GPAM platform/implementation being evaluated**

# Used Fuel Disposition

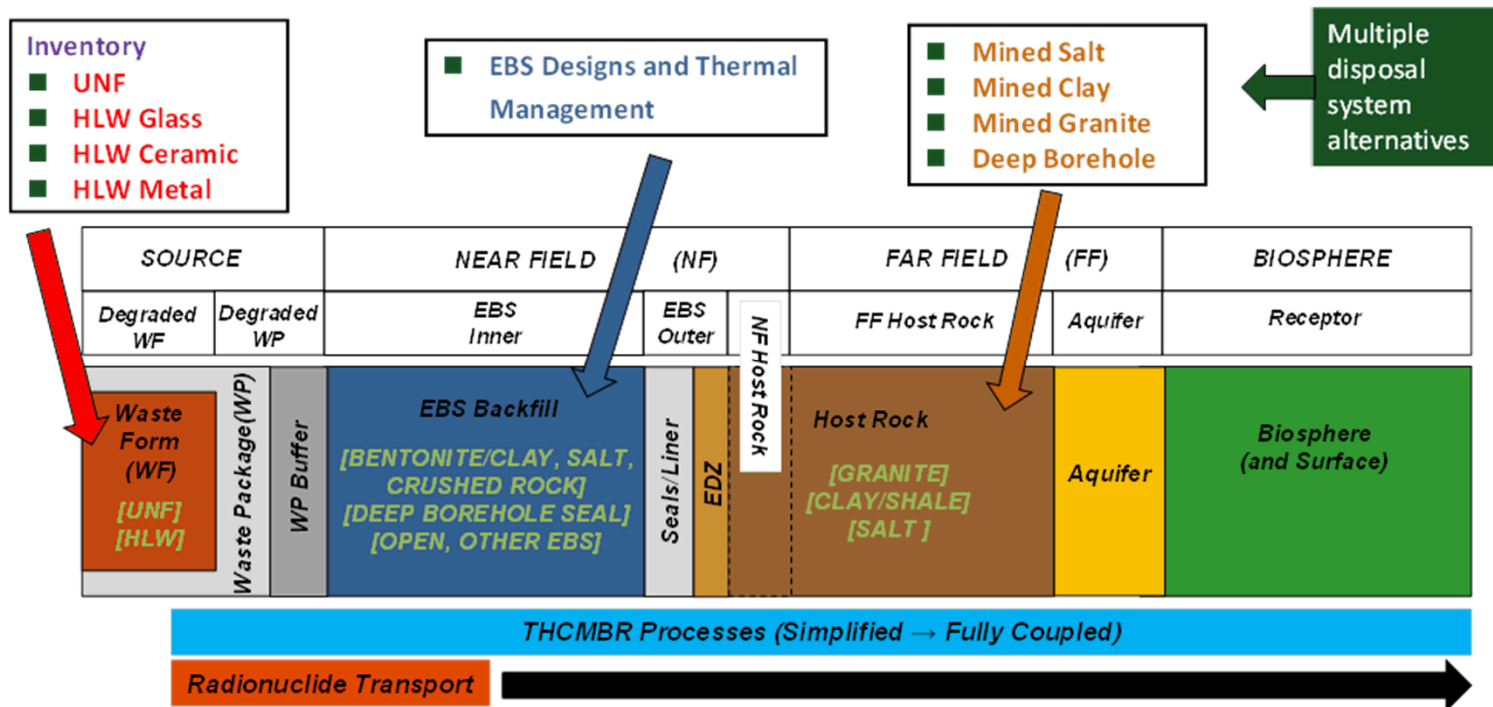
# UFD&RM Activities and Models Integration Summary



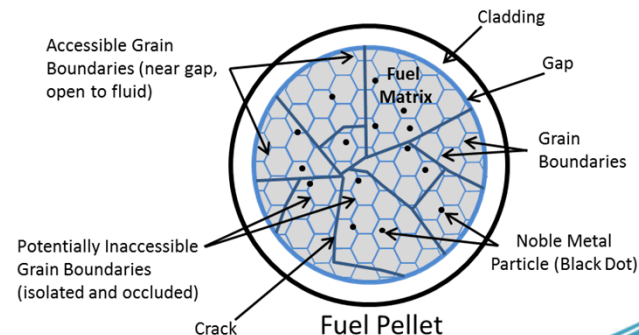
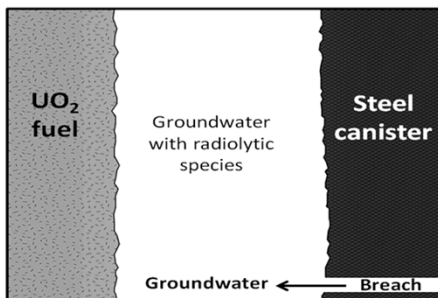
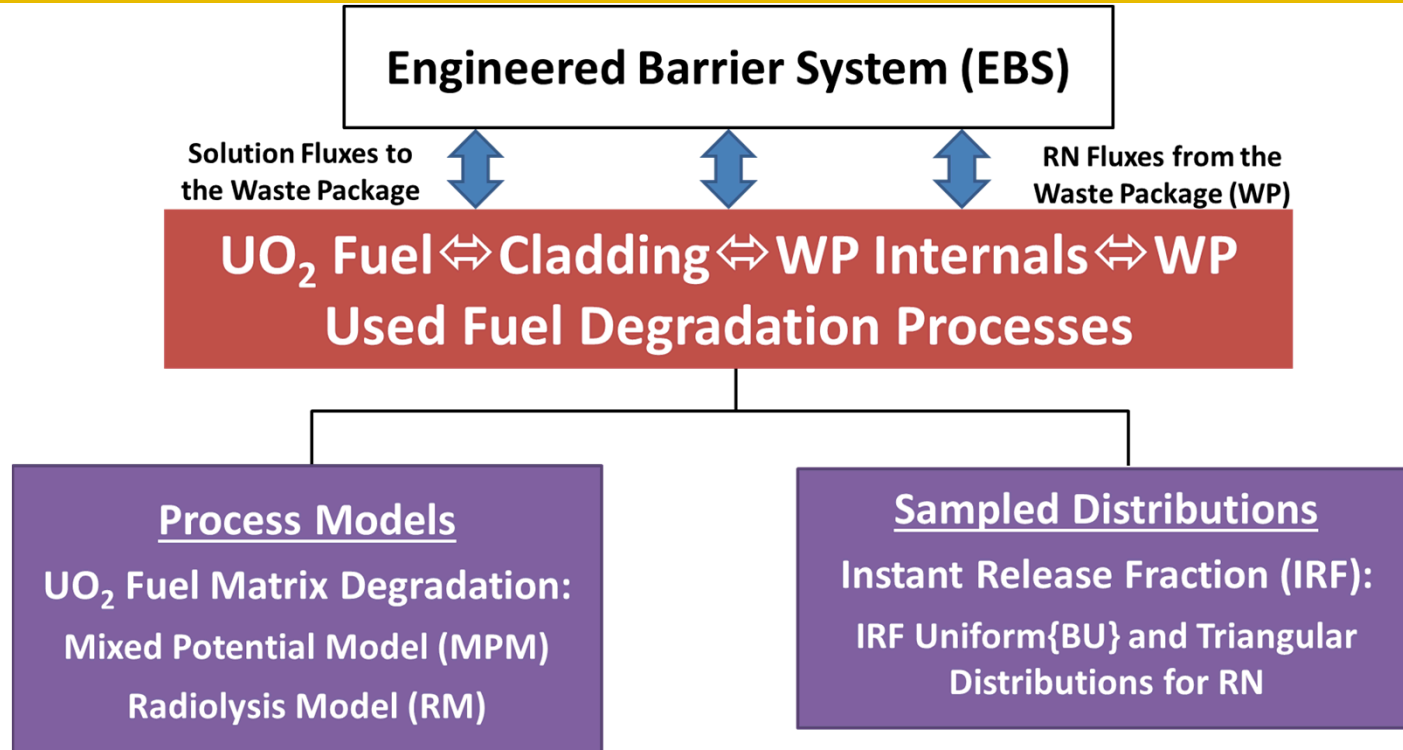
# Used Fuel Disposition

# GPAM – Conceptual Framework

- Description of the Generic Performance Assessment Model (GPAM) concepts, including interfaces, showing features, and processes throughout the representation
- Can accommodate a range of processes and process model fidelities (from EBS and Natural Systems evaluations and FEP screening)



# UFD&RM ↔ EBS Interface



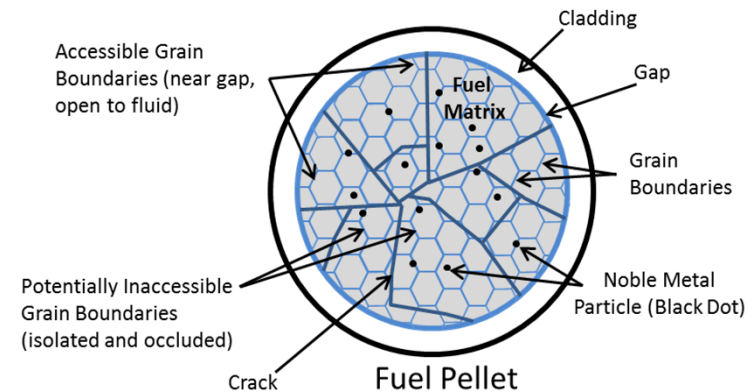
- **Used Fuel Degradation and Radionuclide Mobilization Model Concepts**

- The *instant release fraction* (IRF) comprised of fission products (including fission gases) located in

- The rod plenum regions (e.g., Kr and Xe)
- The fuel gap (between pellet and cladding – Figure)
- The accessible grain boundaries/pellet fractures

- The **matrix** inventory that includes the UF matrix itself and radionuclides located in

- The inaccessible grain boundaries/pellet fractures
- The solid solutions (e.g., Pu, Np) within the matrix
- The epsilon phase particles in the matrix (which undergo their own degradation rate once exposed by matrix degradation)



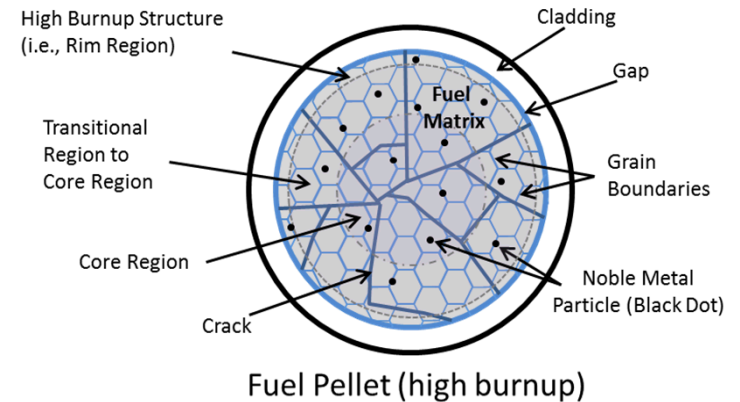
*Figure - Schematic of a fuel pellet cross section showing the relative locations of radionuclide inventories for the gap, grain boundaries, fuel matrix, and noble metal particles. Also shown schematically are the general locations of accessible and inaccessible grain boundaries.*

- **Used Fuel Degradation and Radionuclide Mobilization Model Concepts (continued)**

- Focus on the major rate limiting processes for radionuclide release (e.g., radiolysis, matrix degradation, noble metal particle degradation)

- **Future Efforts**

- *Couple physical/chemical degradation of cladding and mechanical evolution of degrading fuel*
- *Address specifics of high burnup fuels (>45 MWd/kgU - Figure)*



*Figure - Schematic of a fuel pellet cross section for high BU UF showing the rim region high-BU structure, transitional region, and core region.*

# UFD&RM Activities Accomplishments/Summary

- **Delineated Constraints for the IRF for UF in Two Sets of Distributions**
  - Triangular distributions representing minimum, maximum, and mean (apex) values for LWR UF with BU at or below 50 MWd/KgU
  - Uniform distributions as a function of BU representing UF with BU up to 75 MWd/KgU
- **Computational Development/Implementation of a Radiolysis Model that**
  - Uses a comprehensive set of radiolysis reactions to better account for potential solution compositions to be encountered in repository environments
  - Allows for heterogeneous  $\text{CO}_2$  speciation thus accounting for the presence of  $\text{HCO}_3^-$
  - Produces modeling results that are in good agreement with those reported in other studies
  - Experiments of alpha radiolysis generating  $\text{H}_2\text{O}_2$  in aqueous solution are ongoing
- **Computational Implementation and Verification/Validation of the Canadian Mixed Potential Model for  $\text{UO}_2$  Fuel Corrosion that**
  - Represents the fundamental electrochemical and thermodynamic properties described by interactions at the fuel – fluid interface
  - Captures key processes such as hydrogen oxidation and the catalysis of oxidation/reduction reactions by noble metal particles on the fuel surface (epsilon phases)
  - Electrochemical experiments with both  $\text{UO}_2$  and “epsilon phase” electrodes are started

- **Computational First-principles Studies of**
  - **The properties of  $\text{UO}_2$  bulk and  $\text{UO}_2$  surface chemistries**  
(Weck et al., 2012, *Dalt. Trans.* 41(32))
    - *Account for the strong on-site Coulomb repulsion between U 5f electrons (strong electron correlation parameter)*
    - *Evaluate chemical interactions of molecular water, dissociated water, dissociated oxygen and co-adsorbed molecular water and monatomic oxygen with the  $\text{UO}_2(111)$  surface*
    - *Reveal that some of the key electronic and chemical properties controlling the surface reactivity are very sensitive to the value of this strong electron correlation parameter.*
  - **The structures of the uranyl peroxide hydrates studtite and metastudtite**  
(Weck et al., 2013, *Dalt. Trans.* DOI: 10.1039/C3DT32536A)
    - *The structures obtained from total energy calculations using density functional theory show good agreement with those characterized by experimental X-ray diffraction methods.*
    - *Such work allows predicting phase stability of  $\text{UO}_2$  corrosion products and quantifying their thermodynamic properties for use with similar studies of  $\text{UO}_2$  bulk and surface chemistry.*
- **Development of an idealized strategy for model integration with PA approaches to analyze generic disposal environments**
  - **it is an ongoing task to**
    - *delineate in detail how these process models will couple to other EBS process models and,*
    - *Determine how such coupled models would be incorporated into the generic performance assessment model (GPAM) for generic evaluations of the safety case.*

- **First U.S. report – November, 2012 (delivered)**

- *Sassani, D.C., Jové Colón, J. C., Weck, P., Jerden, J. L., Jr., Frey, K. E., Cruse, T., Ebert, W. L., Buck, E. C., Wittman, R. S., Skomurski, F. N., Cantrell, K. J., McNamara, B. K., and Soderquist, C. Z., 2012, Integration of EBS Models with Generic Disposal System Models, FCRD-UFD-2012-000277, SAND2012-7762 P, 145 p.*

- **Used fuel degradation in a repository environment (granite initial system)**

- *Fast/instant release fractions for radionuclides*
    - *Matrix degradation rate*
    - *Radiolysis model*

- **Integration strategy for GPAM**

- **Relevance to storage environment evaluations**

- **Second U.S. report (April, 2014) - areas of possible emphasis/discussion**

- **Cladding model(s) integration with used fuel degradation**

- **Other potential waste forms**

- **Experimental work**

- **Schedule**

# Used Fuel Disposition Campaign

## Quantifying weak interactions between iodide and clay minerals

**Andrew Miller**

**Yifeng Wang**

**Jessica Kruichak**

**Melissa Mills**

**Hernesto Tellez**

**Sandia National Laboratories**



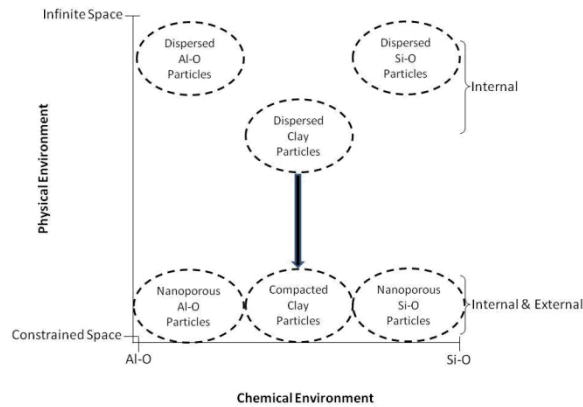
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# Used Fuel Disposition

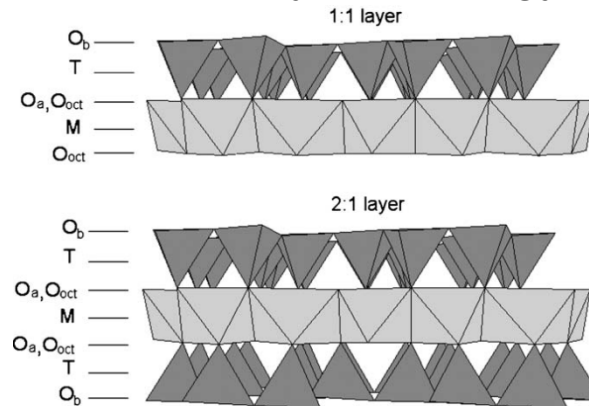
# This talk relates clay physical/chemical relationships with iodine uptake behavior.

## Ion behavior in nanopores



Miller, A.W., Wang, Y. (2012). *Environ.Sci. Technol.* DOI: 10.1021/es203025q.

## Clay mineralogy

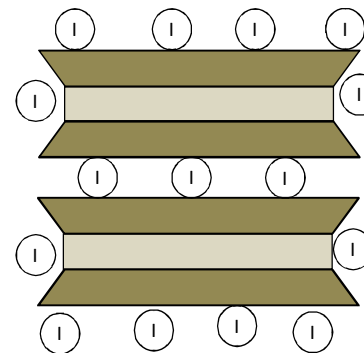


Handbook of Clay Science, Eds.: Bergaya, F., Theng, B.K.G., Lagaly, G.; Elsevier, 2006.

## Experimental conditions/results

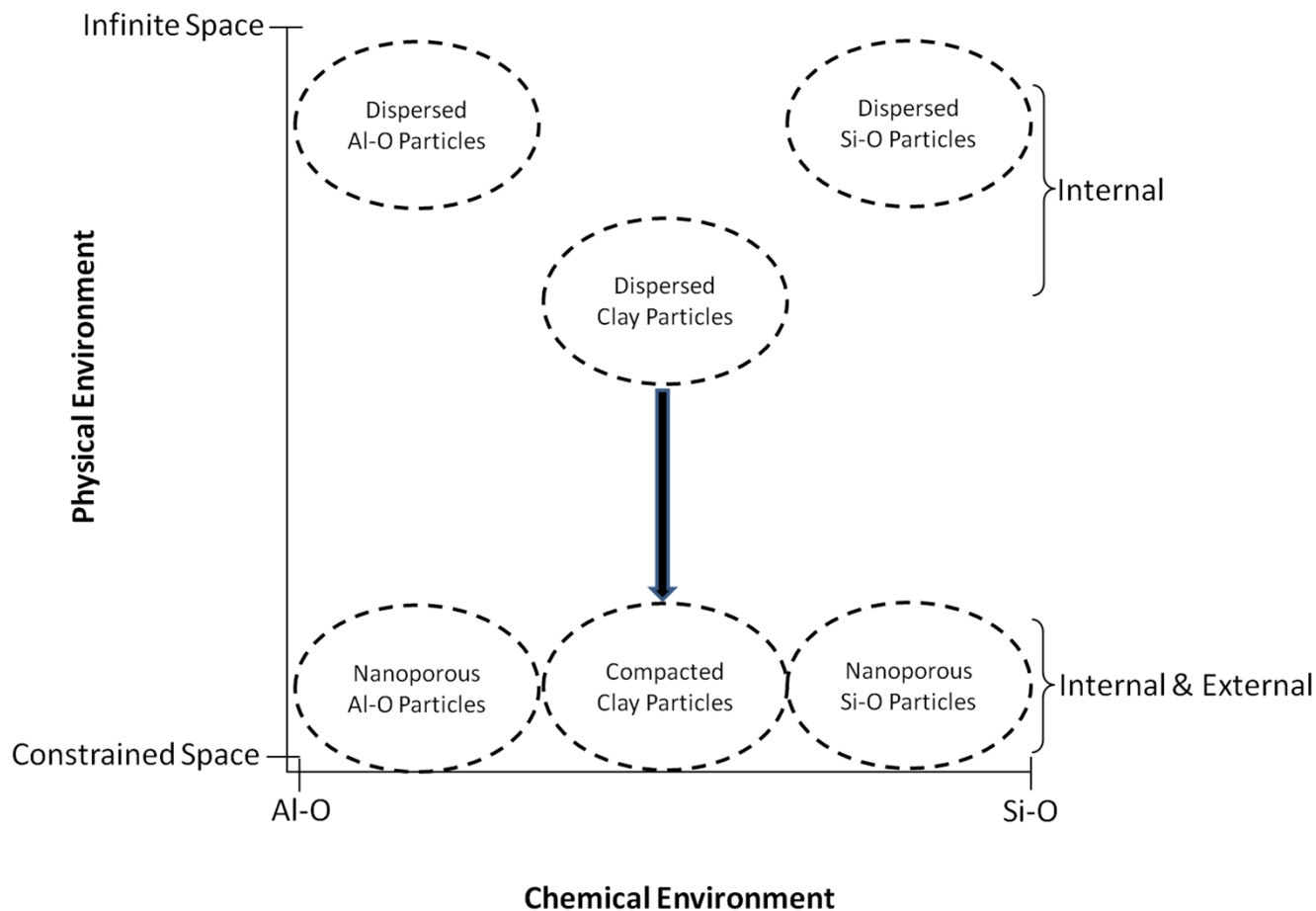


## Path forward



# Used Fuel Disposition

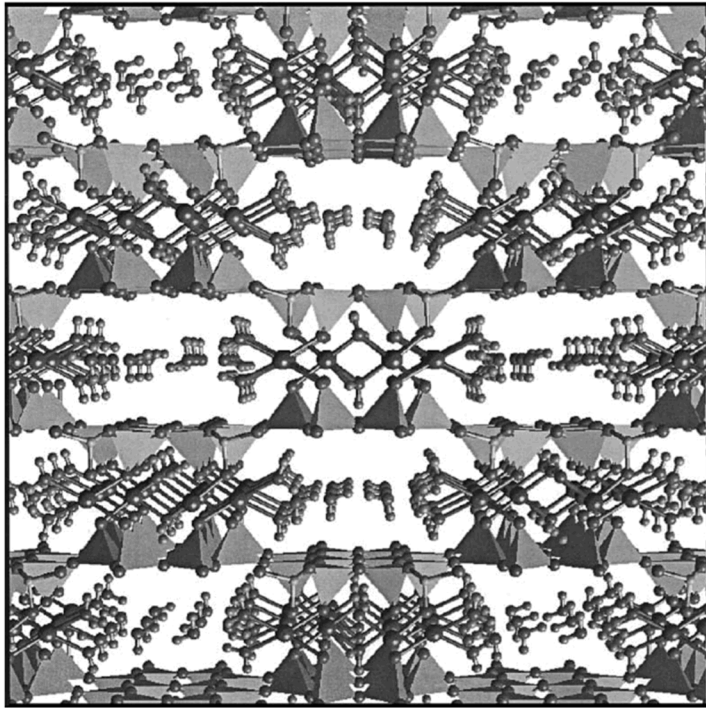
## Clay particle proximity has the potential to change observed reactivity.





Used  
Fuel  
Disposition

Fibrous clays have columnar  
voids for water inclusion.



Fois et al., 2003. *Microporous and Mesoporous Materials*. 57, 263-272.



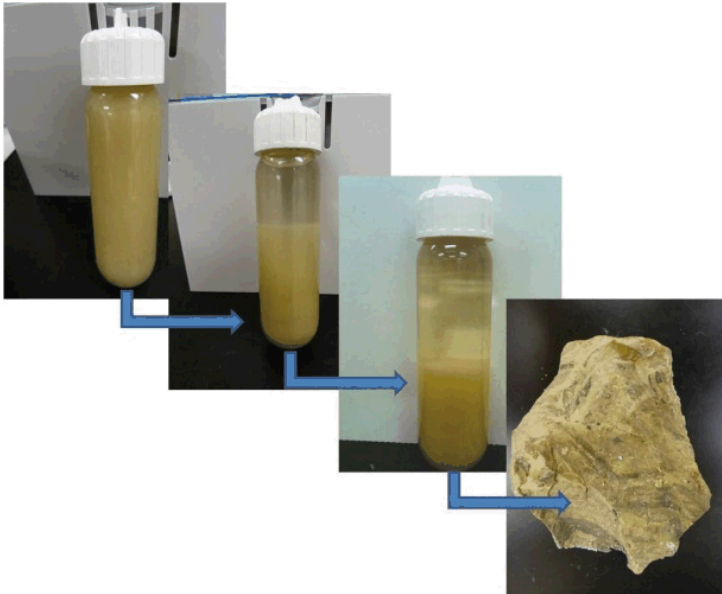
<http://backreaction.blogspot.com/2008/03/cookies-palygorskite-and-maya-blue.html>

# Used Fuel Disposition

## Surface titrations and batch uptake experiments characterize the clay surface.

**7 clays under consideration:** All clays obtained from the clay bank repository (Purdue Univ.)

- Kaolinite
- Ripidolite
- Illite
- Illite/Smectite
- Montmorillonite
- Palygorskite
- Sepiolite



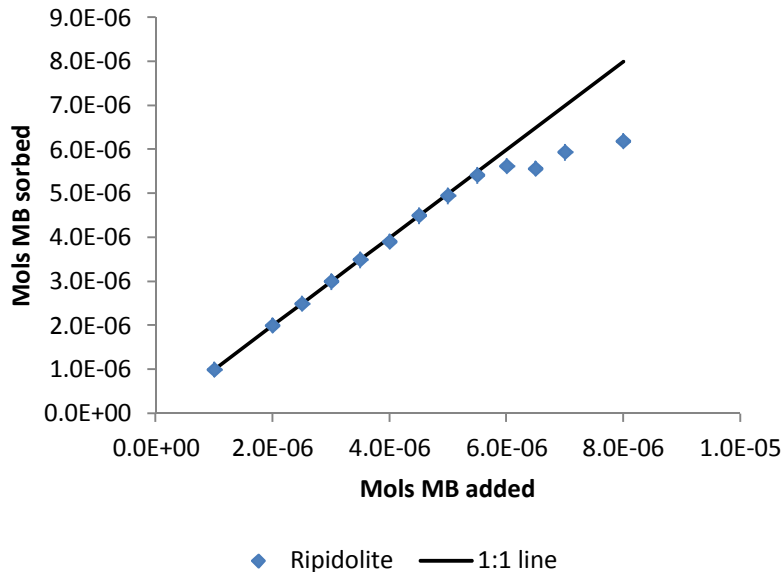
### Uptake experiments:

- **Methylene Blue (MB)**
  - Na-exchanged clays
  - Variable amounts of MB were added until clay surface was saturated
- **Iodide**
  - Solid:Liquid ratio: 100g/L
  - No specific pH control; 'natural' pH of clay
  - Seven day reaction time

| Concentration (M) | NaCl | NaBr | KCl |
|-------------------|------|------|-----|
| 1.0               | X    |      |     |
| 0.1               | X    | X    | X   |
| 0.01              | X    |      |     |

# Used Fuel Disposition

## All of the clays were characterized for cation exchange capacity and surface area.



|                        | MB CEC<br>(meq/100g) | BaCl <sub>2</sub> CEC<br>(meq/100g) | BET S.A<br>(m <sup>2</sup> /g) | Calc. MB S.A<br>(m <sup>2</sup> /g) |
|------------------------|----------------------|-------------------------------------|--------------------------------|-------------------------------------|
| <b>Kaolinite</b>       | 1.50                 | 4.61                                | 11.31                          | 11.76                               |
| <b>Ripidolite</b>      | 3.00                 | 6.03                                | 8.02                           | 23.49                               |
| <b>Illite</b>          | 14.98                | 27.61                               | 31.46                          | 117.21                              |
| <b>Illite.Smectite</b> | 24.69                | 30.39                               | 29.82                          | 193.23                              |
| <b>Montmorillonite</b> | 109.53               | 151.92                              | 28.29                          | 857.17                              |
| <b>Sepiolite</b>       | 17.41                | 8.98                                | 201.43                         | 136.27                              |
| <b>Palygorskite</b>    | 39.96                | 29.22                               | 141.52                         | 625.45                              |

**Used  
Fuel  
Disposition**

**Iodide uptake is dependent on ionic  
composition of swamping electrolyte.**

|         | CEC<br>meq/100g | K <sub>D</sub> Value (L/g) |       |       | Standard deviation |      |       |      |
|---------|-----------------|----------------------------|-------|-------|--------------------|------|-------|------|
|         |                 | NaCl                       | NaBr  | KCl   | NaCl               | NaBr | KCl   |      |
| Layered | Kaolinite       | 4.61                       | 1.61  | 0.02  | -0.01              | 0.28 | 0.63  | 0.22 |
|         | Ripidolite      | 6.03                       | 1.13  | -0.16 | -0.31              | 0.38 | 0.72  | 0.17 |
|         | Illite          | 27.61                      | 0.54  | 0.13  | -0.50              | 0.12 | 0.002 | 0.24 |
|         | Illite.Smectite | 30.39                      | 0.38  | -0.01 | -0.49              | 0.08 | 0.11  | 0.11 |
|         | Montmorillonite | 151.92                     | -0.32 | -0.58 | -1.69              | 0.35 | 0.07  | 0.90 |
| Fibrous | Sepiolite       | 8.98                       | 0.01  | 0.79  | 0.11               | 0.28 | 0.14  | 0.30 |
|         | Palygorskite    | 29.22                      | 0.24  | 1.26  | 0.99               | 0.30 | 0.05  | 0.17 |

**Used  
Fuel  
Disposition**

**Iodide uptake depends on swamping  
electrolyte concentration.**

|         | CEC<br>meq/100g | K <sub>d</sub> Value (L/g) |              |              | Standard deviation |              |              |      |
|---------|-----------------|----------------------------|--------------|--------------|--------------------|--------------|--------------|------|
|         |                 | NaCl<br>0.01M              | NaCl<br>0.1M | NaCl<br>1.0M | NaCl<br>0.01M      | NaCl<br>0.1M | NaCl<br>1.0M |      |
| Layered | Kaolinite       | 4.61                       | 0.48         | 1.61         | 0.11               | 0.26         | 0.28         | 0.29 |
|         | Ripidolite      | 6.03                       | 0.14         | 1.13         | 0.44               | 0.21         | 0.38         | 0.17 |
|         | Illite          | 27.61                      | -0.46        | 0.54         | 0.27               | 0.41         | 0.12         | 0.21 |
|         | Illite.Smectite | 30.39                      | -0.16        | 0.38         | 0.30               | 0.25         | 0.08         | 0.08 |
| Fibrous | Montmorillonite | 151.92                     | -1.35        | -0.32        | 0.60               | 0.54         | 0.35         | 0.09 |
|         | Sepiolite       | 8.98                       | 1.38         | 0.01         | -0.01              | 4.03         | 0.28         | 0.30 |
|         | Palygorskite    | 29.22                      | -0.23        | 0.24         | 0.70               | 0.54         | 0.30         | 0.26 |

**Used  
Fuel  
Disposition**

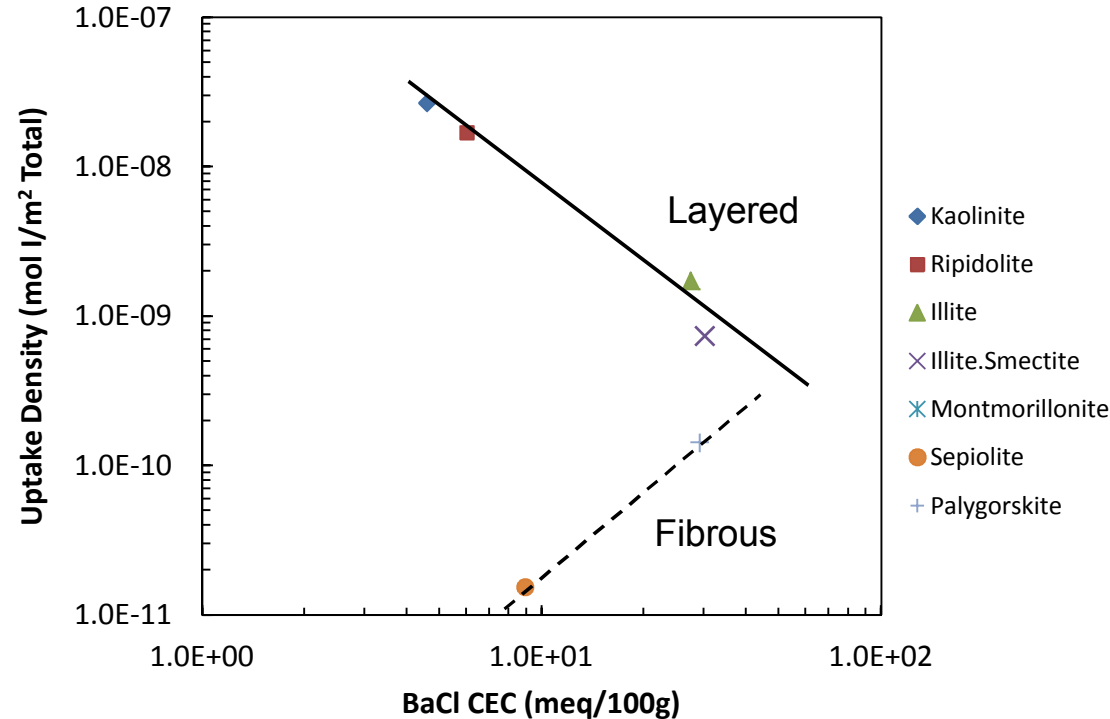
**Iodide behavior in divalent salts is  
less consistent.**

0.05M Electrolyte

|         |                 | CEC<br>meq/100g | K <sub>d</sub> Value (L/g) |                   |                   | Standard deviation |                   |                   |
|---------|-----------------|-----------------|----------------------------|-------------------|-------------------|--------------------|-------------------|-------------------|
|         |                 |                 | CaCl <sub>2</sub>          | CaBr <sub>2</sub> | MgCl <sub>2</sub> | CaCl <sub>2</sub>  | CaBr <sub>2</sub> | MgCl <sub>2</sub> |
| Layered | Kaolinite       | 4.61            | 0.34                       | -0.34             | 0.09              | 0.35               | 0.28              | 0.43              |
|         | Ripidolite      | 6.03            | 0.16                       | -0.05             | 0.22              | 0.33               | 0.01              | 0.66              |
|         | Illite          | 27.61           | 1.02                       | -0.48             | 0.37              | 0.22               | 0.32              | 0.01              |
|         | Illite.Smectite | 30.39           | 0.87                       | -0.30             | 0.90              | 0.16               | 0.09              | 0.34              |
|         | Montmorillonite | 151.92          | 0.56                       | -2.16             | -1.70             | 0.18               | 0.53              | 0.47              |
| Fibrous | Sepiolite       | 8.98            | -0.43                      | 0.52              | -0.35             | 0.12               | 0.25              | 0.37              |
|         | Palygorskite    | 29.22           | 0.41                       | 0.80              | 0.48              | 0.78               | 0.41              | 0.10              |

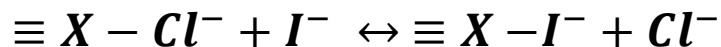
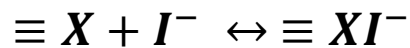
# Used Fuel Disposition

## Iodide uptake normalized to interior surface area suggests interlayer interactions.



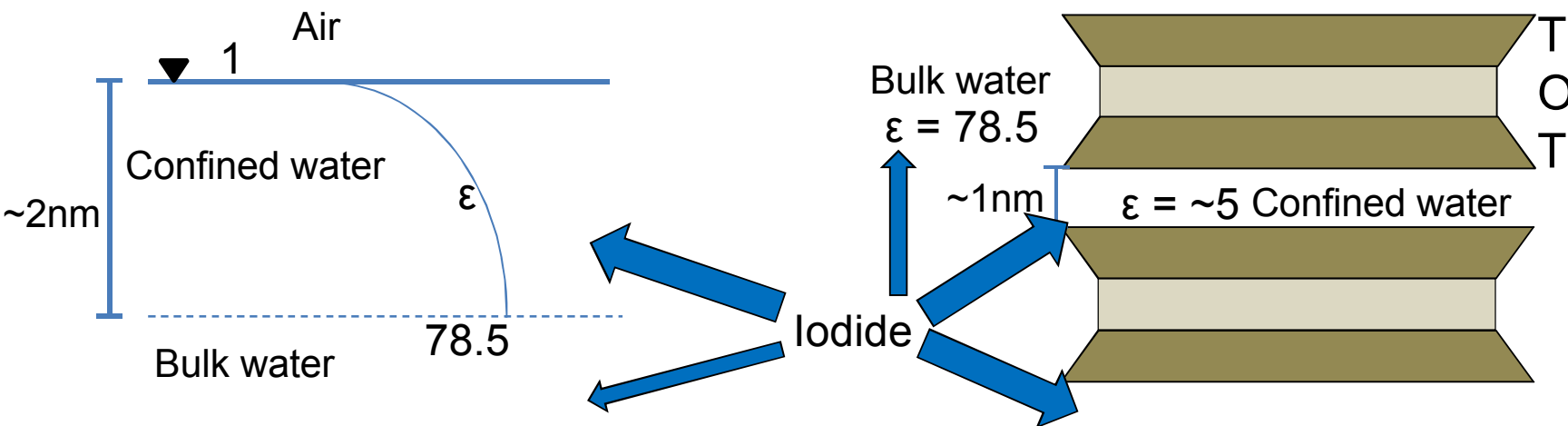
| Clay Mineral | Ideal Formula  |
|--------------|--|
| Kao          | $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  |
| Rip          | $\text{Mg}_5\text{Al}(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_8$   |
| Ill          | $\text{K}_{0.6}(\text{H}_3\text{O})_{0.4}\text{Al}_{1.3}\text{Mg}_{0.3}\text{Fe}^{2+}_{0.1}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2 \cdot (\text{H}_2\text{O})$ |
| Ill/Smec     |  |
| Mont         | $\text{Na}_{0.2}\text{Ca}_{0.1}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})_{10}$  |
| Sepio        | $\text{Mg}_4\text{Si}_6\text{O}_{15} \cdot 6(\text{H}_2\text{O})$  |
| Paly         | $\text{Mg}_{1.5}\text{Al}_{0.5}\text{Si}_4\text{O}_{10}(\text{OH}) \cdot 4(\text{H}_2\text{O})$  |

Ideal formulas from webmineral.com



# Used Fuel Disposition

## Ion pair formation in the interlayer may be able to describe interactions.



| Element | Ionic Radii | Hyd Energy (kJ/mol) |
|---------|-------------|---------------------|
| Na      | 1.16        | -406                |
| K       | 1.52        | -322                |
| Cs      | 1.81        | -287                |
| Ca      | 1.14        | -1577               |
| Cl      | 1.81        | -363                |
| Br      | 1.96        | -336                |
| I       | 2.2         | -295                |

| log K                   | NaCl | NaBr | KCl  |
|-------------------------|------|------|------|
| Ion pair of electrolyte | 0.82 | 0.73 | 0.53 |
| Ion pair I with cation  | 0.6  | 0.6  | 0.4  |

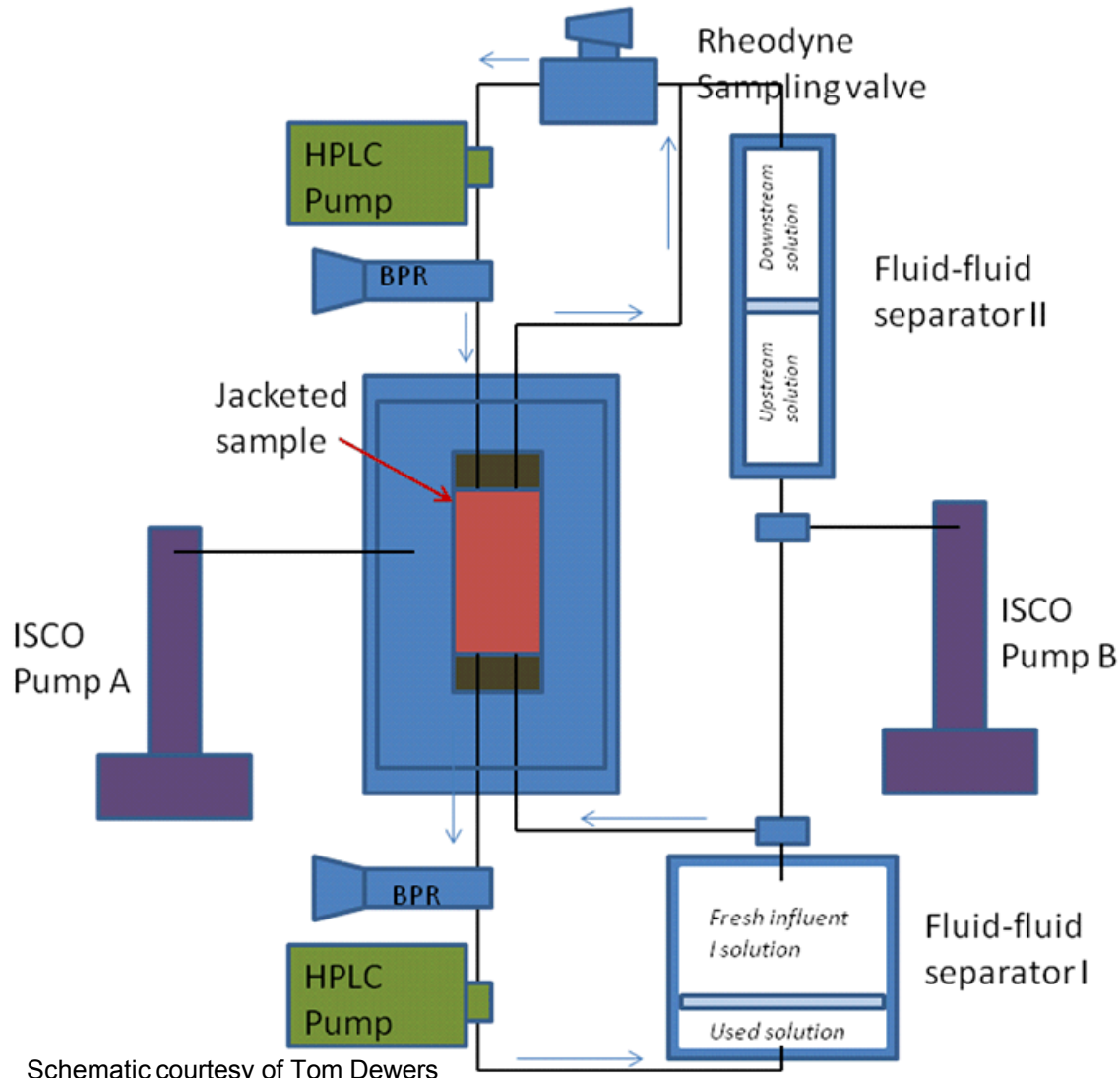
$$K^{eff} = f(\dots \Delta F_h \dots)$$

$$\Delta F_h = f(\dots \epsilon, D \dots)$$

$$\epsilon, D = f(\dots \sigma_{fixed} \dots)$$

# Used Fuel Disposition

## Diffusion studies will be completed in a constant pressure system.



Schematic courtesy of Tom Dewers

**Used  
Fuel  
Disposition**

**In summary, iodide interactions are heavily influenced by CEC, ionic strength and ionic identity.**

---

The data suggests unexpected interlayer concentrations of iodide.

Little to no conversion to iodate was observed.

Iodide uptake is heavily related to CEC.

Iodide uptake is heavily related to ionic composition of electrolyte.

Iodide uptake is dependent on clay textures and structures

**Future Work:**

- Mathematical interpretation of iodide uptake as a function of ionic strength and fixed charge
- Diffusion experiments with varied clay minerals, compactions and ionic strengths/compositions

|                        | 0.1M Electrolyte |                     |                    |              |                     |                    |              |                     |                    |
|------------------------|------------------|---------------------|--------------------|--------------|---------------------|--------------------|--------------|---------------------|--------------------|
|                        | NaCl             |                     |                    | NaBr         |                     |                    | KCl          |                     |                    |
|                        | Before spike     | Before Centrifuging | After Centrifuging | Before spike | Before Centrifuging | After Centrifuging | Before spike | Before Centrifuging | After Centrifuging |
| <b>Kaolinite</b>       | 4.23             | 4.21                | 4.39               | 4.43         | 4.47                | 4.28               | 4.18         | 4.12                | 4.07               |
| <b>Ripidolite</b>      | 8.73             | 8.51                | 8.10               | 8.76         | 8.63                | 8.20               | 8.79         | 8.59                | 7.81               |
| <b>Illite</b>          | 8.45             | 8.27                | 8.16               | 8.48         | 8.31                | 7.95               | 8.28         | 8.08                | 8.01               |
| <b>Illite/Smectite</b> | 4.00             | 4.06                | 4.24               | 4.22         | 4.26                | 4.03               | 3.91         | 3.85                | 3.82               |
| <b>Montmorillonite</b> | 8.15             | 8.05                | 8.05               | 8.19         | 8.14                | 8.05               | 8.09         | 8.03                | 7.90               |
| <b>Sepiolite</b>       | 7.89             | 7.66                | 7.83               | 7.98         | 7.63                | 7.75               | 7.92         | 7.64                | 7.80               |
| <b>Palygorskite</b>    | 7.98             | 7.76                | 7.90               | 8.05         | 7.84                | 7.82               | 7.84         | 7.63                | 7.87               |

|                        | NaCl Electrolyte |                     |                    |              |                     |                    |              |                     |                    |
|------------------------|------------------|---------------------|--------------------|--------------|---------------------|--------------------|--------------|---------------------|--------------------|
|                        | 0.01M            |                     |                    | 0.1M         |                     |                    | 1.0M         |                     |                    |
|                        | Before spike     | Before Centrifuging | After Centrifuging | Before spike | Before Centrifuging | After Centrifuging | Before spike | Before Centrifuging | After Centrifuging |
| <b>Kaolinite</b>       | 4.70             | 4.83                | 4.73               | 4.23         | 4.21                | 4.39               | 4.04         | 4.27                | 4.19               |
| <b>Ripidolite</b>      | 8.79             | 8.57                | 8.15               | 8.73         | 8.51                | 8.10               | 8.74         | 8.59                | 8.37               |
| <b>Illite</b>          | 8.68             | 8.46                | 8.30               | 8.45         | 8.27                | 8.16               | 8.37         | 8.22                | 7.87               |
| <b>Illite/Smectite</b> | 4.38             | 4.57                | 4.40               | 4.00         | 4.06                | 4.24               | 3.57         | 3.65                | 3.74               |
| <b>Montmorillonite</b> | 8.65             | 8.55                | 8.50               | 8.15         | 8.05                | 8.05               | 7.78         | 7.77                | 7.73               |
| <b>Sepiolite</b>       | 7.92             | 7.64                | 7.83               | 7.89         | 7.66                | 7.83               | 7.78         | 7.50                | 7.71               |
| <b>Palygorskite</b>    | 8.17             | 7.93                | 7.99               | 7.98         | 7.76                | 7.90               | 7.83         | 7.75                | 7.75               |

# Used Fuel Disposition Campaign

## Thermodynamic Modeling of Clay Hydration and C-S-H Cement Leaching

**Carlos F. Jové Colón (SNL)**

# Used Fuel Disposition

## Interactions at EBS Interfaces

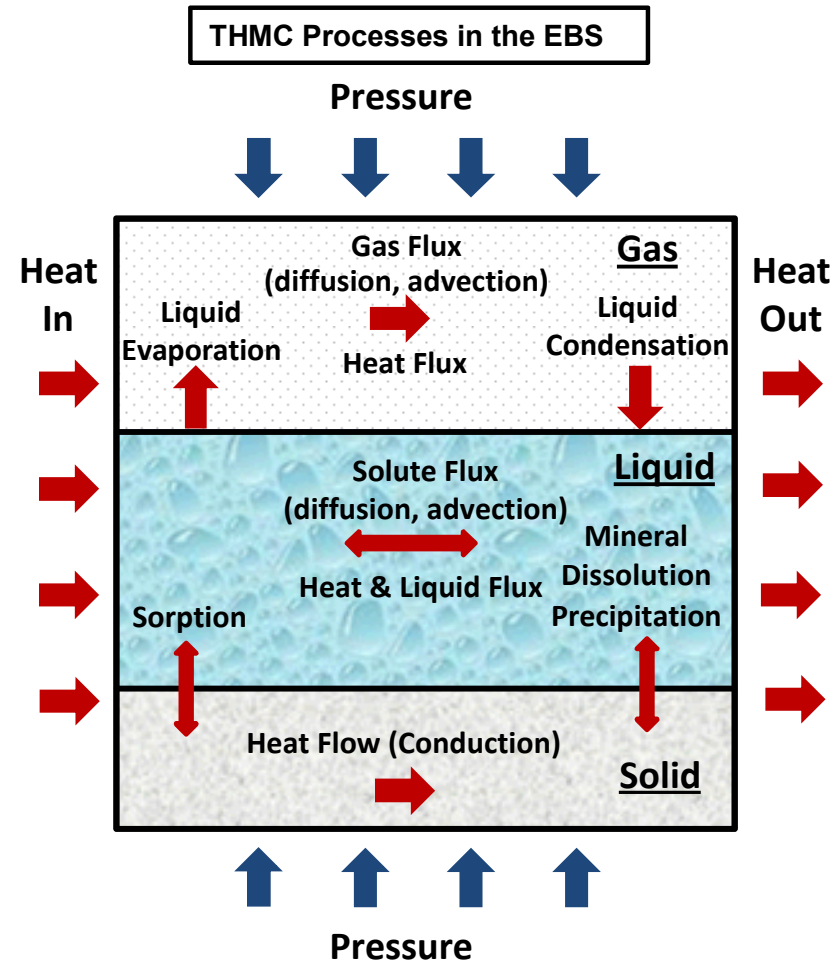
- Knowledge gaps and R&D prioritization in EBS (based on the UFDC Disposal R&D Roadmap, Nutt et al. 2011) :

- Highest ranked issues:

- Waste Form
- THM Processes
- Waste Container
- Radionuclide speciation and solubility
- Buffer/Backfill and Seals Barrier Materials - (Chemical Processes)**
  - Seals: Cementitious Phases
  - Buffer/Backfill: Clay

- High rank of THMC processes is relevant to interactions at EBS interfaces:

- Shares a boundary with far-field region
- Loci for important degradation processes in the near-field
  - Fluid interactions with EBS materials
  - Effects on barrier material stability



Modified After Olivella et al. (2011)

## ■ Clay Hydration Model:

- **Cantera** code implementation with the Margules parameterization to represent the non-ideal solid solution:

- *Margules parameterization based on sub-regular solid solution for two clay end-members following the approaches advanced by Ransom and Helgeson (1994) and Vieillard et al. (2011):*

$$\begin{aligned} & \text{Smectite (dehyd.)} + nH_2O = \text{Smectite (hyd., } nH_2O) \\ & H^{EX} = X_{\text{smect. hyd.}} X_{\text{smect. dehyd.}} (W_{H1} + W_{H1} X_{\text{smect. dehyd.}}) \\ & S^{EX} = X_{\text{smect. hyd.}} X_{\text{smect. dehyd.}} (W_{S1} + W_{S1} X_{\text{smect. dehyd.}}) \\ & G^{EX} = H^{EX} - TS^{EX} \end{aligned}$$

## ■ Thermodynamic Modeling of Sorption and Ion exchange:

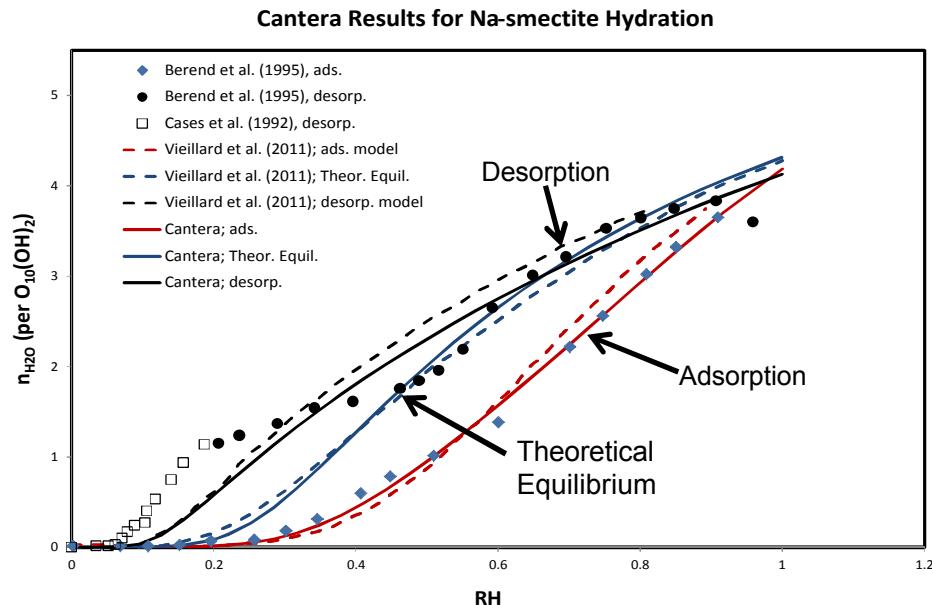
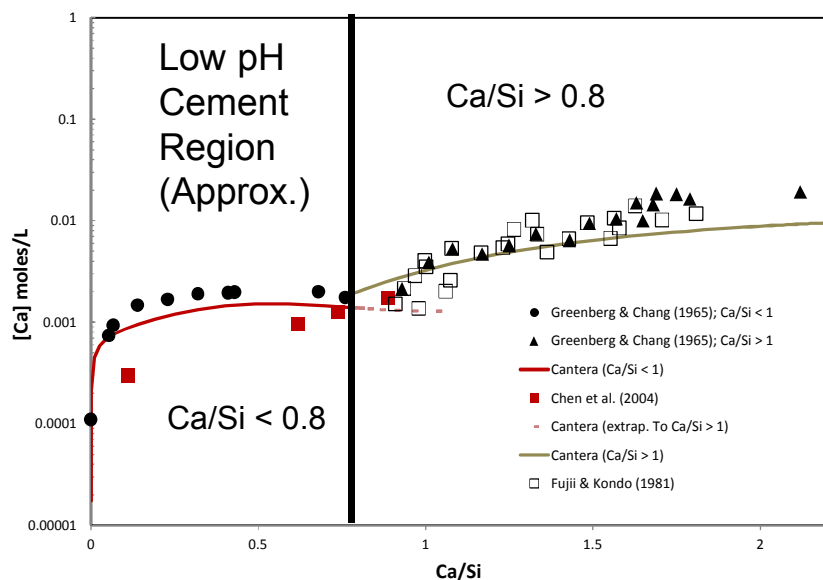
- *Cantera code implementation of surface complexation using a non-electrostatic thermodynamic model based on pseudo steady-state kinetics (work in progress)*
- *Similarly, Cantera code implementation to represent the thermodynamics of ion exchange using the Margules parameterization*

# C-S-H Leaching Model Using Cantera

- Cantera code implementation with the Margules class to represent the sub-regular solid solution behavior

$$\begin{aligned}H^{EX} &= X_{\text{SiO}_2(am)} X_{\text{Ca(OH)}_2} (W_{H1} + W_{H1} X_{\text{SiO}_2(am)}) \\S^{EX} &= X_{\text{SiO}_2(am)} X_{\text{Ca(OH)}_2} (W_{S1} + W_{S1} X_{\text{SiO}_2(am)}) \\G^{EX} &= H^{EX} - TS^{EX}\end{aligned}$$

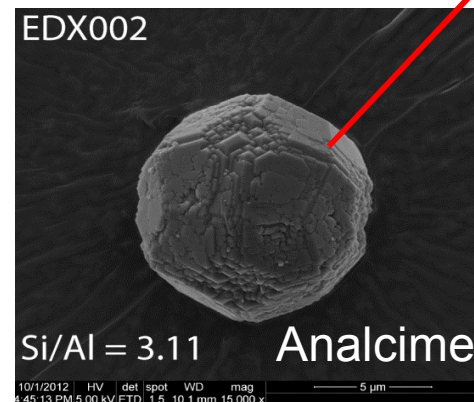
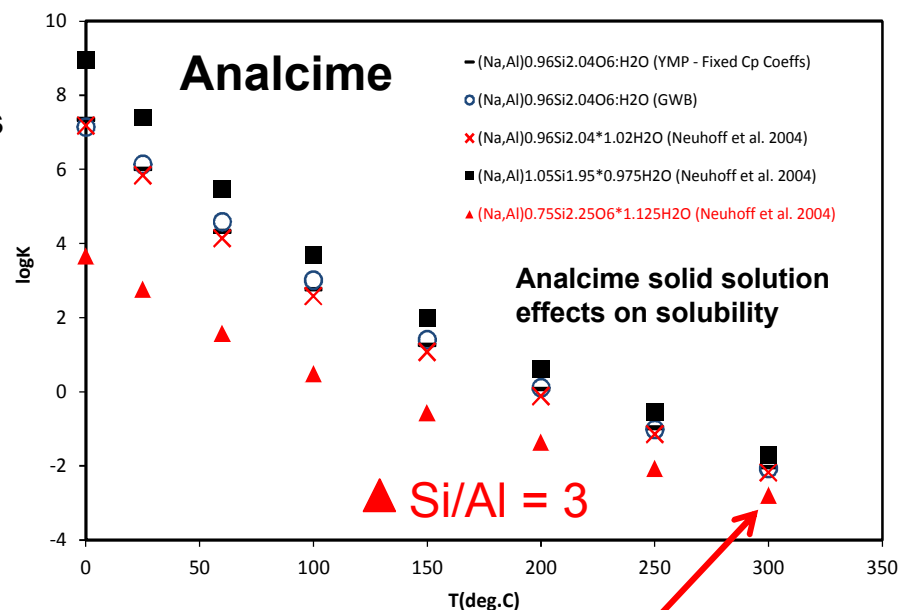
- Pitzer model class to represent the aqueous phase
- Solid solution model implementation:
  - Two separate C-S-H solid solution domains on the basis of two ranges of Ca/Si ratios in the solid: Ca/Si < 0.8 and Ca/Si > 0.8
  - Based on two end member solids: SiO<sub>2(am)</sub> and Ca(OH)<sub>2</sub>
  - The model is consistent with the binary non-ideal solid solution model advanced by Sugiyama and Fujita (2006)
- Retrieval and evaluation of Margules parameters was conducted using the code coupling of Cantera with the DAKOTA optimization code
- Results show solute leaching curves as a function of Ca/Si ratio in the solid are in very good agreement with experimental data trends for aqueous Ca, Si, and pH
- International Collaboration: Established contact with Dr. Urs Maeder (Univ. of Bern) to obtain sample from the CI experiment on cement-clay interaction at Mont Terri



- ✓ Thermodynamic data compilation and evaluation for cementitious solids (YMP and CEMDATA07)
- ✓ Cantera Margules implementation to represent non-ideal solid solution behavior of cement leaching and clay hydration
- ✓ Retrieval and evaluation of thermodynamic parameters using code coupling of Cantera with DAKOTA optimization toolkit
- ✓ Unified approach to thermodynamic modeling using object-oriented C++ code platform
- ✓ Sorption database development: (a) Focus on the compilation of “raw” metal sorption data on oxides and clays, (b) use of these data to evaluate and test sorption models

## FY13

- Cantera code suite implementation of ion exchange and surface complexation using Gibbs energy minimization (GEM)
- Expand smectite hydration thermodynamic modeling to various clay compositions (Na,, K, Ca, Mg) and existing clay thermodynamic database (in collaboration with LLNL):
  - ❖ Evaluate volumetric relations as a f(RH)
- Thermodynamic modeling of hydrothermal clay-fluid interactions (in collaboration with LANL):
  - ❖ Utilize experimental observations from hydrothermal experiments and reaction path modeling to evaluate mineral-fluid interactions (e.g., analcime formation)
- International collaboration: In situ cement interaction experiments for clay–cement, clay-bentonite, and bentonite-cement interfaces at the Mont Terri URL. Current phase: sample characterization – Small Angle Neutron Scattering (SANS) at LANL



## **FY13**

- **Continue thermal analysis for multi-layered EBS (in collaboration with LLNL)**
- **Continue assessment of thermodynamic data for clays and cementitious materials at elevated temperatures (in collaboration with LLNL)**
- **Thermodynamic description of clay interactions at high temperatures and pressures (with LANL experimental work)**
- **Explore the use of Gibbs energy minimization models for sorption and ion exchange – Implementation with the open source Cantera suite of codes**
- **Establish collaboration with the cement-clay interaction (CI) experiment at Mont Terri**