Advanced Conceptual and Numerical Methods for Modeling Subsurface Processes Regarding Nuclear Waste Repository Systems

IAEA Network of Centers of Excellence

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Modeling Repository Source-Term: Chemical and Radionuclide Release Processes – the Yucca Mountain Example

David C. Sassani, Ph.D.

Principle Member of Technical Staff

Sandia National Laboratories

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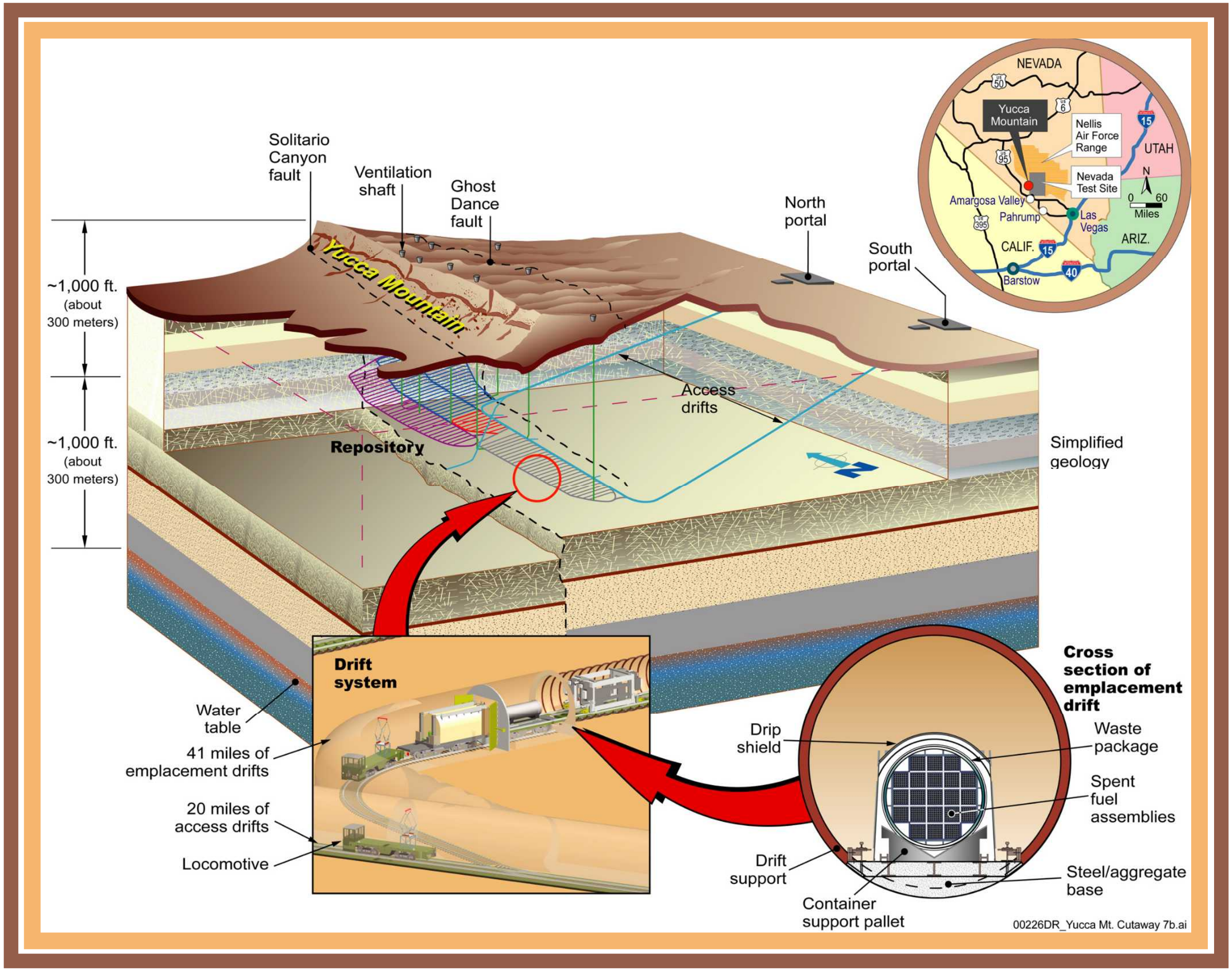
Overview

- The Performance Assessment Context
- Source Term Models in Performance Assessment
- Chemical Environment Models
- Waste form Degradation/Release Models
  - Nuclear Fuel (e.g., UO_2 based) Degradation
  - High Level Waste Glass Degradation
  - Solubility Models
- Colloid Stability and Transport Models
- Engineered Barrier System Transport Models
- Additional Considerations
- Summary

Repository Reference Design Concept



Performance Assessment (PA)

- PA is a system-level analysis using integrated numerical models of events and natural processes to evaluate long-term performance of the natural and engineered components of a repository system
  - Long-term performance means performance after the operational period and emplacement of final seals
- PA models are based on the data collected during field (surface and underground), and laboratory studies of natural and engineered system components, including natural analogs
- PA and supporting technical bases captures the current state of knowledge including the characterization of uncertainty

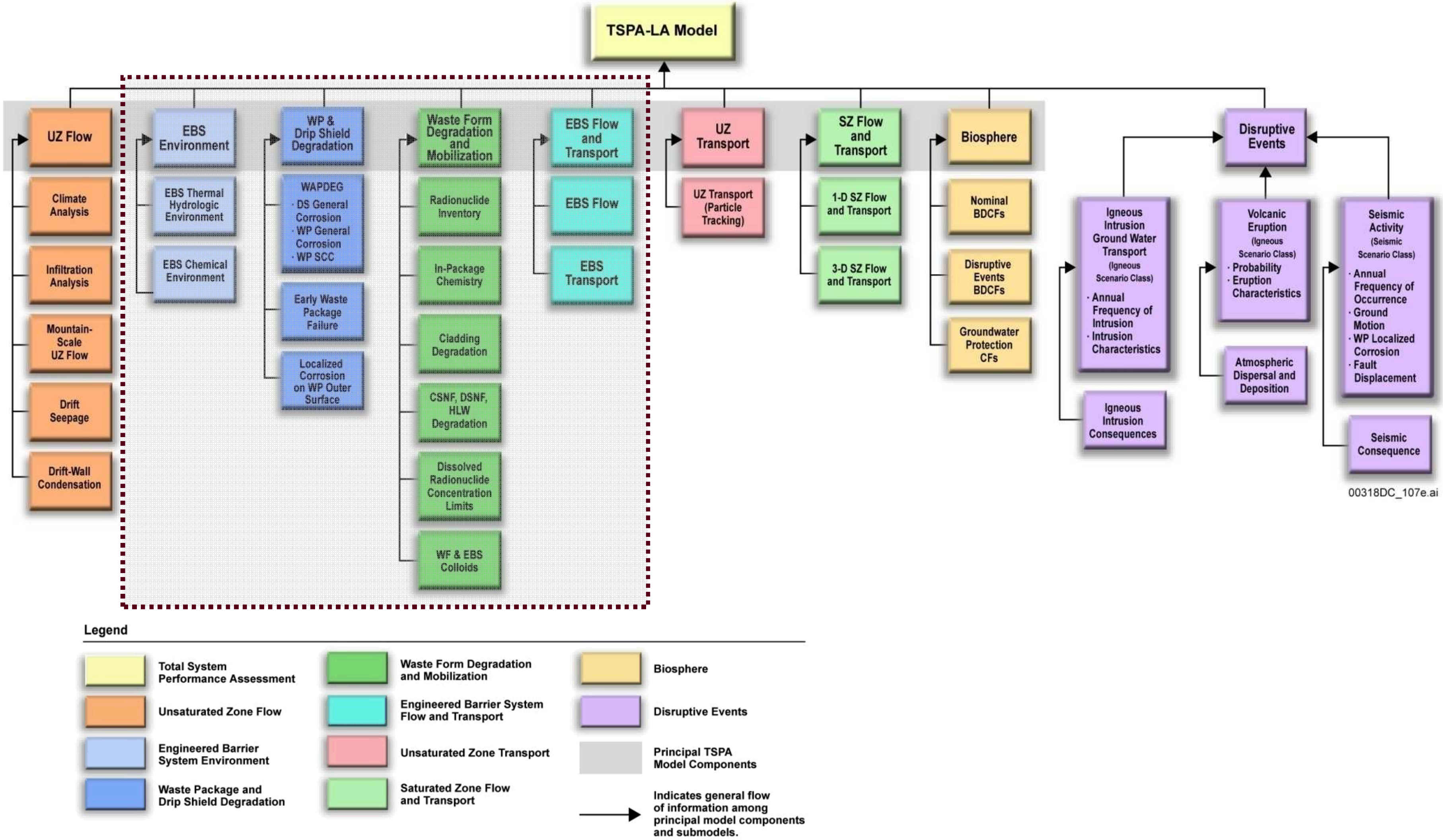
Purpose of PA

- Performance Assessments provide answers to four questions:
    1. What events and processes can take place at the facility?
    2. How likely are these events or processes?
    3. What are the consequences of these events or processes?
    4. How reliable are the answers to the first 3 questions?
- PA evaluates the uncertainty in the evolution of the geologic setting and engineered barrier system

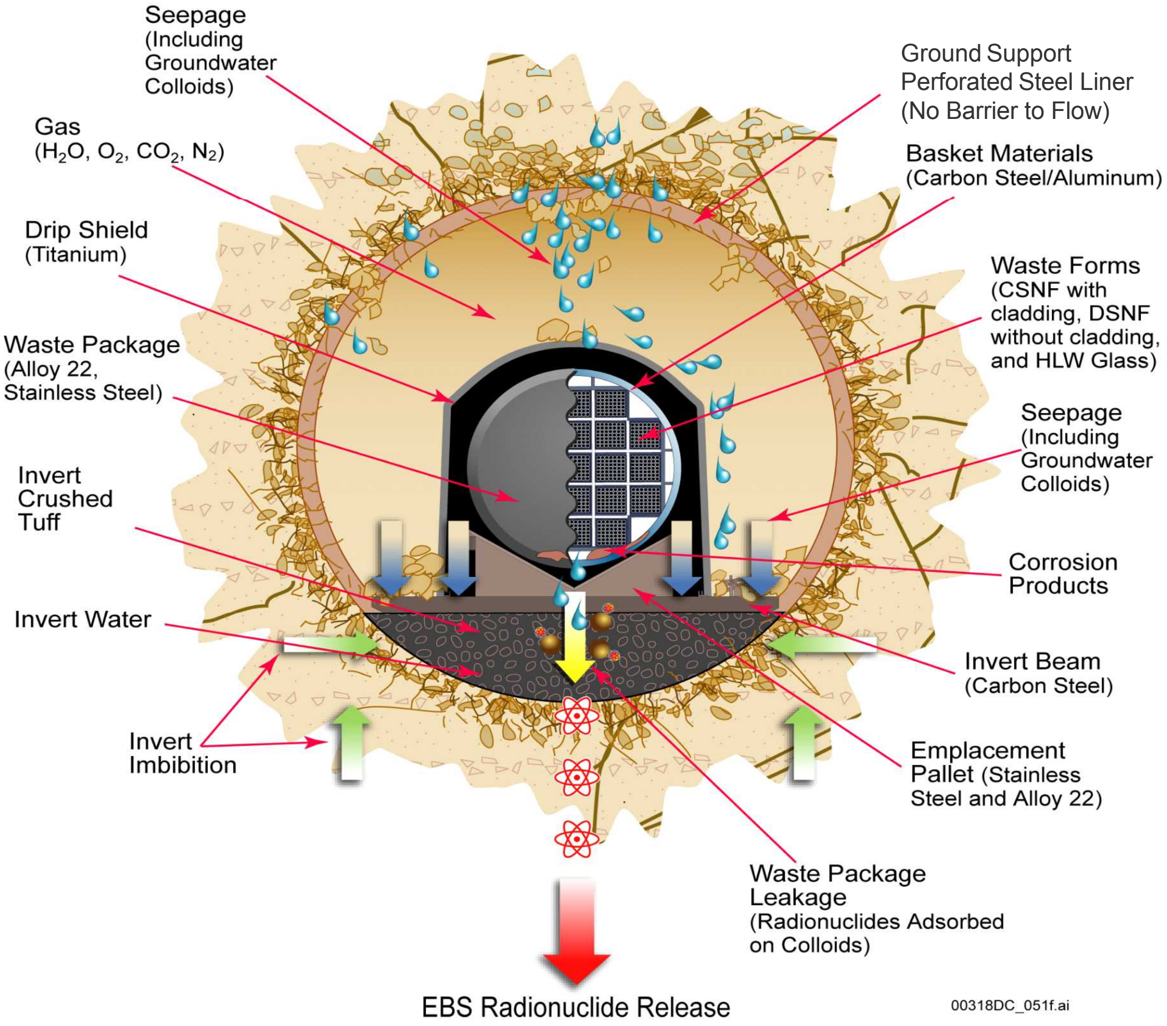
  Includes the significant features, events, and processes

  Uses a range of defensible and reasonable parameter distributions and propagates the uncertainty to evaluate the effects and consequences through Monte Carlo simulation
- PA captures major process couplings/linkages via conditional or parametric dependencies in abstracted models, or explicitly with fundamental process models

Example Model Components in Yucca Mtn. PA



General Engineered Barrier System Design Features and Materials and Natural Processes



Source Term Models in Performance Assessment: A Yucca Mountain (YM) Example

YM Source Term Abstractions Objectives

- Account for physical and chemical processes that occur inside a failed waste package (WP) and affect the availability of radionuclides to be transported through and out of the failed WPs
- Break into two specific locations within the WP
  - Within the waste forms (Cell 1)
  - Downstream transport with corrosion products (Cell 2)
  - Hand off radionuclide fluxes to radionuclide transport model within the engineered barrier system (EBS)

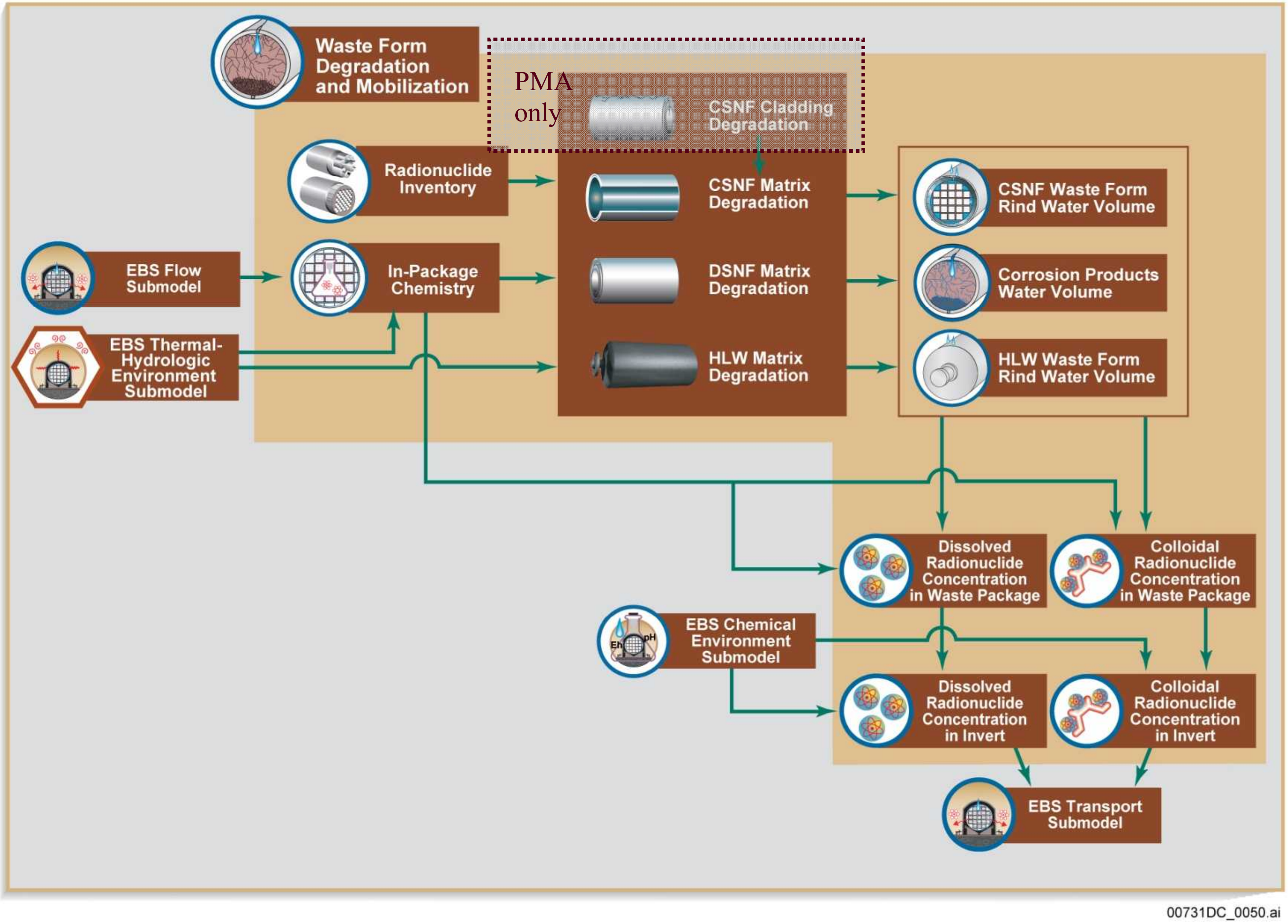
YM Model Assumptions

- The repository is in an oxidizing condition and oxygen fugacity equals 0.2 bar
  - Exception for solubility model for Pu
- In-package oxygen, carbon dioxide, and water vapor maintain equilibrium with the ambient atmosphere outside of the WP
- No credit taken for cladding (Zircaloy or stainless)
  - Except for Performance Margin Analysis (PMA)
    - Zircaloy cladding is assumed to split along its length in a single model time step
      - for fuel that has failed prior to emplacement
      - for all fuel failed by a disruptive event
    - No credit taken for stainless steel cladding
- All radionuclides are transported in the aqueous phase (either dissolved or colloidal, i.e., no gaseous transport) between the repository and the accessible environment

YM Model Assumptions (continued)

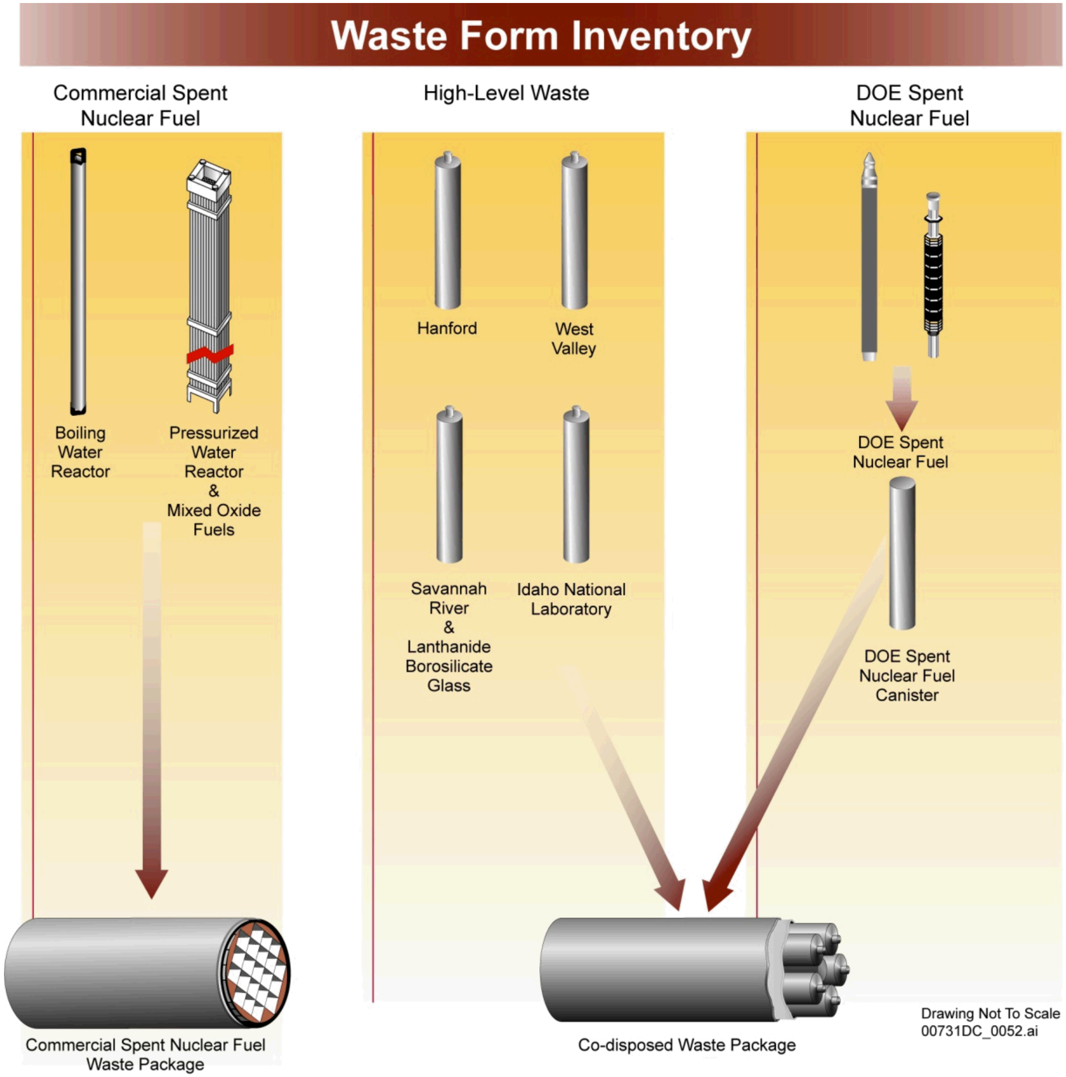
- Bulk water chemistry in a waste package is calculated by a well-mixed batch reactor model
  - Applicable to thin films of water greater than a limiting number of monolayers
    - ~ 10 monolayers (corresponds to RH about 95%)
  - Thinner films are assumed to be too discontinuous for transport (and not representative of bulk water)
- Thermodynamic database for dilute solutions is used in the in-package chemistry speciation calculations
  - Evaluated higher ionic strength as function of RH
    - incorporation of H_2O into reaction products
    - consideration of simple brine compositions
- Control of pH in Cell 2 via surface adsorption/desorption reactions on corrosion products

Identity and Linkage of YM Abstractions



Inventory— YM Implementation

- Inventory averaged over WP types
- CSNF WP contains:
  - PWR, BWR, MOX fuel
  - Zircaloy and stainless steel clad fuel
- Co-disposal WP contains:
  - Defense spent nuclear fuel (DSNF in multicanister overpack [MCO])
  - HLW (lanthanide borosilicate [LaBS] glass)



Chemical Environment Models : A Yucca Mountain (YM) Example

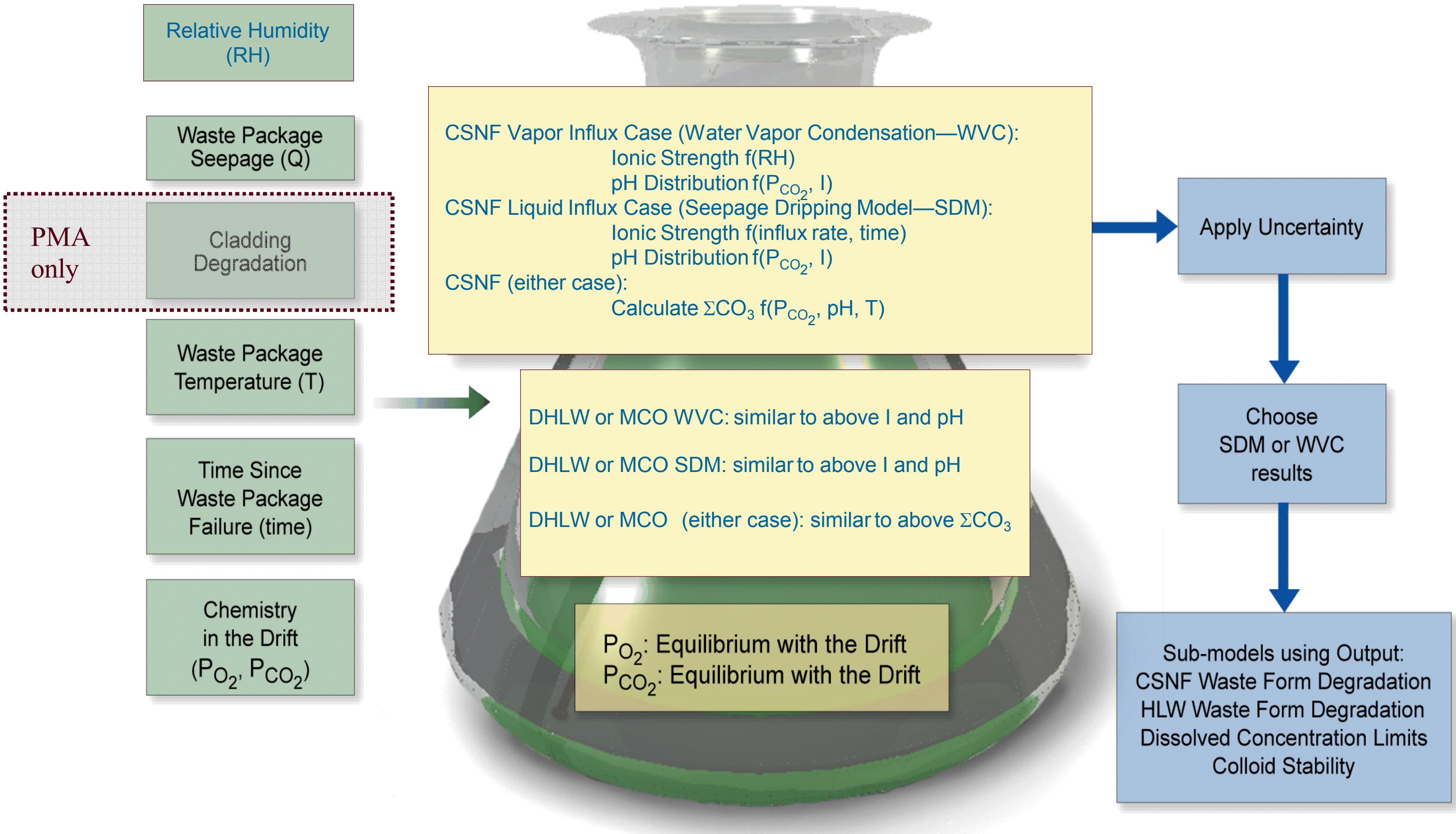
YM In-Package Chemistry Processes

- The chemical processes considered in the model include:
  - Reaction-path tracing of the in-package chemical system
  - Conservation of mass
  - Kinetic dissolution of the waste package components and spent nuclear fuel using linear rate laws
  - Kinetic dissolution of waste forms (CSNF and HLWG) using transition-state theory rate laws (i.e., nonlinear rate laws, which are dependent on the fluid chemistry)
  - Equilibrium precipitation and dissolution of metal corrosion products and complex mineral phases
  - Thermal (i.e., temperature) effects on fluid chemistry
  - Equilibrium oxidation and reduction reactions (atmospheric oxygen fugacity)
  - Chemical interaction of input solution with codisposed waste (DSNF with HLWG)
  - Effect of variable input water compositions on the resulting fluid composition
  - Chemical effects of void space (proximity of waste package components with atmospheric conditions, carbon dioxide fugacity set by in-drift chemical environment)
  - Influence of surface complexation on the fluid pH.
- The physical processes considered in the model include:
  - Water ingress and egress (egress for the liquid influx only) through the waste package
  - Mixing of water in contact with waste package components.

YM In-Package Chemistry Model Summary

- Models for CSNF and Codisposal Waste Packages
  - Batch reactor model (EQ6) with flow through
    - Water Vapor Condensation (WVC) Case:
      - Vapor-Influx only
      - The condensation of vapor onto the waste package internals is simulated as pure H_2O and enters at a rate determined by the water vapor pressure for representative temperature and relative humidity conditions.
    - Seepage Dripping Model (SDM) Case:
      - Liquid-Influx
      - The water entering a waste package from the drift is simulated as typical groundwater and enters at a rate determined by the amount of seepage available to flow through openings in a breached waste package.
  - Surface Complexation model (CSNF only)
    - Steel corrosion products protonation/deprotonation reactions serve as buffer mechanism for in-package pH

YM In-Package Chemistry Submodel



Relative Humidity (RH)

Waste Package Seepage (Q)

PMA only

Cladding Degradation

Waste Package Temperature (T)

Time Since Waste Package Failure (time)

Chemistry in the Drift (P_{O_2}, P_{CO_2})

CSNF Vapor Influx Case (Water Vapor Condensation—WVC):
Ionic Strength f(RH)
pH Distribution f(P_{CO_2}, I)
CSNF Liquid Influx Case (Seepage Dripping Model—SDM):
Ionic Strength f(influx rate, time)
pH Distribution f(P_{CO_2}, I)
CSNF (either case):
Calculate ΣCO_3 f(P_{CO_2}, pH, T)

DHLW or MCO WVC: similar to above I and pH

DHLW or MCO SDM: similar to above I and pH

DHLW or MCO (either case): similar to above ΣCO_3

P_{O_2}: Equilibrium with the Drift
P_{CO_2}: Equilibrium with the Drift

Apply Uncertainty

Choose SDM or WVC results

Sub-models using Output:
CSNF Waste Form Degradation
HLW Waste Form Degradation
Dissolved Concentration Limits
Colloid Stability

Determine pH, Ionic Strength, ΣCO_3, P_{O_2}, P_{CO_2}
in a failed waste package

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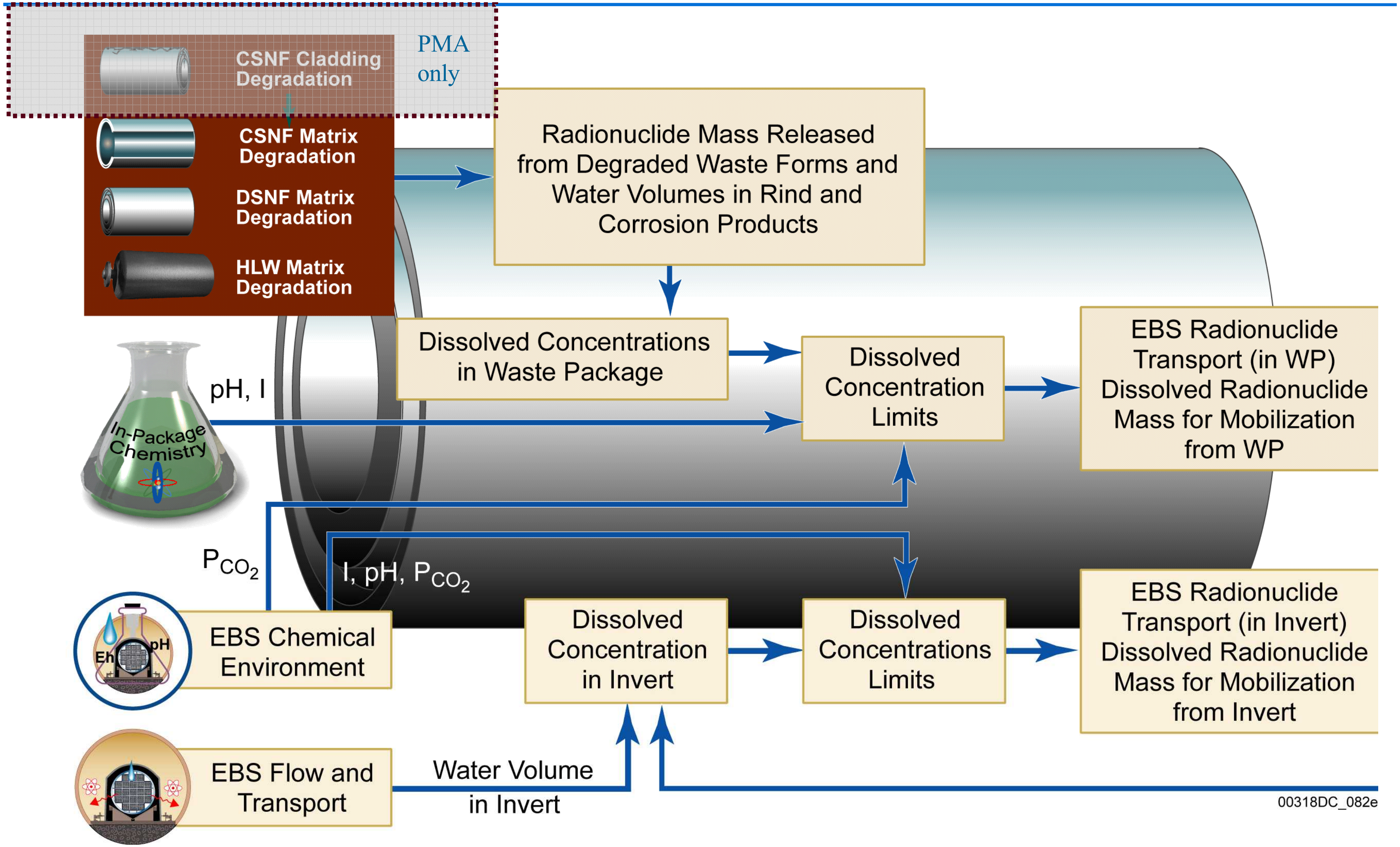
YM In-Package Chemistry—Implementation

- PCO_2, PO_2, and RH in equilibrium with drift environment
- pH distribution depends on
  - Waste form (CSNF, DHLW, MCO)
  - H_2O entry conditions
    - Vapor influx only
    - Vapor and liquid influx
  - Ionic strength, PCO_2
- Ionic strength (range evaluated) as $f\{RH\}$
  - Fuel type
  - H_2O entry conditions and time since breach
- Total dissolved carbonate $f\{pH, T, PCO_2\}$
  - Directly coupled to pH via equilibria

Connections within the YM Source-Term Model



CSNF Cladding Degradation

PMA only

CSNF Matrix Degradation

DSNF Matrix Degradation

HLW Matrix Degradation

Radionuclide Mass Released from Degraded Waste Forms and Water Volumes in Rind and Corrosion Products

Dissolved Concentrations in Waste Package

Dissolved Concentration Limits

EBS Radionuclide Transport (in WP) Dissolved Radionuclide Mass for Mobilization from WP

In-Package Chemistry

pH, I

P_{CO_2}

I, pH, P_{CO_2}

EBS Chemical Environment

Dissolved Concentration in Invert

Dissolved Concentrations Limits

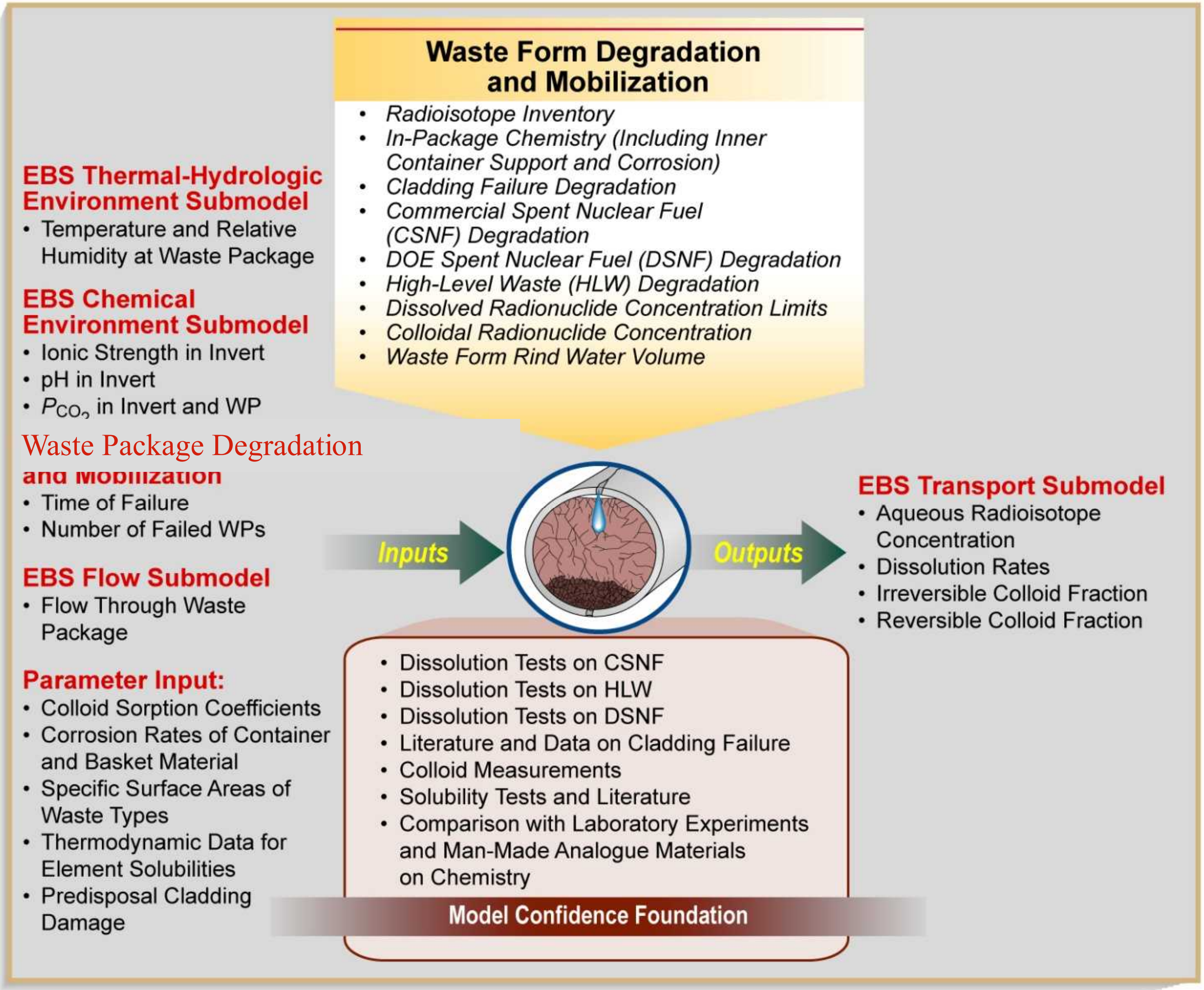
EBS Radionuclide Transport (in Invert) Dissolved Radionuclide Mass for Mobilization from Invert

EBS Flow and Transport

Water Volume in Invert

Waste form Degradation/Release Models: A Yucca Mountain (YM) Example

Inputs, Outputs, Basis for YM Model Confidence



Waste Form Degradation and Mobilization

- *Radioisotope Inventory*
- *In-Package Chemistry (Including Inner Container Support and Corrosion)*
- *Cladding Failure Degradation*
- *Commercial Spent Nuclear Fuel (CSNF) Degradation*
- *DOE Spent Nuclear Fuel (DSNF) Degradation*
- *High-Level Waste (HLW) Degradation*
- *Dissolved Radionuclide Concentration Limits*
- *Colloidal Radionuclide Concentration*
- *Waste Form Rind Water Volume*

EBS Thermal-Hydrologic Environment Submodel
- Temperature and Relative Humidity at Waste Package

EBS Chemical Environment Submodel
- Ionic Strength in Invert
- pH in Invert
- P_{CO_2} in Invert and WP

Waste Package Degradation

and Mobilization
- Time of Failure
- Number of Failed WPs

EBS Flow Submodel
- Flow Through Waste Package

Parameter Input:
- Colloid Sorption Coefficients
- Corrosion Rates of Container and Basket Material
- Specific Surface Areas of Waste Types
- Thermodynamic Data for Element Solubilities
- Predisposal Cladding Damage

EBS Transport Submodel
- Aqueous Radioisotope Concentration
- Dissolution Rates
- Irreversible Colloid Fraction
- Reversible Colloid Fraction

- Dissolution Tests on CSNF
- Dissolution Tests on HLW
- Dissolution Tests on DSNF
- Literature and Data on Cladding Failure
- Colloid Measurements
- Solubility Tests and Literature
- Comparison with Laboratory Experiments and Man-Made Analogue Materials on Chemistry

Model Confidence Foundation

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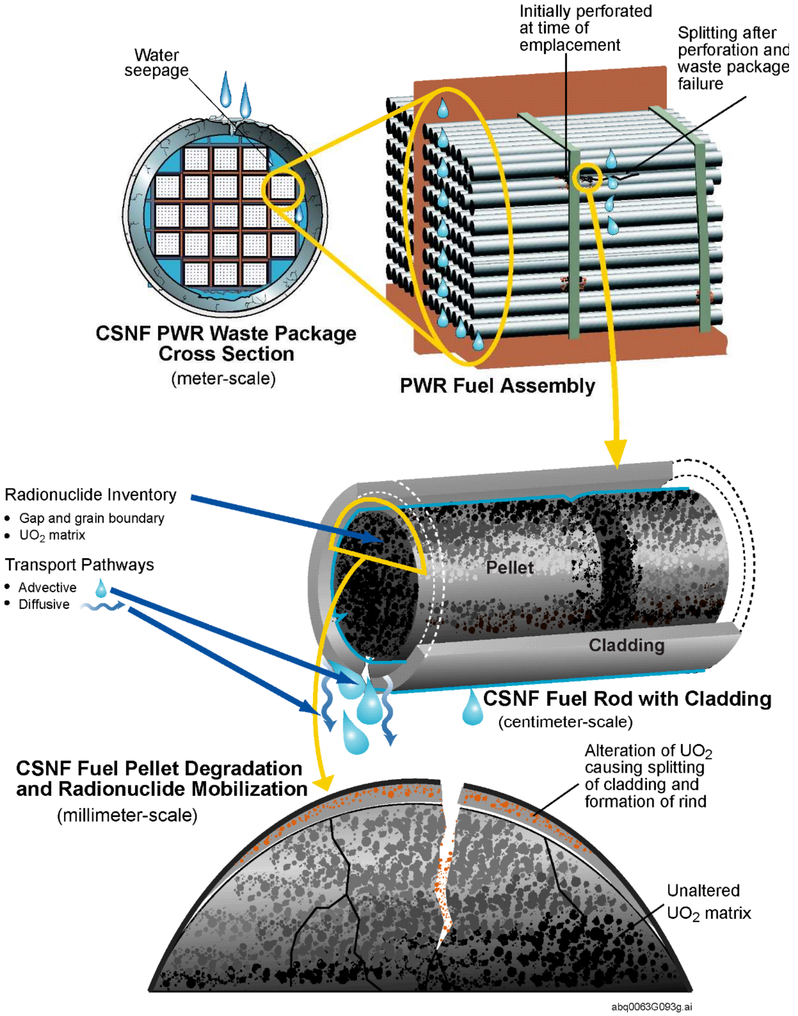
YM CSNF Degradation Process at Various Scales



Water seepage

Initially perforated at time of emplacement

Splitting after perforation and waste package failure

CSNF PWR Waste Package Cross Section
(meter-scale)

PWR Fuel Assembly

Radionuclide Inventory
- Gap and grain boundary
- UO_2 matrix

Transport Pathways
- Advective
- Diffusive

Pellet

Cladding

CSNF Fuel Rod with Cladding
(centimeter-scale)

CSNF Fuel Pellet Degradation and Radionuclide Mobilization
(millimeter-scale)

Alteration of UO_2 causing splitting of cladding and formation of rind

Unaltered UO_2 matrix

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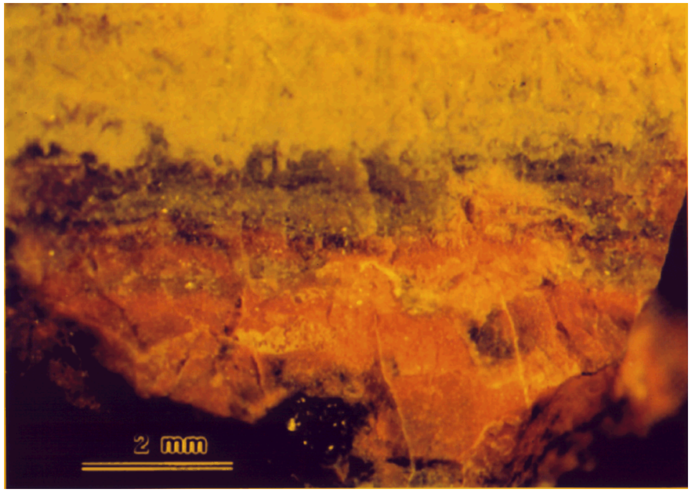
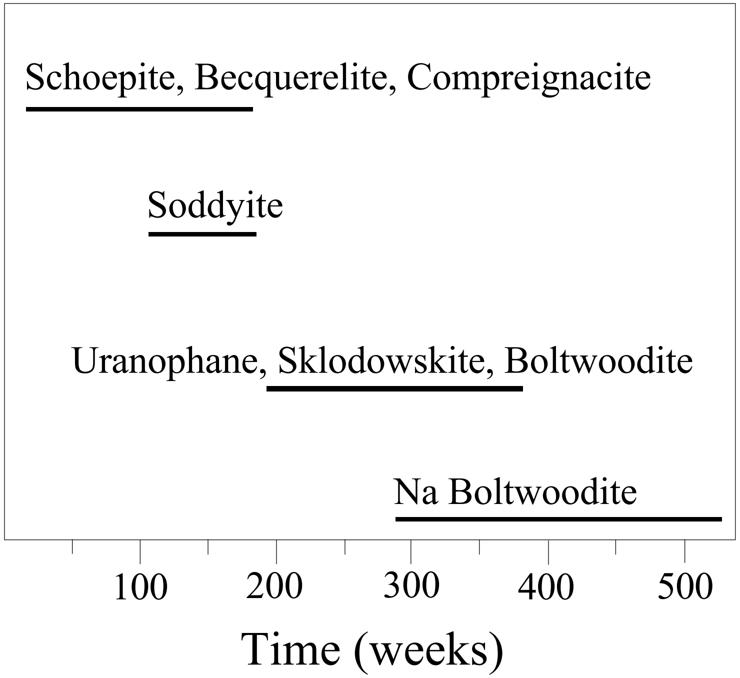
UO_{2+x} Corrosion and Uranyl Phase Paragenesis



Finch and Ewing (1992) *Journal of Nuclear Materials*



Natural uranyl mineral paragenesis is well defined from numerous observations of uraninite alteration in geologic systems

Uranyl mineral relations observed in laboratory testing on UO_2 and spent fuel parallel observations of natural alteration

Data from experiments, Argonne National Lab

Wronkiewicz, Bates, Gerding, Veleckis & Tani (1992): J. Nucl. Mater. 190, 107-127

Wronkiewicz, Bates, Wolf, & Buck (1996): J. Nucl. Mater. 238, 78-95

Finch, Buck, Finn & Bates (1999): MRS Proc. 556, 431-438

YM Spent Fuel Degradation Model

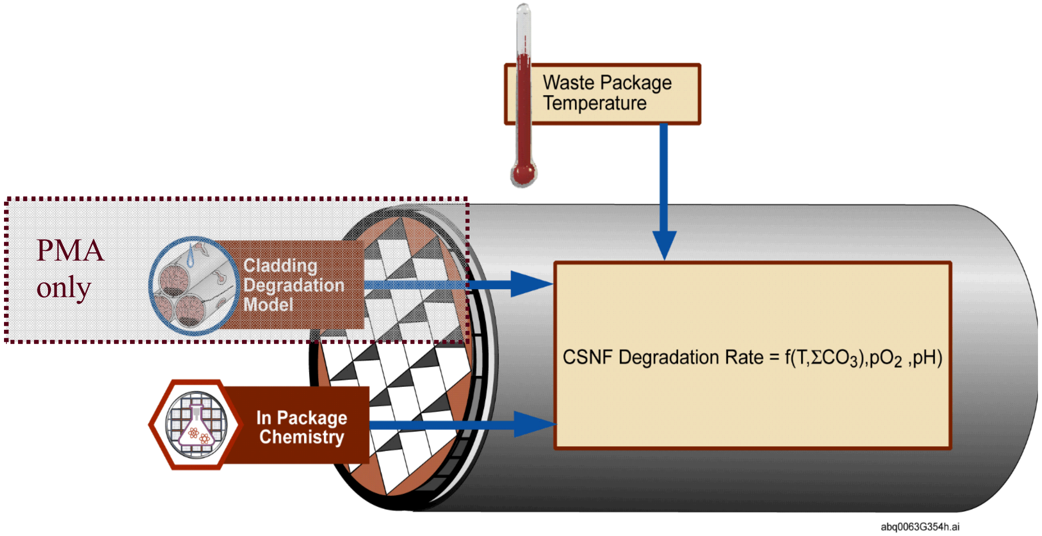
- Gap and Grain Boundary Instantaneous Release Fractions

Triangular Probability Distribution Functions of Instantaneous Release Fractions

	^{137}Cs (%)	^{129}I (%)	^{99}Tc (%)	^{90}Sr (%)
Apex	3.63	11.24	0.10[a]	0.09
Minimum	0.39	2.04	0.01[b]	0.02
Maximum	11.06	26.75	0.26	0.25

NOTES: [a]Rounded up from 0.06. [b]Changed from zero to provide a nonzero minimum.

- Hardware inventory also instantly released (^{14}C)
- Matrix Dissolution Rates Depend on Chemical Conditions and Temperature (Flow Through Tests)



YM Spent Fuel Matrix Degradation

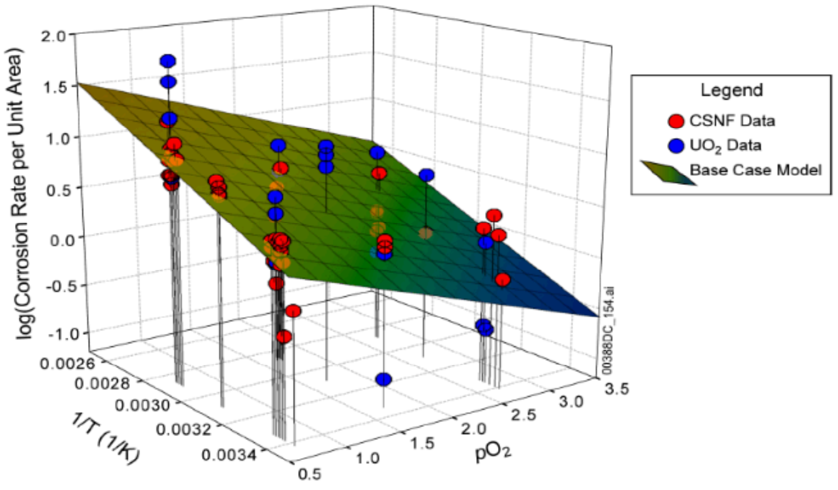
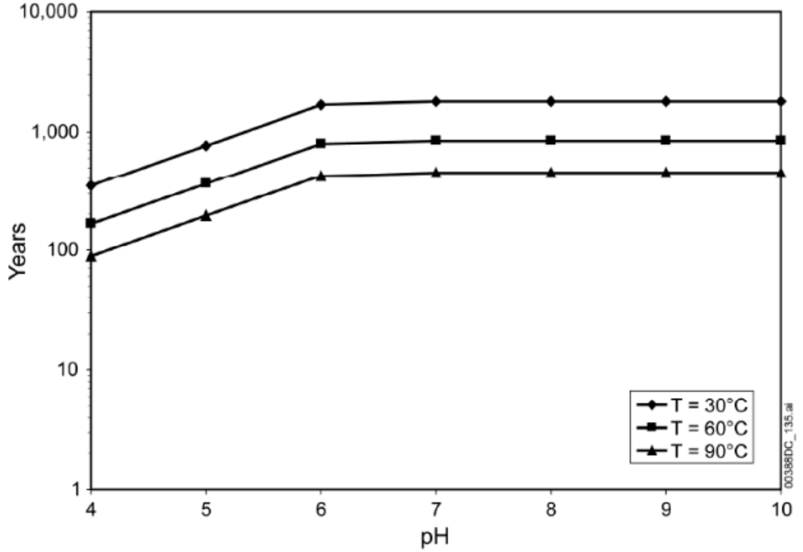


Figure 6-3. Comparison of the Base-Case Model ($pCO_3 = 2.7$) to the Input CSNF and UO_2 Data



- Overall rate depends on temperature, chemical conditions, surface area
  - Under acidic conditions
    - pH, oxygen fugacity
  - Under basic conditions
    - oxygen fugacity, total dissolved carbonate
  - Flow-through testing of Commercial Spent Nuclear Fuel (CSNF) dissolution and UO_2 dissolution at various conditions
- Provides rate radionuclides are potentially available for release
- Concentrations resulting from degradation are calculated for comparison to limitations from solubility controls

CSNF WF Degradation—YM Implementation

- No cladding credit in the compliance case – waste form available to degrade once package breaches
- Instantaneous release of the gap/grain boundary inventory (Cs, Tc, Sr, I) and hardware inventory (C)
  - Range 0.01% – 26%
- Fractional degradation rate for CSNF matrix
  - All radionuclides released congruently as matrix dissolves
  - Function of T, pH, pO_2, total dissolved carbonate concentration
  - Coefficients in the regression equation include epistemic uncertainty

OSTI Source Term Targeted Thrust (STTT)

- SNF dissolution mechanisms and rates
  - Single-Pass Flow-Through (SPFT) testing to assess
    - rate change with degradation
    - congruent release

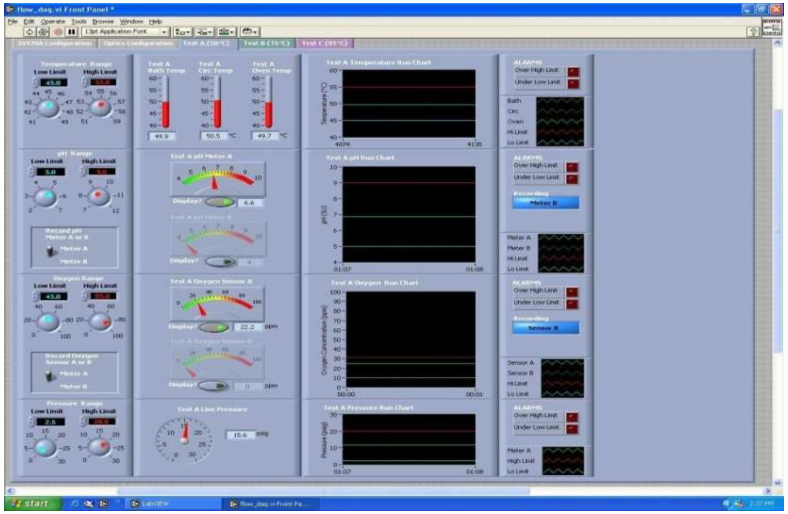
Brady Hanson and Edgar Buck (PNNL)

Judah Friese (PNNL)

Linfeng Rao (LBNL)

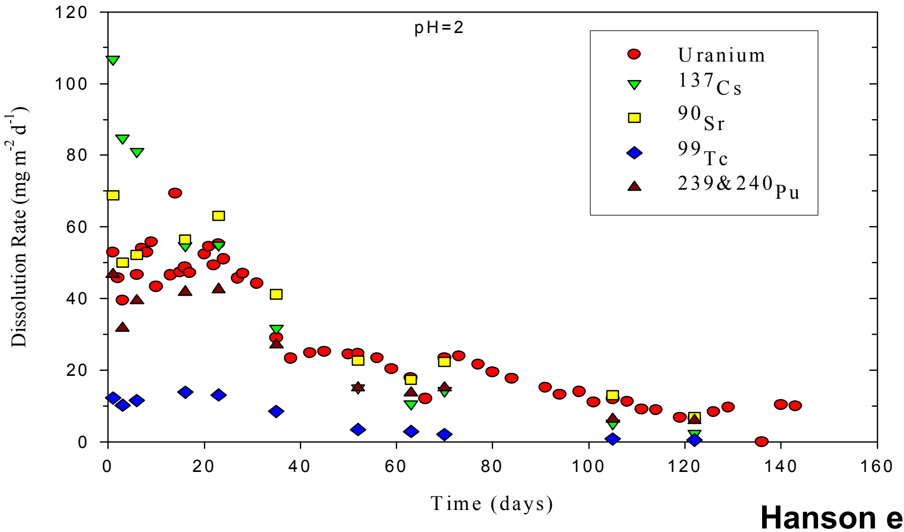
Jim Jerden (ANL)

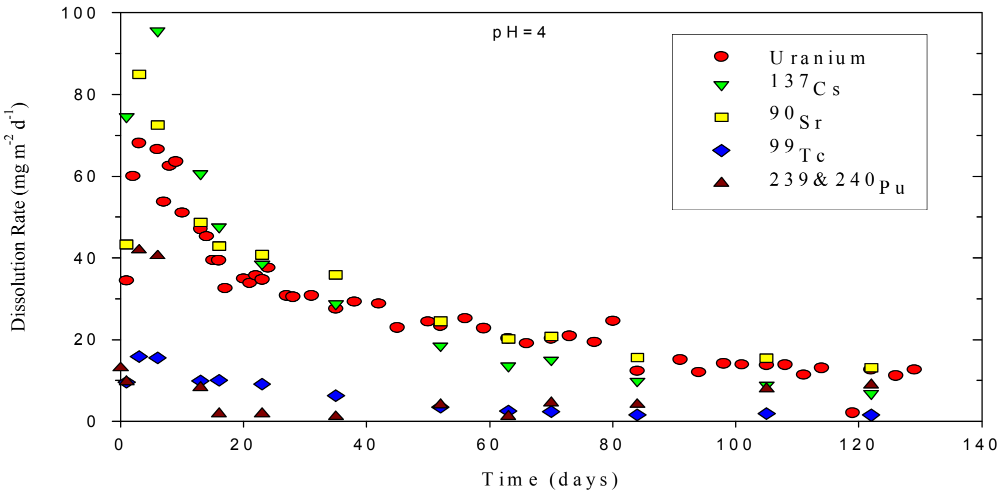
Single-Pass Flow-Through (SPFT) Setup



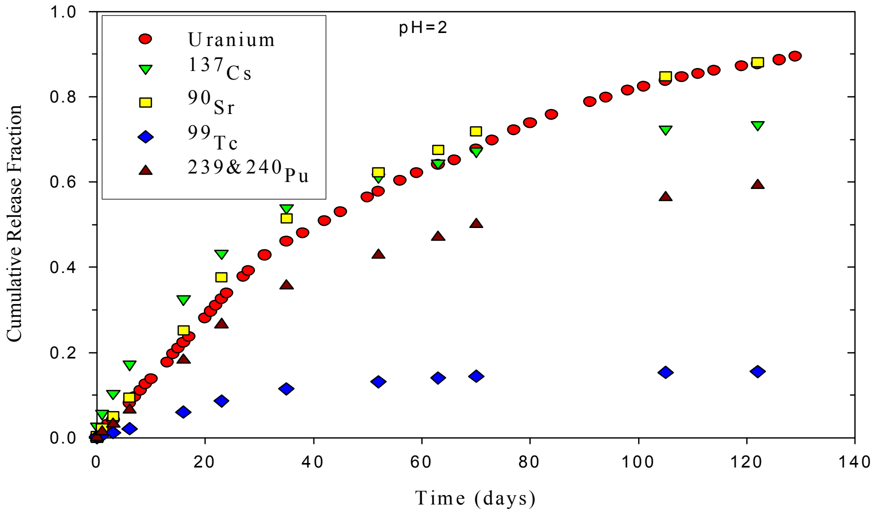
28 columns simultaneously (PNNL)

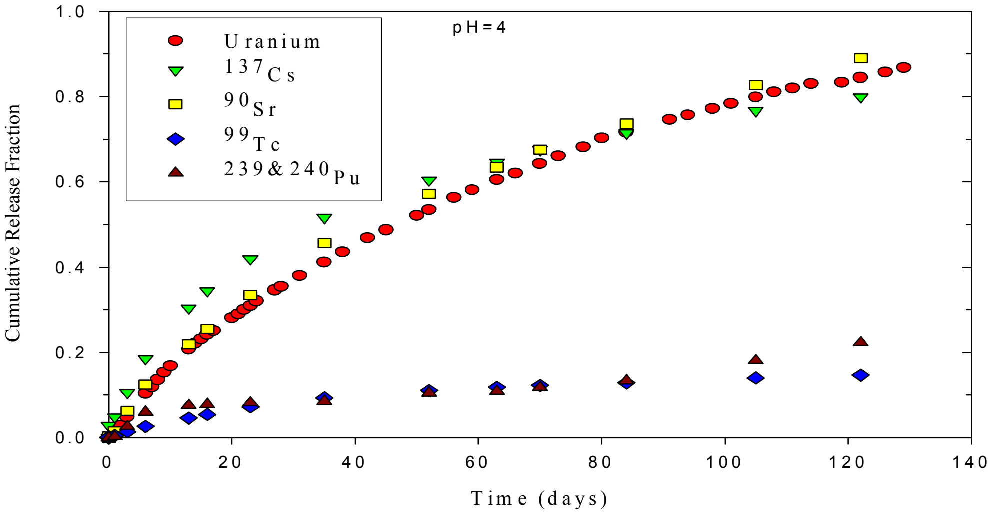
Low pH SPFT on CSNF



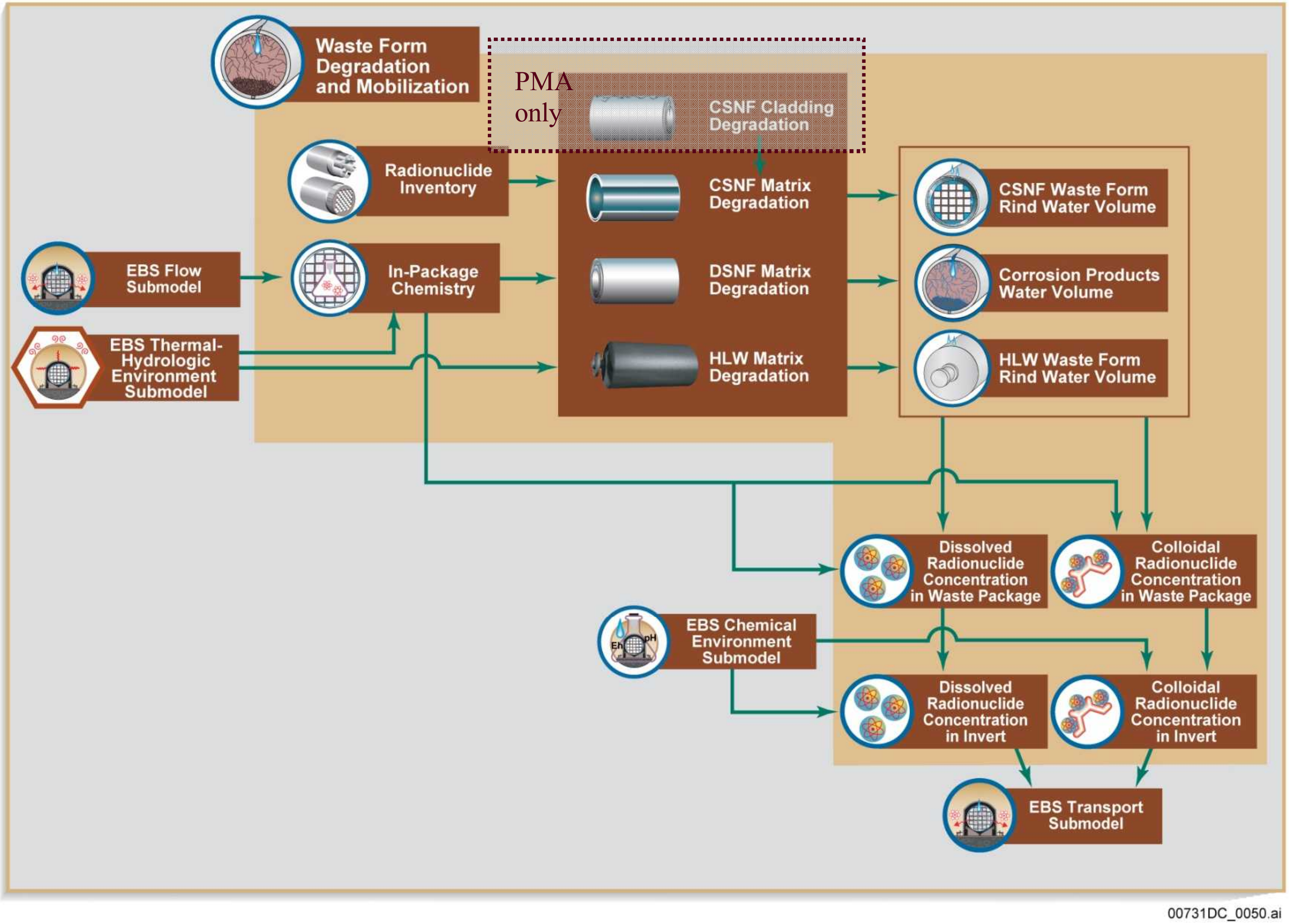


Hanson et al. MRS 2004



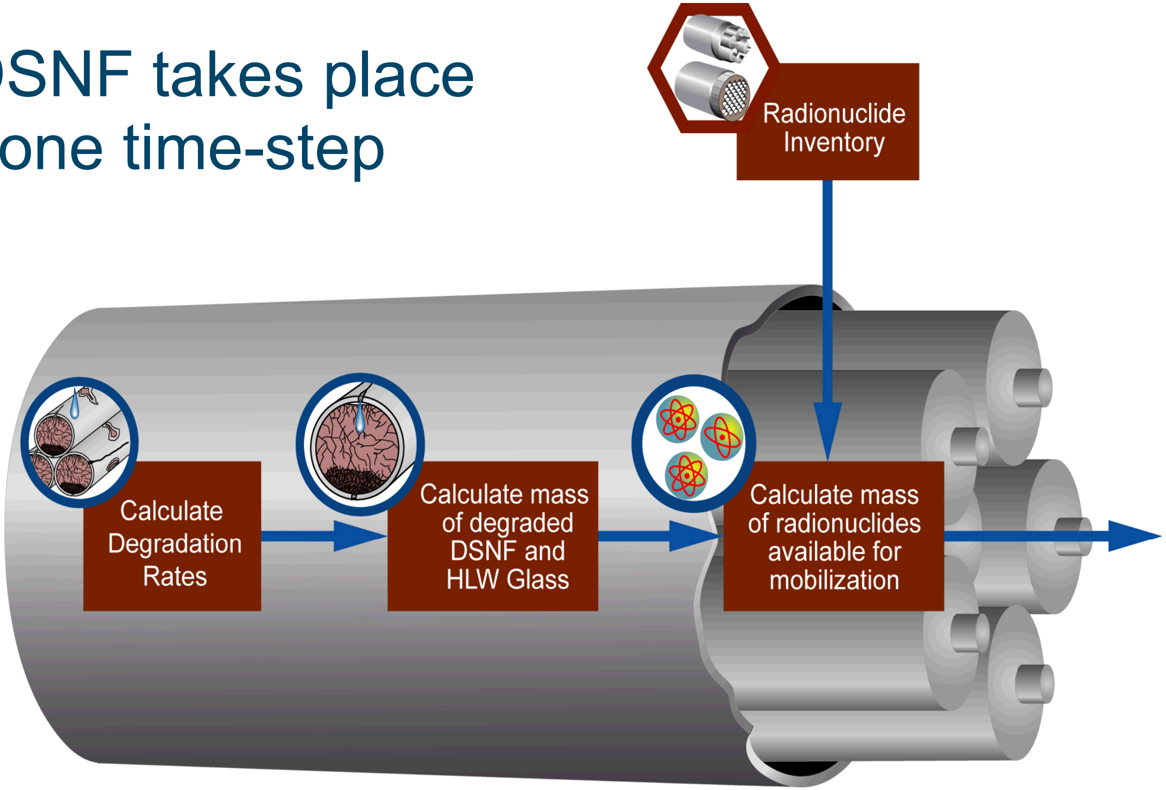


Identity and Linkage of YM Abstractions



DSNF WF Degradation—YM Implementation

- Model uses one surrogate for ten DSNF groups
- Degradation of DSNF takes place rapidly, that is in one time-step



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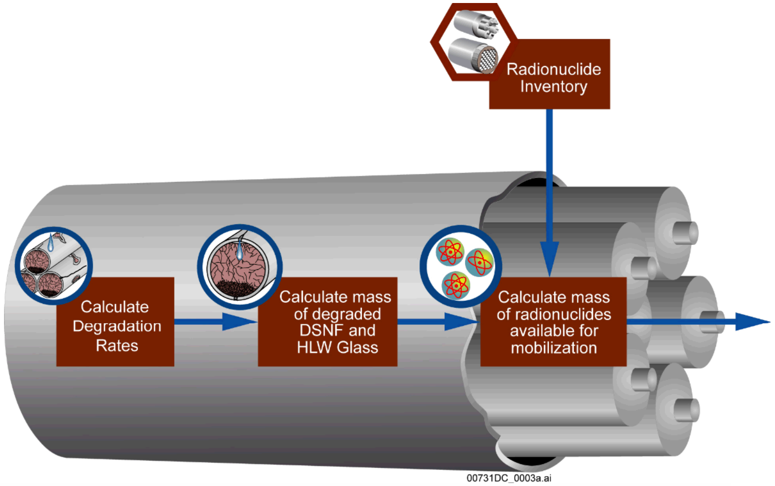
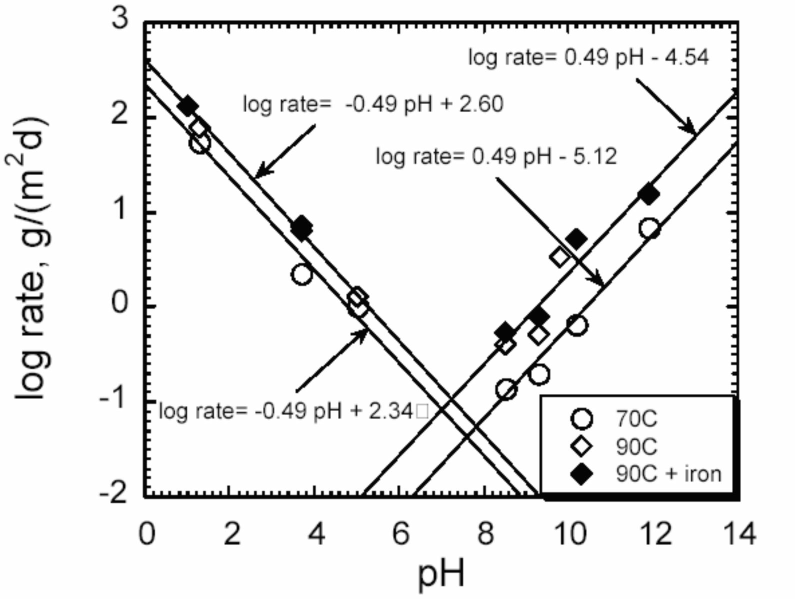
HLW Glass Degradation—YM Implementation

- One surrogate to represent full range of disposed glass degrading in humid air, dripping, or immersion conditions



- Fractional degradation rate for HLW glass
  - RH < 44%: Rate = 0 yr^{-1}
  - Function of T, pH
  - Coefficients in the regression equation include epistemic uncertainty



Other HLW Glass Degradation Processes

- YM HLW Dissolution Model is Conservative
  - Includes only far from equilibrium rates (highest)
- Glass Degradation Processes are more Complex
  - Diffusion controls
  - Gel layer development
  - Secondary phase coverage
- YM Model does not Include these Additional Processes
  - Included in other Process Models and PA Models

Integrated Predictive Simulation Capability (IPSC)

Vision: As an integral part of nuclear energy generation and management, we will develop an integrated, science-based predictive simulation package for assessing performance of potential nuclear reactor waste storage or disposal options, from the waste form itself through the entire surrounding engineered environment and representing the range of important multi-scale effects, with uncertainty quantification.

Nuclear Energy Advanced Modeling and Simulation (NEAMS) (US DOE NE)

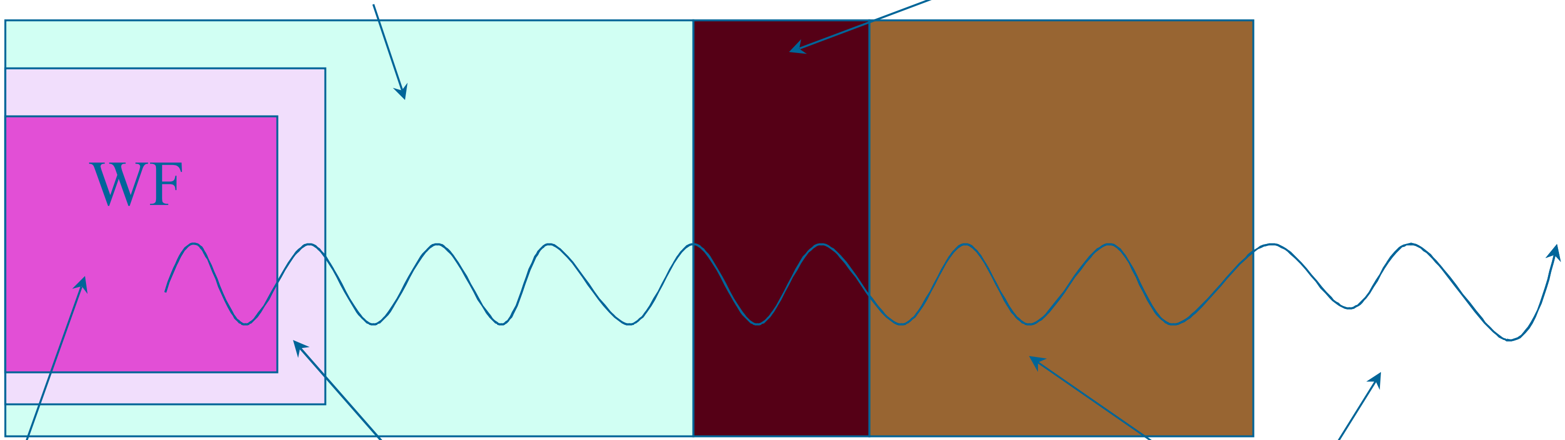
Radionuclide Migration

What happens at barriers?
- corrosion, cracking, sorption

What happens away from surface?
- transport, colloids, 2ndary phases

aqueous solution pH, redox, cations, anions

Cladding/canisters/package



barrier layers, complexes, gels

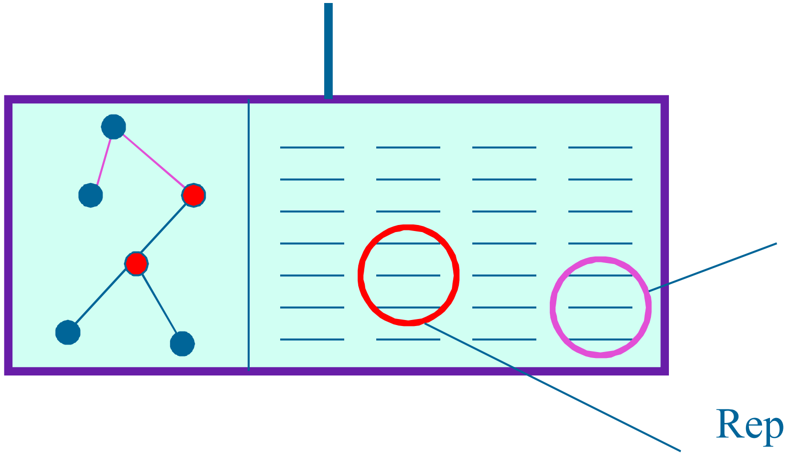
glass, ceramic,
metal

EBS fill, geologic setting
- transport, sorption, …

what happens at the surface?
- leaching, transport, dissolution, …

what happens in the bulk?
-composition, phases, grains, cracking, …

Upscaling from Atomistic to Continuum



Replace phenomenological. data with sub-scale data

Replace phenomenological. data with sub-scale data

Two challenges:
  1) accuracy of parameters
  2) adequacy of physics abstractions

Model parameters always refit (calibrated) for validation of application
    Internal consistency (e.g. thermodynamic)
    Model incompleteness
Physics abstraction mixes parameters (dependencies)
    and may not be (quantitatively) reducible to sub-scale processes

Bridging this divide is unsolved challenge

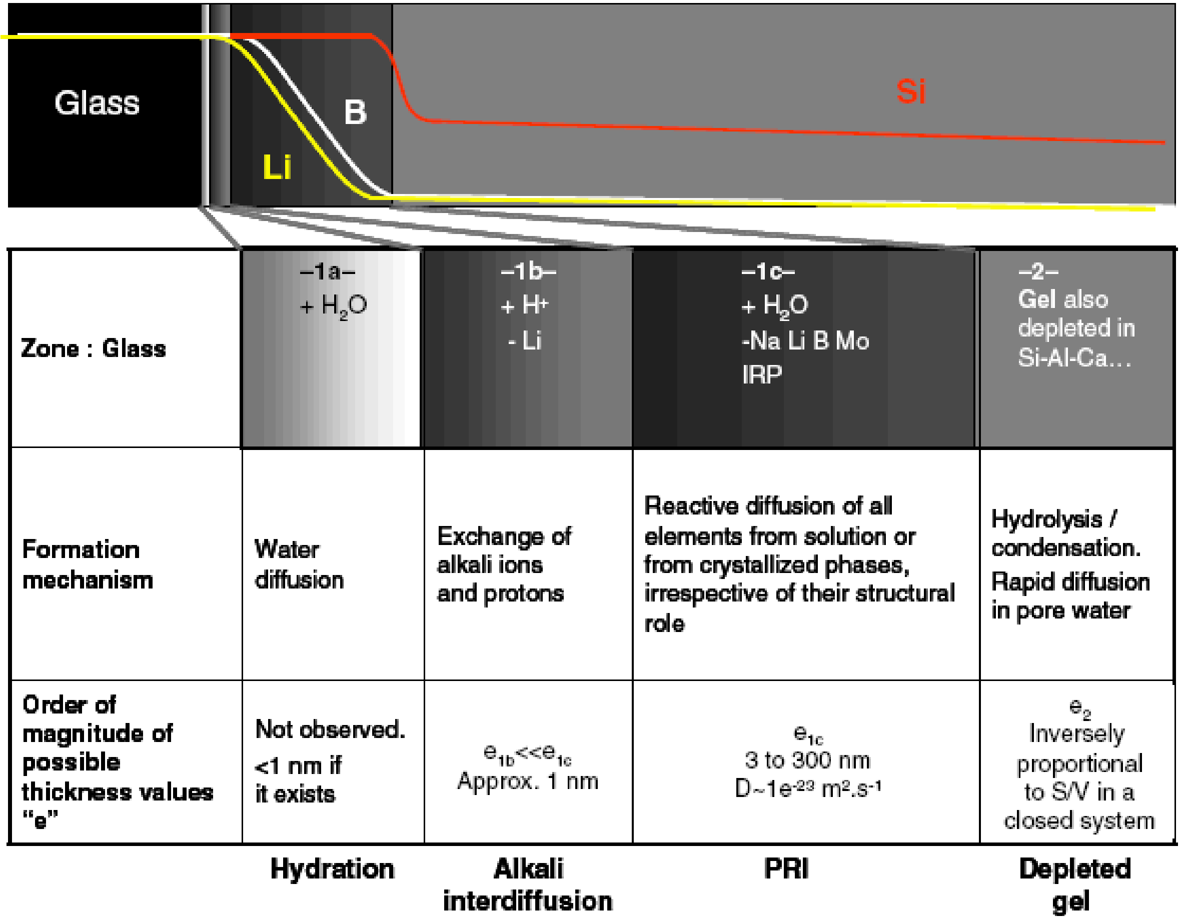
NEAMS IPSC Glass Waste Background

- Seven different models for long-term behavior of glass in wet environments are being used in performance assessment
- Why? → **Single biggest reason is due to a lack of understanding in controlling mechanisms!**
- Subject of world-wide interest, e.g., EU funded study on model comparison (GLAMOR)

Model	Boksay	r(t)	GM	FitSim	Pescatore	Diss+IX	GRAAL
Author	Boksay	Grambow	Vernaz	Aerstens	Pescatore	McGrail	Gin
Parameters	V,D	k0, Dsi, C*, rf, α(ab)	k0, Dsi, C*, rf, α(ab), Dh2o, Kd/Db	D1, D2, Cx	Dsi, ηR, k0, C*	k0, η, C*, r(ab)	k0, Dsi, C*, rf, α(ab), Dh2o, Kd/Db
Linear rate	no	yes	yes	no	yes	yes	yes
Si in solution	yes	yes	yes	no	yes	yes	yes
Diffusion layer	yes	no	yes	yes	no	yes	yes
Profiles in WF	yes	no	yes	yes	no	yes	yes
Diffusion in 'gel'	no	Si	Si	B+A	no	no	Si
Diffusion in 'D-layer'	B+A	no	B+A	B+A	no	B+A	B+A
Final gel	finite	finite	finite	inf	none	finite	finite
Final barrier	inf	none	inf	inf	none	finite	inf

From Vienna et al., 2009

Glass Alteration Phases and Zonation



Zone : Glass	–1a– + H_2O	–1b– + H^+ - Li	–1c– + H_2O -Na Li B Mo IRP	–2– Gel also depleted in Si-Al-Ca…
Formation mechanism	Water diffusion	Exchange of alkali ions and protons	Reactive diffusion of all elements from solution or from crystallized phases, irrespective of their structural role	Hydrolysis / condensation. Rapid diffusion in pore water
Order of magnitude of possible thickness values “e”	Not observed. <1 nm if it exists	$e_{1b} << e_{1c}$ Approx. 1 nm	e_{1c} 3 to 300 nm D~1e-23 $m^2.s^{-1}$	e_2 Inversely proportional to S/V in a closed system
	Hydration	Alkali interdiffusion	PRI	Depleted gel

Fig. 8. Diagram of the different amorphous phases likely to be observed and their formation mechanisms.

from P. Frugier et al. / Journal of Nuclear Materials 380 (2008) 8–21

GRAAL Model Mechanisms

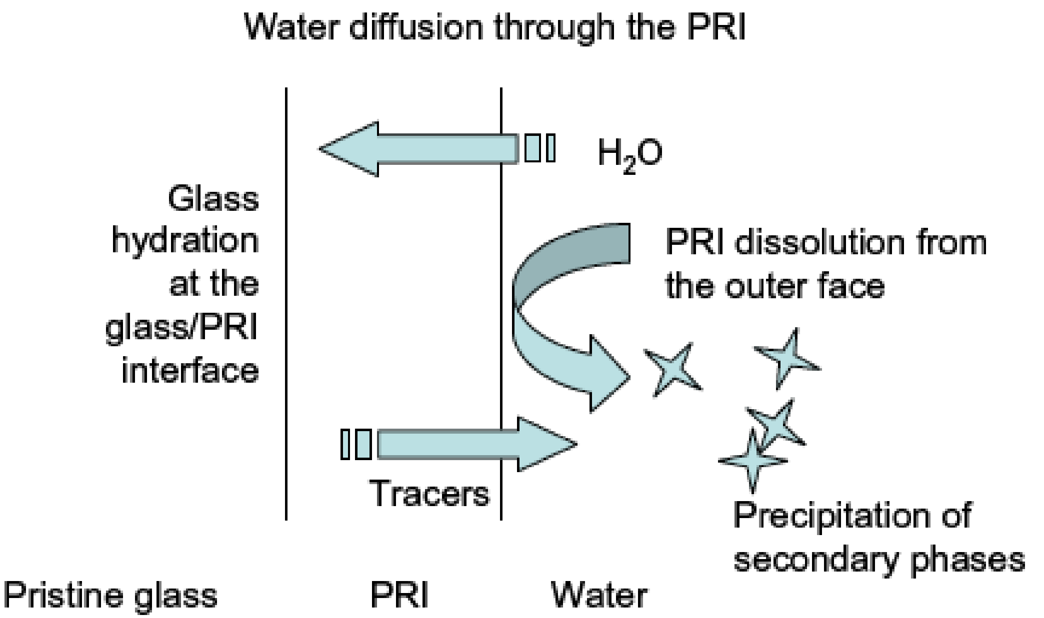
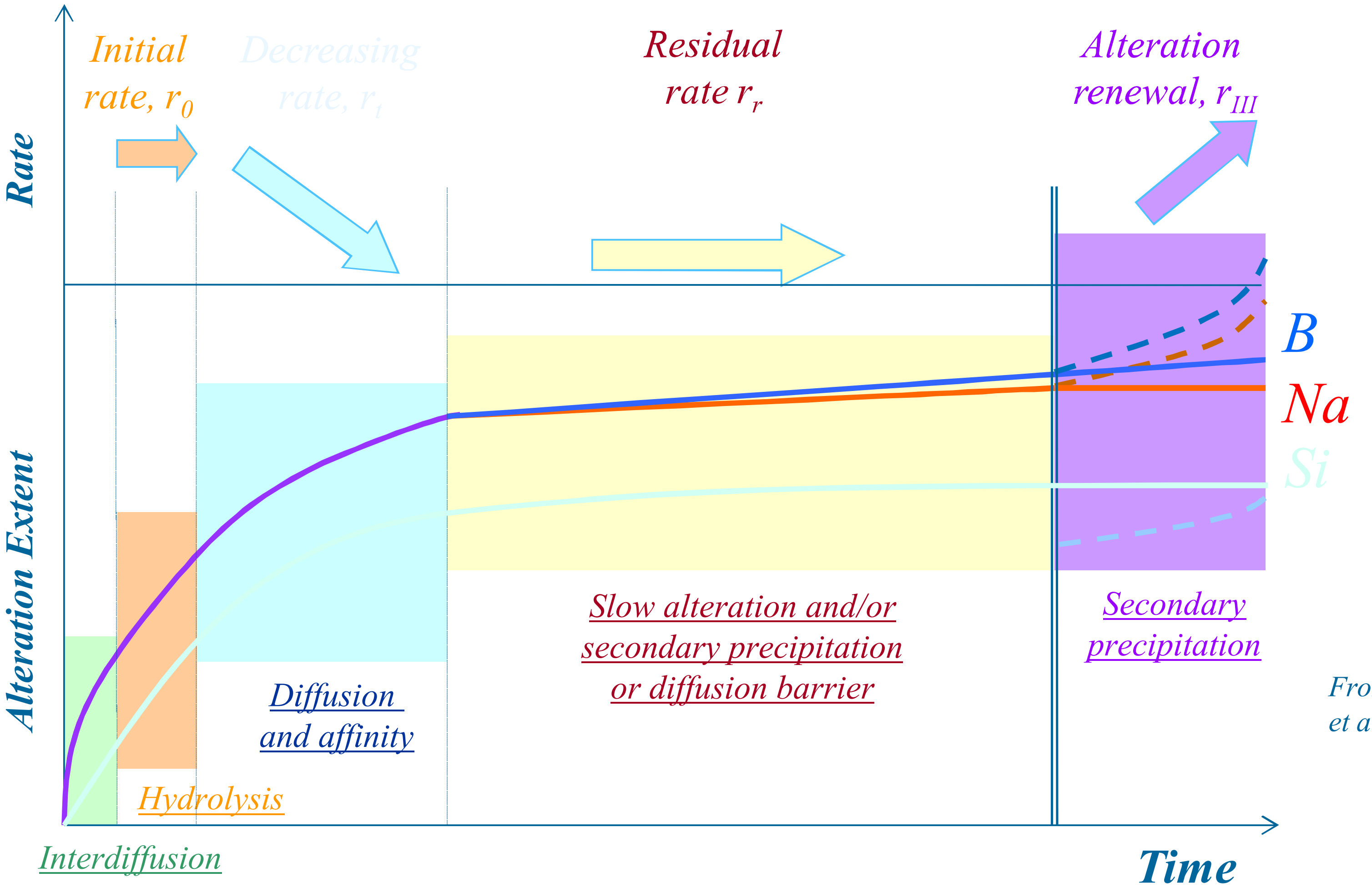


Fig. 1. Simplified diagram of the predominant mechanisms of SON68 glass alteration taken into account in the GRAAL model.

from P. Frugier et al. / Journal of Nuclear Materials 392 (2009) 552–567

Glass/Mineral Dissolution Process



From Vienna et al., 2009

Kinetic Rate Laws for Mineral Dissolution (Brantley, 2007)

- Silicate and Oxide Dissolution Mechanisms
  - Alteration of Silicate Surface
    - Leaching accompanied by surface condensation and reconstruction reactions
    - Dissolution, reprecipitation, and reconstruction
  - Surface Complexation Models (SCM)
    - $r = k_H a^n_{H+} + k_{OH} a^m_{OH-}$
    - Proton-promoted SCM appears inadequate to explain dissolution of mixed oxides such as feldspars
    - Ab initio calculations document that protonation of terminal =SiOH and =AlOH groups strengthens bonds connecting these groups to underlying mineral

Kinetic Rate Laws Cont.

Effect of Dissolved Cations and Anions

General kinetic rate equation for far-from equilibrium dissolution of silicates (Oelkers and Gislason, 2001) containing cation *M_i*. Assumes that a precursor species controls dissolution.

Background electrolytes in solution generally decrease rate of dissolution of feldspars, but increase the rate of quartz dissolution. A model is proposed by Dove et al., 2005.

$$r = k \prod_{i=1, i \neq k}^{i} \left[\frac{K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}} \right)^s}{\left(1 + K_i \left(\frac{a_{H^+}^{v_i}}{a_{M_i}^{v_i}} \right)^s \right)} \right]$$

- Exchange reaction between protons and M_i forms precursor species
- Two endmembers
  - Rate affected by dissolved M_i concentration (e.g., basaltic glass)
  - Rate independent of dissolved M_i concentration (e.g., anorthite)

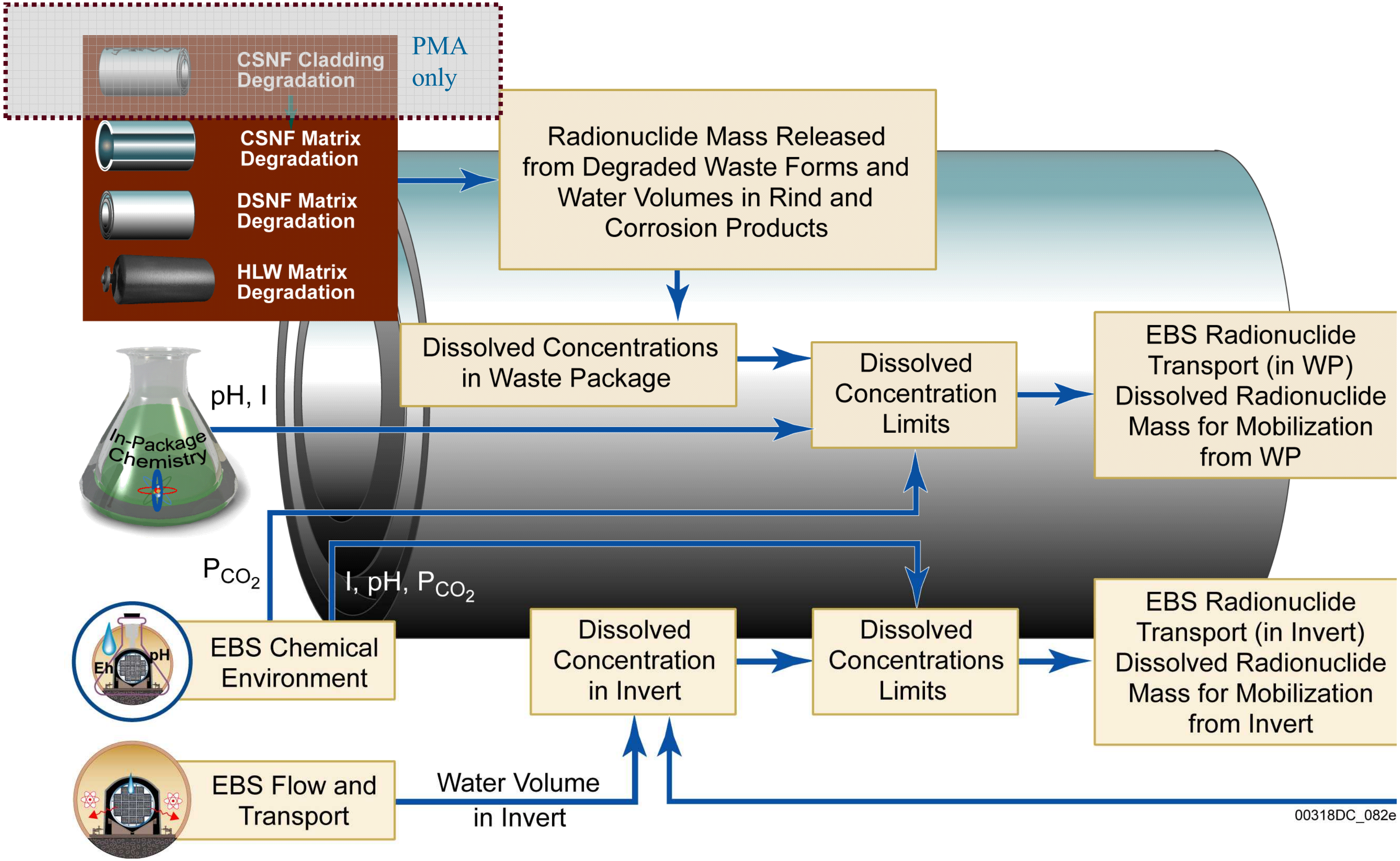
Oelkers and Gislason, 2001

Kinetic Rate Laws Cont. (II)

- Rate Constants as a Function of Mineral Composition
  - Amorphous silica
    - w/ and w/out NaCl (Icenhower and Dove, 2000)
  - Non-framework silicates
    - The trend in dissolution rate constants can be predicted from the ratio of non-tetrahedrally to tetrahedrally-coordinated cations, X/Si, which varies with connectedness (Brantley, 2004).
- Chemical affinity
  - Linear rate laws (far-from-equilibrium)
  - Non-linear rate laws
    - Dissolution stepwaves (Lasaga and Luttge, 2001)
    - These rate laws all represent complex reaction mechanisms for composite reactions.
    - Dissolution rates are controlled by nucleation of pits (dislocation, etch, etc.; Dove et al, 2005)
    - Aluminum Inhibition and Affinity (Oelkers, 2001a): Incorporate both aqueous aluminum activity and chemical affinity into rate expression.

$$\boxed{r = k_{+}(a_{SiO2(aq)})(a_{H2O})^{2}(1-\Omega)}$$

Connections within the YM Source-Term Model



Solubility— YM Implementation

- Solubility Models for Ac, Am, Np, Pa, Pu, Ra, Se, Sn, Th, and U
  - Solubilities are functions of pH and P_{CO2} presented as look-up tables for the solubility controlling phase(s)
  - Uncertainty associated with thermodynamic properties is included
  - Uncertainty associated with variations in water chemistry is included
- No solubility limit for other radioelements
- Solubility controlling phase(s)
  - PuO_2 (hyd, aged)
  - NpO_2 within the WPs (while reductants exist)
  - Np_2O_5 within the invert
  - Schoepite + Na-boltwoodite (U phases) within co-disposal WPs and invert, within CSNF WPs for igneous scenario
  - Schoepite within CSNF WPs for other scenarios

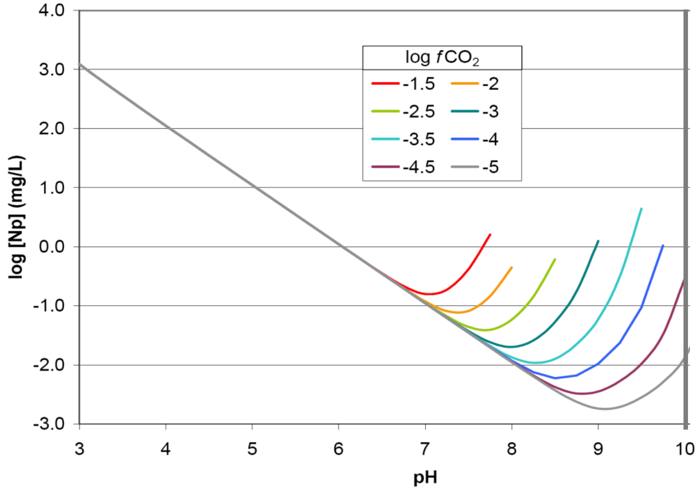
YM Np Solubility Models Considered

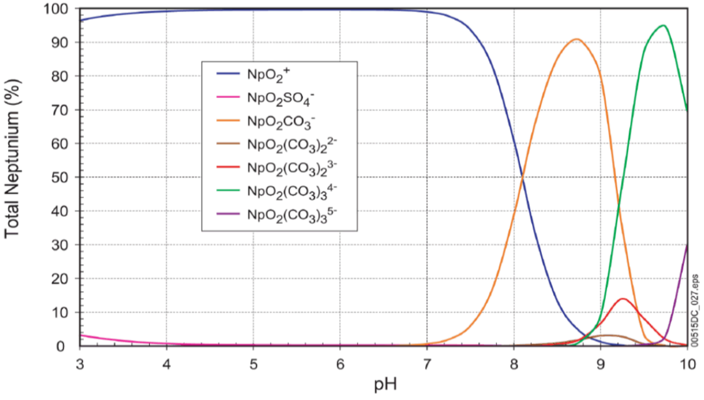
- Pure Phase Models (thermodynamic data – OECD/NEA database)
  - Np_2O_5 – Np(V) oxide (metastable but forms in oversaturation studies)
  - NpO_2 – Np(IV) oxide stable even at atmospheric oxygen fugacity
  - Solution dominated by NpO_2^+ species (reduction reaction for NpO_2)
- Secondary Phase Models
  - Coprecipitation of Np within uranyl alteration phases
  - Expected that NpO_2^+ would substitute for UO_2^{++} (Burns et al., 1997)
    - Coupled substitution for charge balance
  - Proximal alteration phases (e.g., schoepite) do not appear effective

YM Np Solubility Models Considered

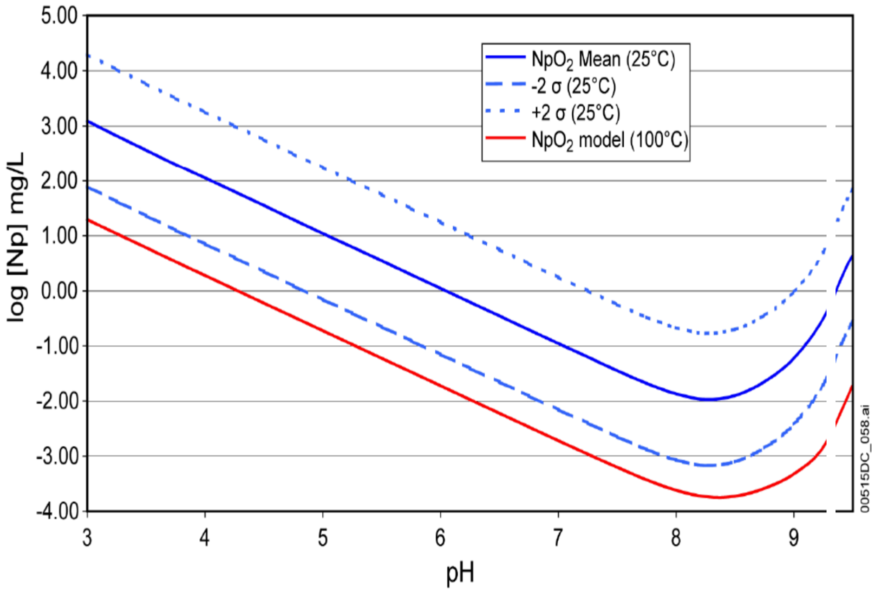
- Application to Expected System
  - Use NpO_2 within the Package
    - Kinetic barriers for reduction not expected to be issue
      - Numerous, massive reductants within package (waste form, steels)
      - Np expected to be Np(IV) within CSNF
      - Gradual increase of dissolved Np concentration from *undersaturation*
    - Once reductants are exhausted switch to Np_2O_5 inside the package
  - Use Np_2O_5 outside the package in the Invert
    - Hedge against uncertain precipitation kinetics of NpO_2

NpO_2 Solubility Model





- Based on thermodynamic data for solid and aqueous species
    - OECD/NEA database, Lemire et al., 2001
- Applied at 25°C to bound retrograde thermal behavior (based on extrapolation of aqueous data)
- Data uncertainty propagated



Additional Support for YM NpO_2 Model

- NpO_2 Formed Directly by Humid Alteration of Np-doped U_3O_8 at Elevated Oxidation Conditions
  (Finch, 2002)

  ~3 weeks at 150°C

  ~16 weeks at 90°C, with Np_2O_5 (less overall reaction progress of U_3O_8 alteration at this temperature)

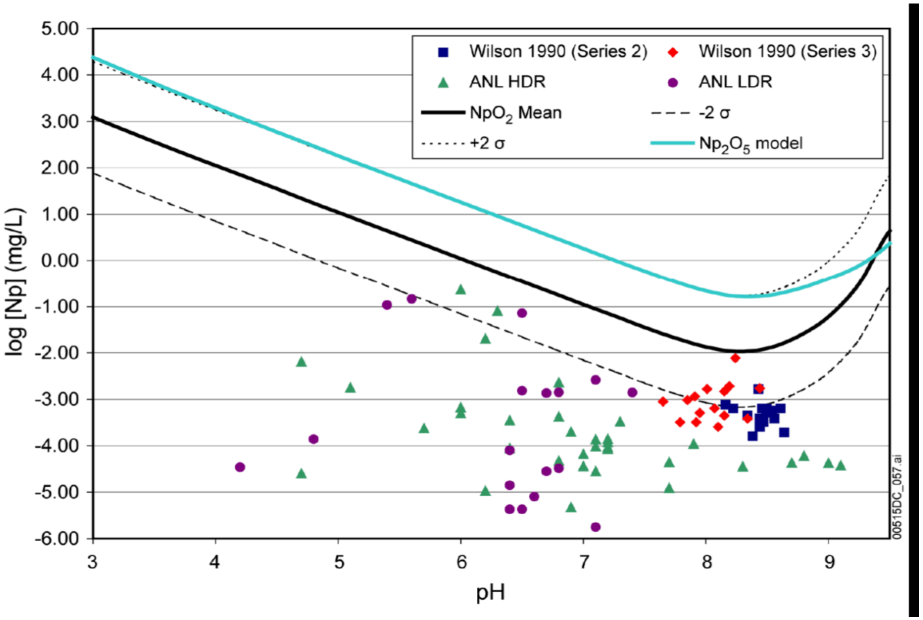
- Direct Precipitation of NpO_2 from Solution
  (Roberts et al., 2003)

  ~3 Months at 200°C

- Comparison to Spent Fuel Dissolution Studies (i.e., more complex systems)

Comparison of Spent Fuel Drip and Batch Dissolution Test Data and YM Solubility Models

- Pure phase NpO_2 model (at 25°C) is consistently higher than observations from spent fuel laboratory tests (at 25 and ~85-90°C)
  - Most recent Argonne National Laboratory (ANL) data (Fall 2004) represent 9 years of drip tests
- Spent fuel observations indicate that reasonably long time (years) should be available for precipitation/formation of NpO_2



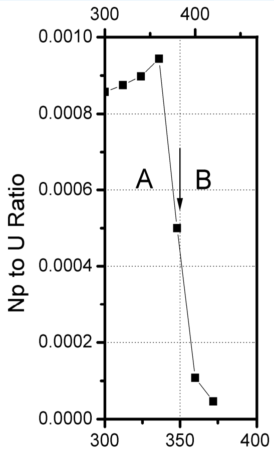
Data Source: Wilson 1990a [DIRS 100949]; Wilson 1990b [DIRS 100793] (Series 2 and Series 3 tests, respectively); and CRWMS M&O 2000 [DIRS 131861]; CRWMS M&O 2000 [DIRS 153105]; and Thomas, 2004 [DIRS 163048] for ANL high-drip and low-drip tests.

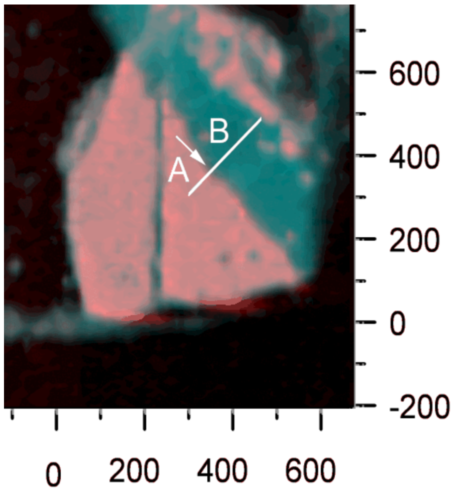
- Several recent studies indicate Np retention in uranyl solids – although mechanism is uncertain
  - Burns et al., (2004), Buck et al., (2004), Friese et al., (2004), Douglas et al., (2005)
- Additional studies on Np in CSNF and NpO_2 formation kinetics

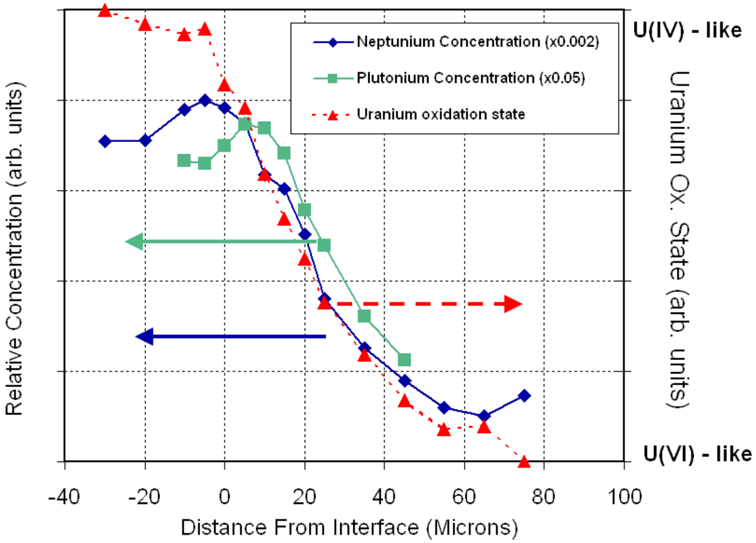
Additional YM Studies for Neptunium

- Detailed Characterization of Np Content in Spent Fuel and Secondary Solid Phases from Drip Tests
  - Oriented core of alteration layers over spent fuel
- Studies of NpO_2 Precipitation Kinetics from Simple Aqueous Solutions
  - Various temperatures investigated to develop rate relation as function of temperature
    - Can be used to estimate lower temperature rates that take longer to evaluate
  - Precipitation not catalyzed by reductants (i.e., direct)
  - Precipitation in presence of reductants
- Could allow application outside the package if direct precipitation rates are high enough at lower temperatures

Np and Pu Across YM CSNF Corrosion Front



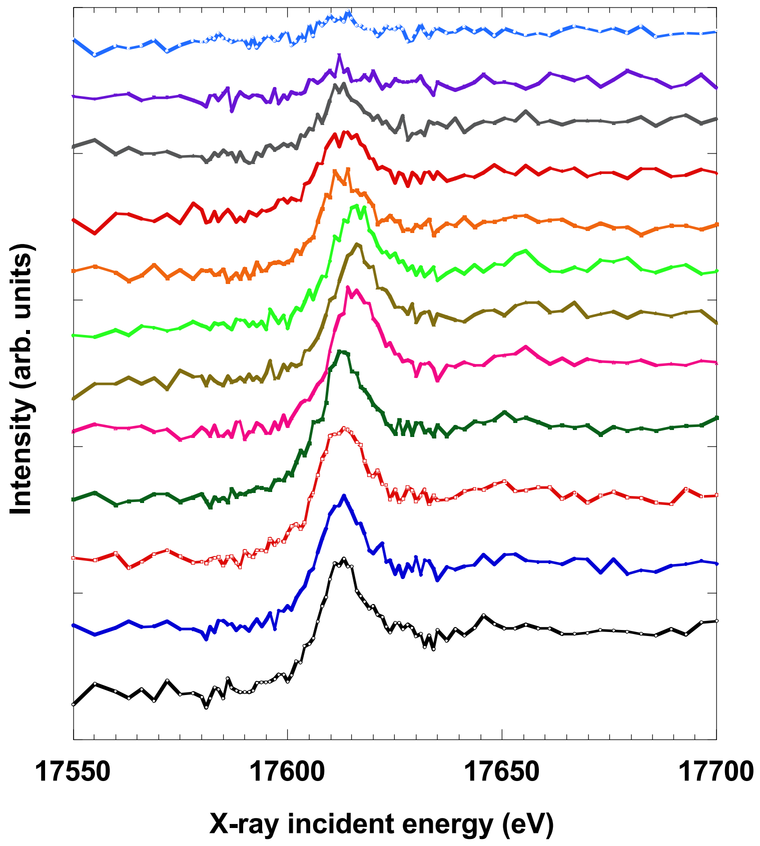


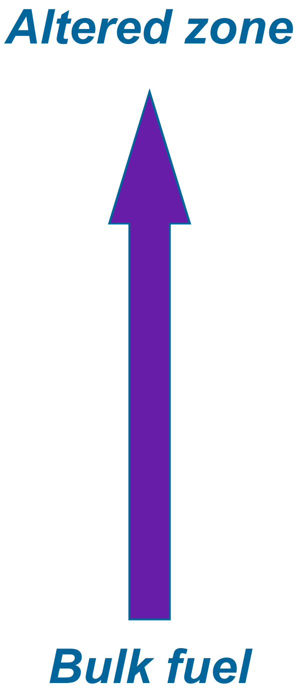


- X-ray Absorption Spectroscopy (ANL) shows Np(IV) in fuel matrix
- Np/U ratio decreases in ~50µm mixed-valence U(IV)/U(VI) region adjacent to the corrosion front
- Np and Pu peak near the surface of the corroded spent fuel
- Results provide evidence that redox conditions at and near the corroding spent fuel surface control Np behavior
- Np may remain within fuel while the alteration occurs (possible solid solution of NpO_2 within UO_2)

Np X-ray Absorption Spectra (ANL) across YM CSNF Corrosion Front

- **Spectral features consistent with Np (IV)**



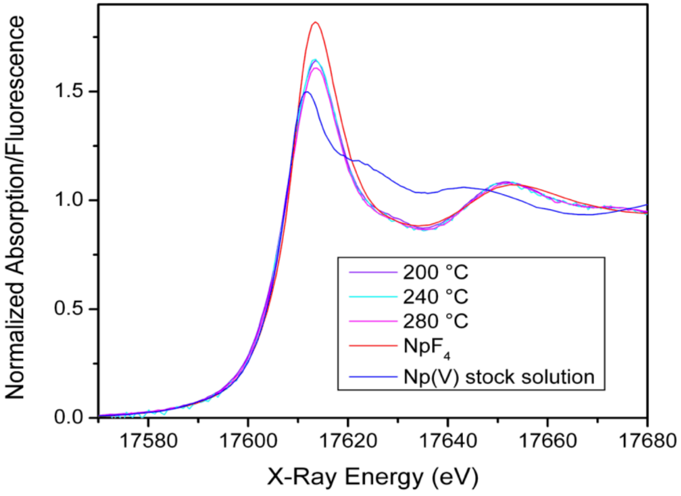


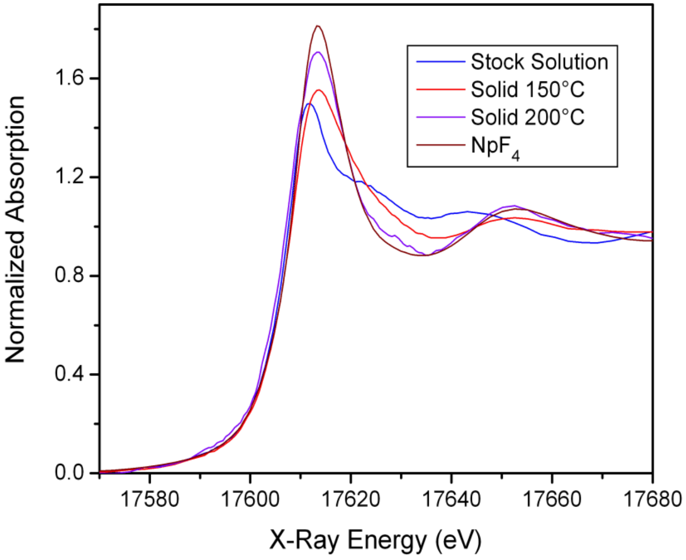
YM Np Precipitation Kinetics Tests (ANL)

125 mL Parr high-pressure vessel with quartz liner

23 mL Parr digestion bomb with a Teflon cup

YM Np Precipitation from Np(V) Solution (ANL)





- Np(V) solutions at pH = 6.5
  - 150, 200, 240, and 280°C
- Note (Roberts et al. 2003) @ 200°C

$NpO_2^+(aq) + 0.5H_2O = NpO_2(s) + H^+(aq) + 0.25O_2(g)$

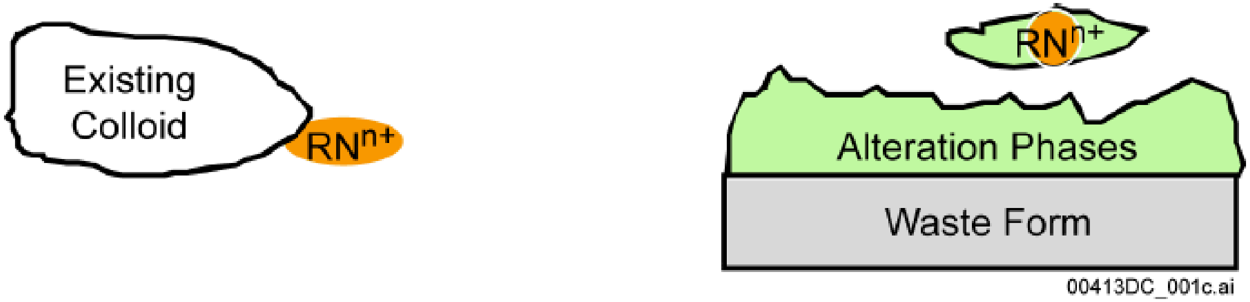
- X-ray absorption spectra of Np solids indicates that solids isolated after 21 days are Np(IV) precipitates (200, 240, and 280°C)
- Mixed valence Np(IV)/Np(V) precipitate observed at 150°C (XAS)
- Direct precipitation
  - Temperature-dependent rate for development of Np(IV) solids
- Catalyzed reduction precipitation occurs at 150°C within weeks

Colloid Models:
A Yucca Mountain (YM) Example

Colloid Models – YM Implementation

- Coloids generated inside the waste package from
  - degradation of the waste forms
    - smectite clay
    - a mixed actinide-bearing rare earth-zirconium oxide
    - Uranophane {$Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$}
  - corrosion of the waste package materials
    - iron oxyhydroxide
- Colloids produced from the steel components in the repository drifts
  - iron oxyhydroxide
- Colloids present in natural waters in the vicinity of Yucca Mountain
  - smectite clay
- Stability of modeled colloids
  - Theoretical calculations and laboratory data used to determine the with Functions of ionic strength and pH
- Attachment of radionuclides to the colloids considered
  - Reversible sorption
  - Irreversible attachment
    - rapid attachment
    - slow dettachment (kinetic)
  - Embedded radionuclides

YM Conceptual Colloid Representation



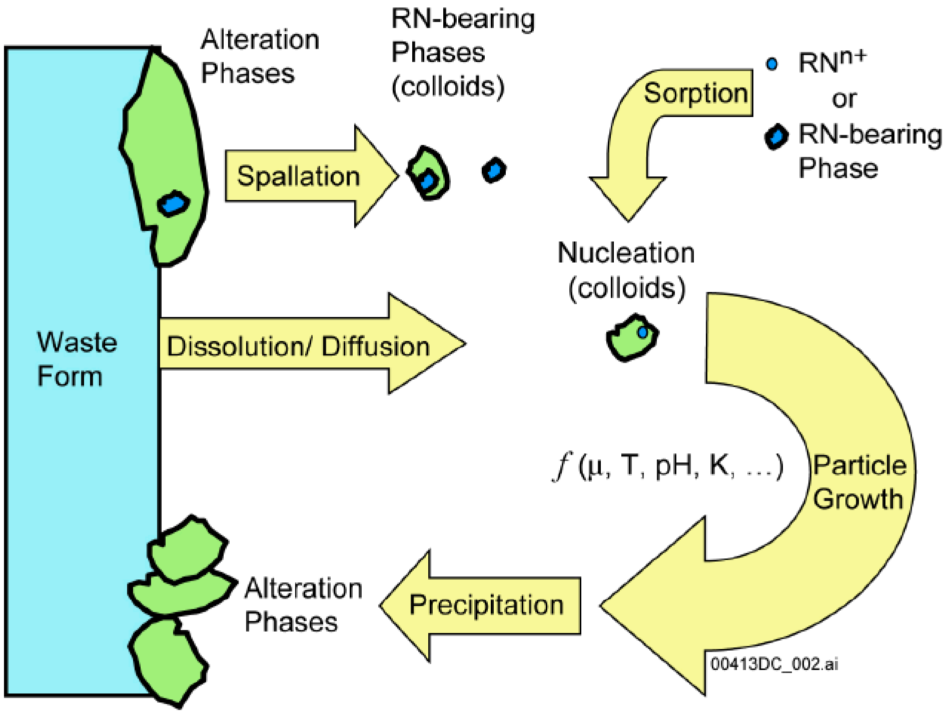
(a) (b)

Source: Adapted from CRWMS M&O 2001 [DIRS 154071], Figure 1.

NOTE: The two major types of modeled radionuclide-bearing colloids are depicted: (a) pseudocolloids (clay or iron oxide) and (b) waste form colloids. The radionuclide (RN^{n+}) associated with the waste form colloids and pseudocolloids can be an ionic species, a real colloid, or a discrete radionuclide-bearing phase.

Figure 6-1. Radionuclide-Bearing Colloid Types

YM Waste Form Colloids and Destabilization

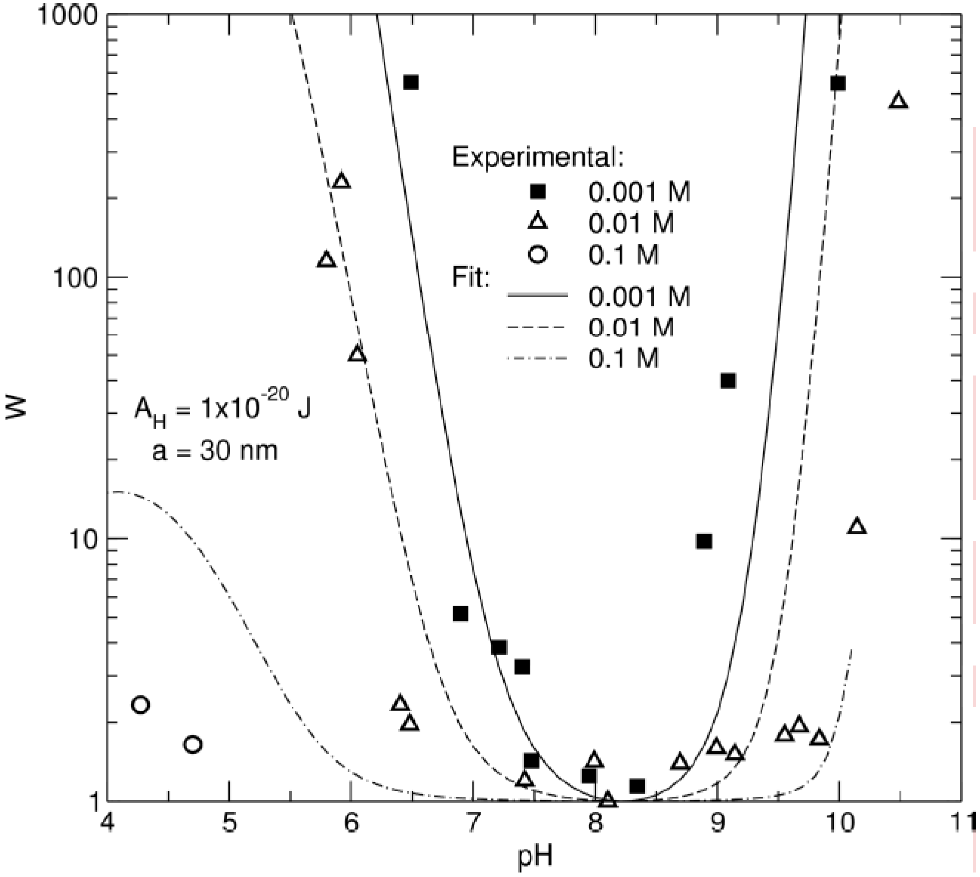


Source: Modified from CRWMS M&O 2001 [DIRS 154071], Figure 2.

NOTE: RN = radionuclide. Schematic of colloid formation from waste-form corrosion whereby several processes are represented: (1) spallation of radionuclide bearing alteration phases from the waste form that are within the colloidal size range, and (2) nucleation of colloids from ions dissolved from the waste form and sorption of ionic radionuclide species or radionuclide-bearing phases. Particle growth occurs by precipitation on nuclei and is controlled by factors such as ionic strength, temperature, pH, and solubility. When particle diameters exceed 1 μm or solution chemistry destabilizes the colloids, deposition or coagulation and gravitational settling of radionuclide-bearing alteration phases occurs.

Figure 6-2. Schematic of Colloid Formation from Waste-Form Corrosion

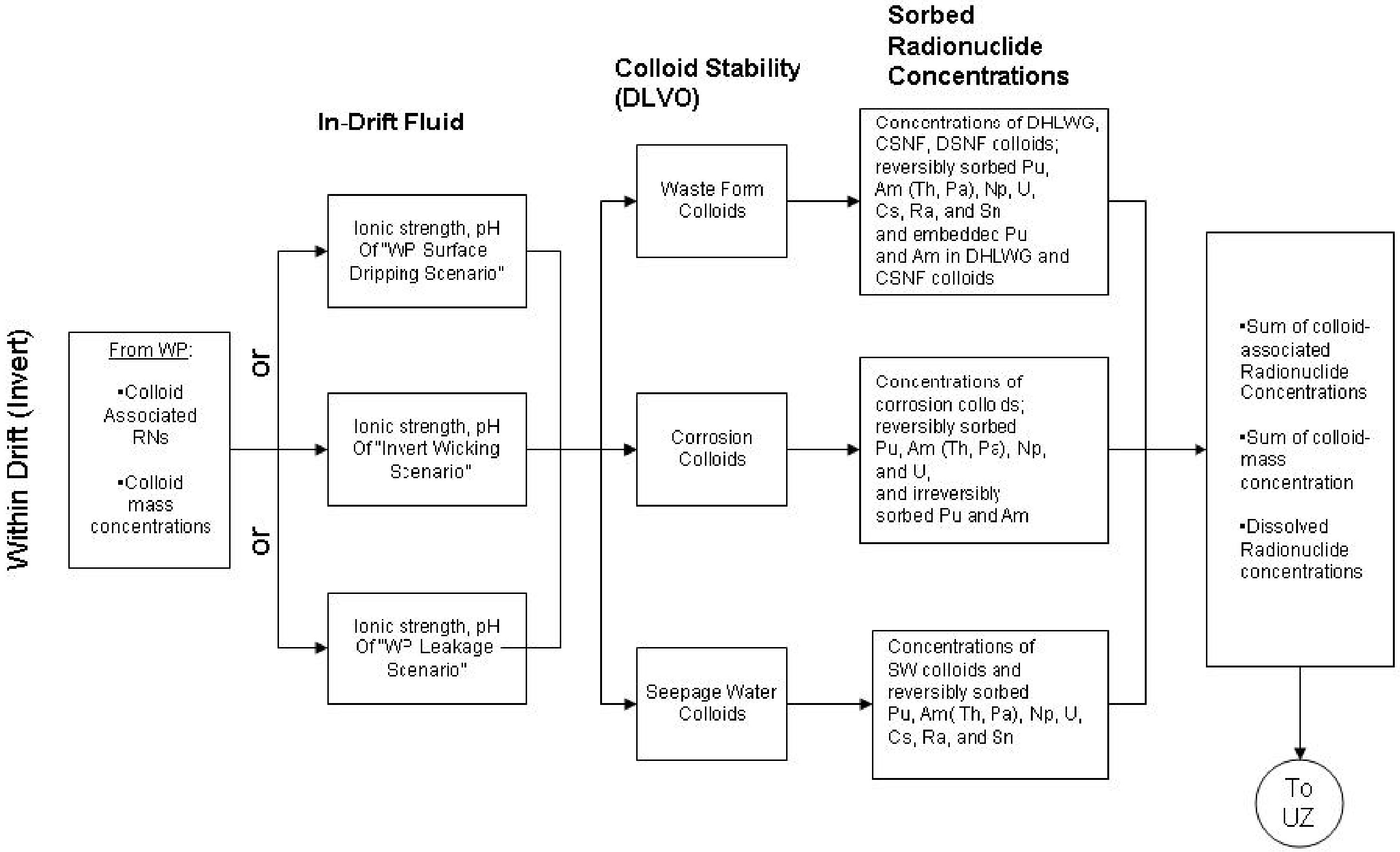
YM Colloid Stability Constraints



Source: Output DTN: MO0705CSIONSTH.000 and Bitea et al. 2003 [DIRS 174504], Figure 6, p. 61.

Figure 6-3. Stability Ratio (*W*) for ZrO_2 Colloids, Showing Experimental Data from Bitea et al. (2003 [DIRS 174504]) with Calculation Fit Using Parameters in Table 6-2

YM Colloid Model Summary



Within Drift (Invert)

From WP:

- Colloid Associated RNs
- Colloid mass concentrations

or

or

In-Drift Fluid

Ionic strength, pH Of "WP Surface Dripping Scenario"

Ionic strength, pH Of "Invert Wicking Scenario"

Ionic strength, pH Of "WP Leakage Scenario"

Colloid Stability (DLVO)

Waste Form Colloids

Corrosion Colloids

Seepage Water Colloids

Sorbed Radionuclide Concentrations

Concentrations of DHLWG, CSNF, DSNF colloids; reversibly sorbed Pu, Am (Th, Pa), Np, U, Cs, Ra, and Sn and embedded Pu and Am in DHLWG and CSNF colloids

Concentrations of corrosion colloids; reversibly sorbed Pu, Am (Th, Pa), Np, and U, and irreversibly sorbed Pu and Am

Concentrations of SW colloids and reversibly sorbed Pu, Am(Th, Pa), Np, U, Cs, Ra, and Sn

- Sum of colloid-associated Radionuclide Concentrations
- Sum of colloid-mass concentration
- Dissolved Radionuclide concentrations

To UZ

NOTE: WP = waste package; RN = radionuclide; SW = seepage water; HLW = high-level waste.

Figure 6-27. Processes within the Drift (invert)

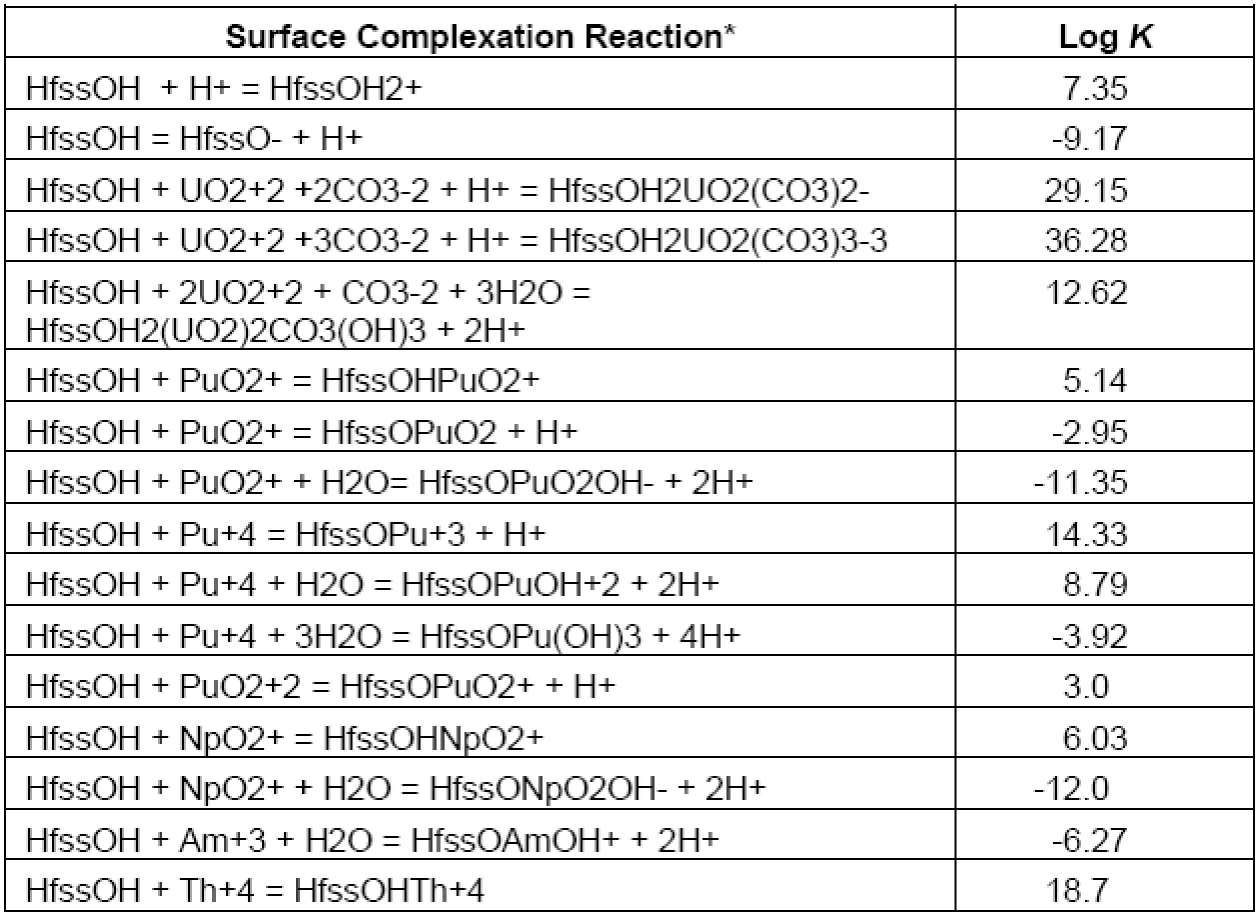
Engineered Barrier System Transport Model: A Yucca Mountain (YM) Example

YM Surface Complexation Model for Competitive Sorption

- PHREEQC
  - Equilibrium solution concentrations for each element sampled over solubility range (100 realizations)
    - U, Pu, Np, Th, and Am
    - Ni also considered for competition
- Surface complexation equilibria calculated using
  - Variable iron oxyhydroxide surface properties sampled (50 realizations) for each constant solution composition
- Output of the surface complexation modeling includes
  - total aqueous concentration and the
  - total sorbed concentration for each of the six elements,
  - the equilibrium pH.
- Results analyzed to generate sorption coefficients that account for the competition for surface sites among these elements

Inputs for YM Surface Complexation Model

Table 6.5-12. Surface Complexation Reactions and log *K* Values



Surface Complexation Reaction*	**Log *K***
HfssOH + H+ = HfssOH2+	7.35
HfssOH = HfssO- + H+	-9.17
HfssOH + UO2+2 +2CO3-2 + H+ = HfssOH2UO2(CO3)2-	29.15
HfssOH + UO2+2 +3CO3-2 + H+ = HfssOH2UO2(CO3)3-3	36.28
HfssOH + 2UO2+2 + CO3-2 + 3H2O = HfssOH2(UO2)2CO3(OH)3 + 2H+	12.62
HfssOH + PuO2+ = HfssOHPuO2+	5.14
HfssOH + PuO2+ = HfssOPuO2 + H+	-2.95
HfssOH + PuO2+ + H2O= HfssOPuO2OH- + 2H+	-11.35
HfssOH + Pu+4 = HfssOPu+3 + H+	14.33
HfssOH + Pu+4 + H2O = HfssOPuOH+2 + 2H+	8.79
HfssOH + Pu+4 + 3H2O = HfssOPu(OH)3 + 4H+	-3.92
HfssOH + PuO2+2 = HfssOPuO2+ + H+	3.0
HfssOH + NpO2+ = HfssOHNpO2+	6.03
HfssOH + NpO2+ + H2O = HfssONpO2OH- + 2H+	-12.0
HfssOH + Am+3 + H2O = HfssOAmOH+ + 2H+	-6.27
HfssOH + Th+4 = HfssOHTh+4	18.7

Inputs for YM Surface Complexation Model

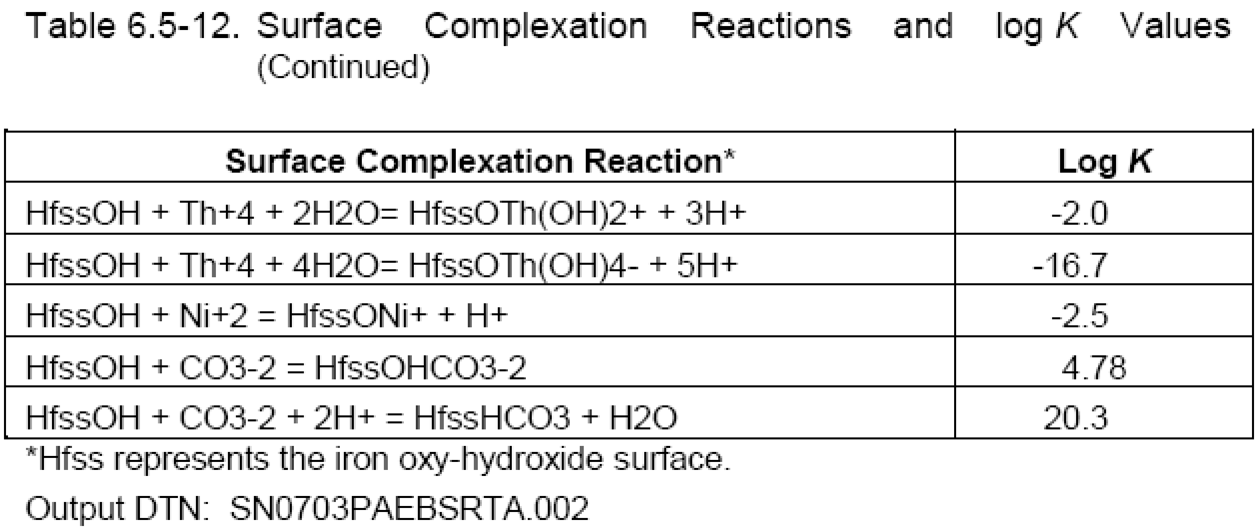


Table 6.5-12. Surface Complexation Reactions and log *K* Values (Continued)

Surface Complexation Reaction*	Log *K*
HfssOH + Th+4 + 2H2O= HfssOTh(OH)2+ + 3H+	-2.0
HfssOH + Th+4 + 4H2O= HfssOTh(OH)4- + 5H+	-16.7
HfssOH + Ni+2 = HfssONi+ + H+	-2.5
HfssOH + CO3-2 = HfssOHCO3-2	4.78
HfssOH + CO3-2 + 2H+ = HfssHCO3 + H2O	20.3

*Hfss represents the iron oxy-hydroxide surface.

Output DTN: SN0703PAEBSRTA.002

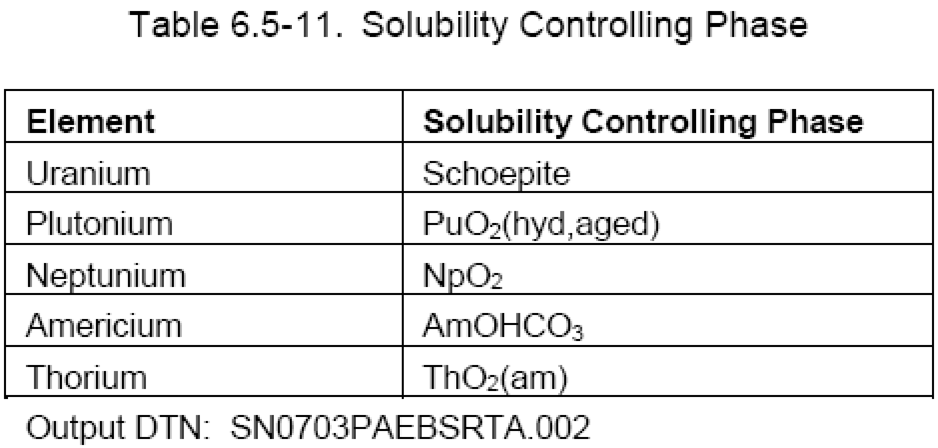
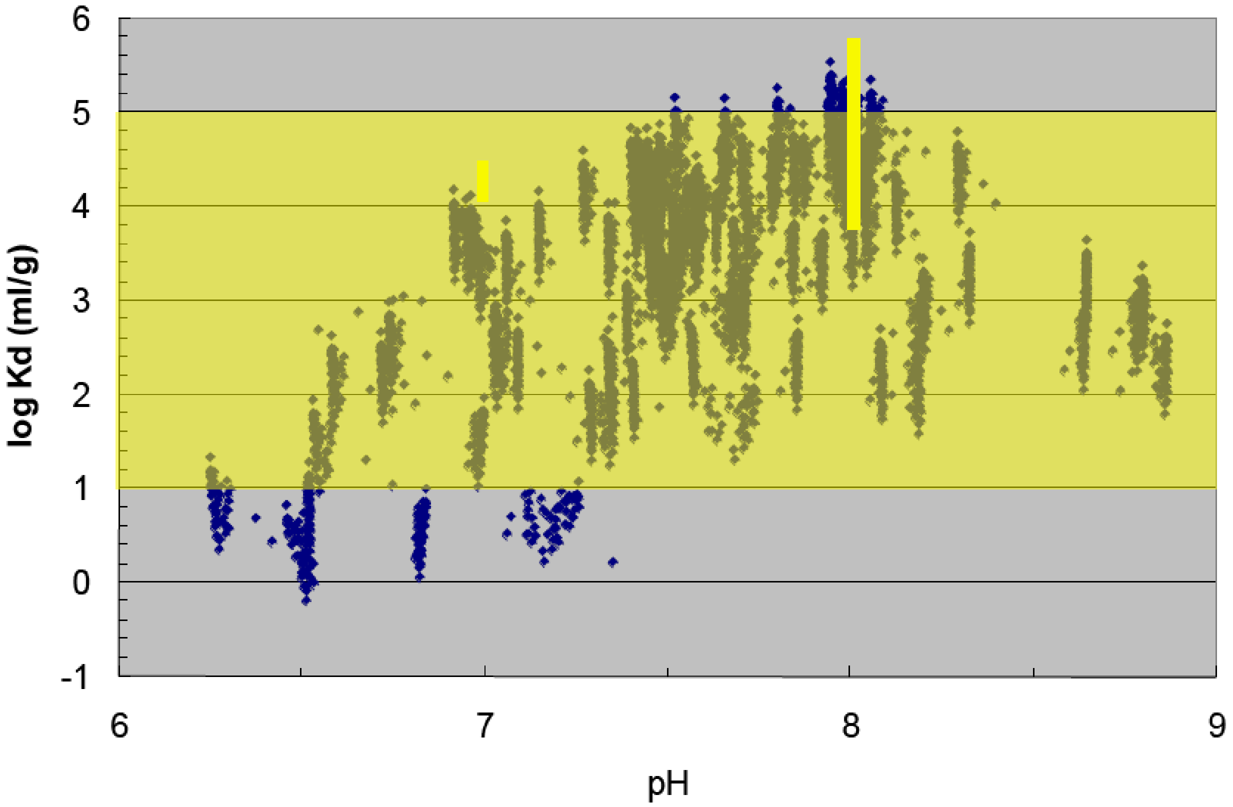


Table 6.5-11. Solubility Controlling Phase

Element	Solubility Controlling Phase
Uranium	Schoepite
Plutonium	PuO_2(hyd,aged)
Neptunium	NpO_2
Americium	$AmOHCO_3$
Thorium	ThO_2(am)

Output DTN: SN0703PAEBSRTA.002

Evaluation of YM Results for Kd of Pu



Sources: Yellow shaded area, EPA 1999 [DIRS 170376]; Yellow bars, Lu et al. 2000 [DIRS 166315] and Sanchez et al. [DIRS 107213]; Blue diamonds, DTN: SN0703PAEBSRTA.002 [DIRS 186557], Excel spreadsheet *Surf_Complx_Validation_figs_REV01.xlsx*, worksheet "Kd-Pu_pH"

NOTE: The yellow bar at pH 8 is the range of Pu K_ds measured on hematite colloids by Lu et al. (2000 [DIRS 166315]); the yellow bar at pH 7 shows estimated Pu K_ds from Sanchez et al. (1985 [DIRS 107213]).

Figure 7.2-12[a]. EPA Pu Soil K_ds and C-SCM Iron Oxide K_ds

Technical Bases for YM Abstractions

- Cladding failure assumed for baseline approach
  - Alternative cladding failure models for the YM performance margin analysis (PMA) were derived from available data on failures during reactor operation
- WF degradation rate models derived from available literature and experimental data

CSNF matrix oxidation and oxidative dissolution processes

HLW glass dissolution

- Chemistry and solubilities modeled using geochemical codes that account for equilibrium and major kinetic effects (EQ3/6 and PHREEQC) and a qualified thermodynamic database

YM Treatment of Uncertainty and Variability

- Treatment of uncertainties
  - No cladding credit for compliance case
    - For PMA – initially failed cladding and unbound inventory
      - Propagates uncertainty in the amount of commercial spent nuclear (CSNF) initially available for degradation and radionuclide release and transport
  - In-package chemistry
    - Uncertainty in the pH and ionic strength affects WF degradation rates, colloid stability, and radioelement solubilities
  - WF degradation rates
    - Propagates uncertainty in the rate that the CSNF fuel and high-level radioactive waste (HLW) glass release radionuclides from the waste forms
  - Solubility
    - Propagates uncertainty in the the amount of inventory that can dissolve within the in-package water
- Treatment of variability via independent variable inputs
  - Various waste package types (CSNF, co-disposed)
  - Seepage conditions
  - Temperature, RH, pCO_2

Additional Considerations

- Approach to Equilibrium
  - End state is path independent
  - Kinetic barriers – many paths
- Coupled Processes
  - Thermal/Mechanical (changing state variables, T and P)
  - Hydrologic (flow/transport paths)
- Chemical Environment
  - Radiolysis products
  - Organic constituents
  - Bisulfide (especially in brines)
  - Data limitations

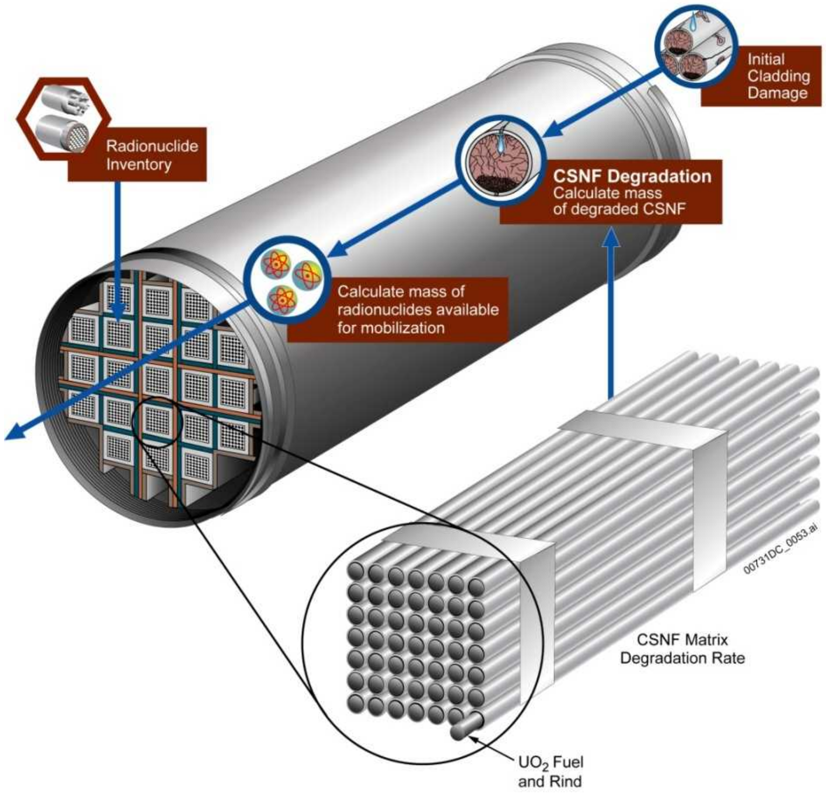
Summary

- Context of Modeling Effort
- Environment Definition - Major Variables
    - Minor variables may play role
- Conceptual Models
    - Kinetic processes
    - Equilibrium constraints
- Fundamental Understanding of Atomic Scale Mechanisms
- Scaling up to Continuum Level Properties
- Experimental Bases
- Inclusion of Uncertainty and Variability

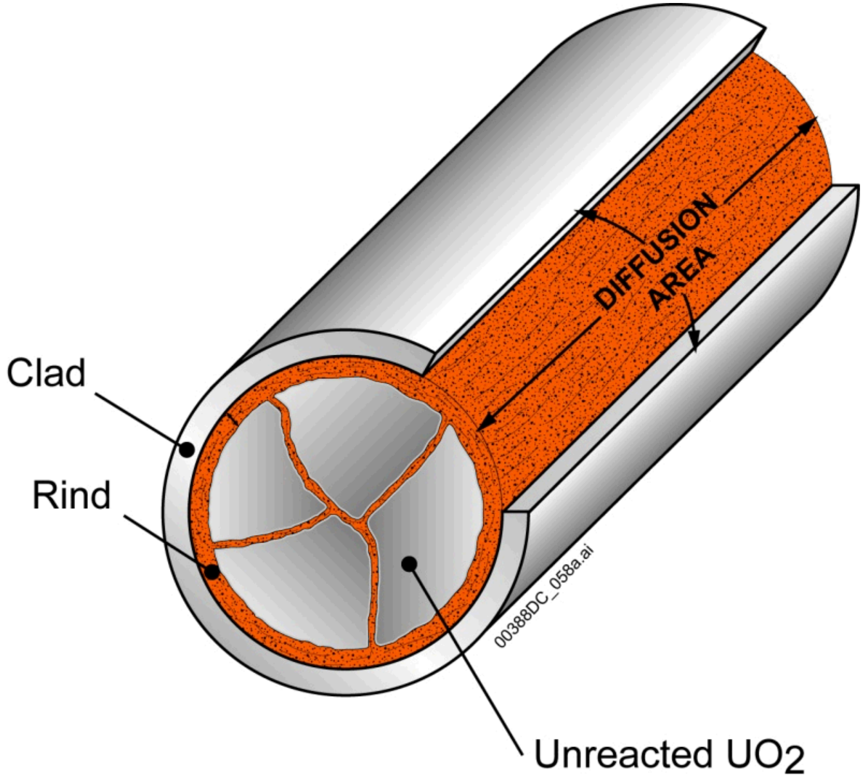
Backup Materials

Cladding—YM Implementation in PMA

- Stainless steel cladding
  - ~1% of the CSNF fuel
  - No performance credit
- Zircaloy cladding – exposed fuel mass depends on cladding failure
  - Performance credit is taken for intact cladding
  - Fuel failed prior to emplacement
    - 0.01% – 1% as-received failures
    - splits along its length in a single model time step
  - Mechanical damage from disruptive events
  - Split cladding exposes fuel mass



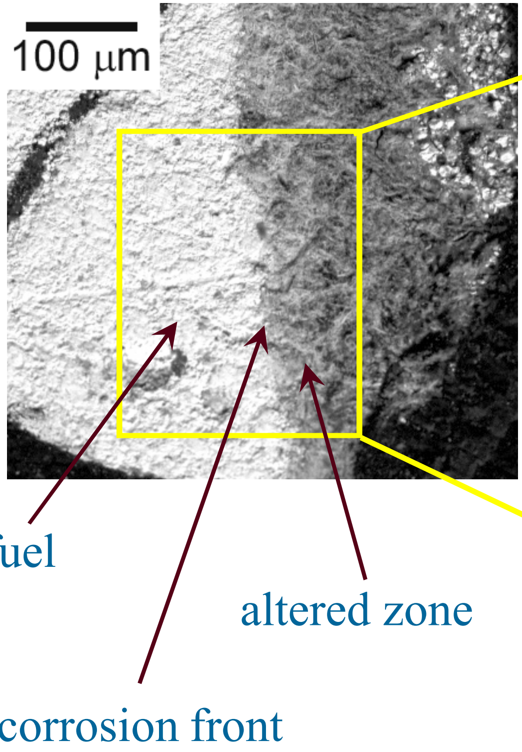
YM Exposed Fuel Mass (PMA Only)

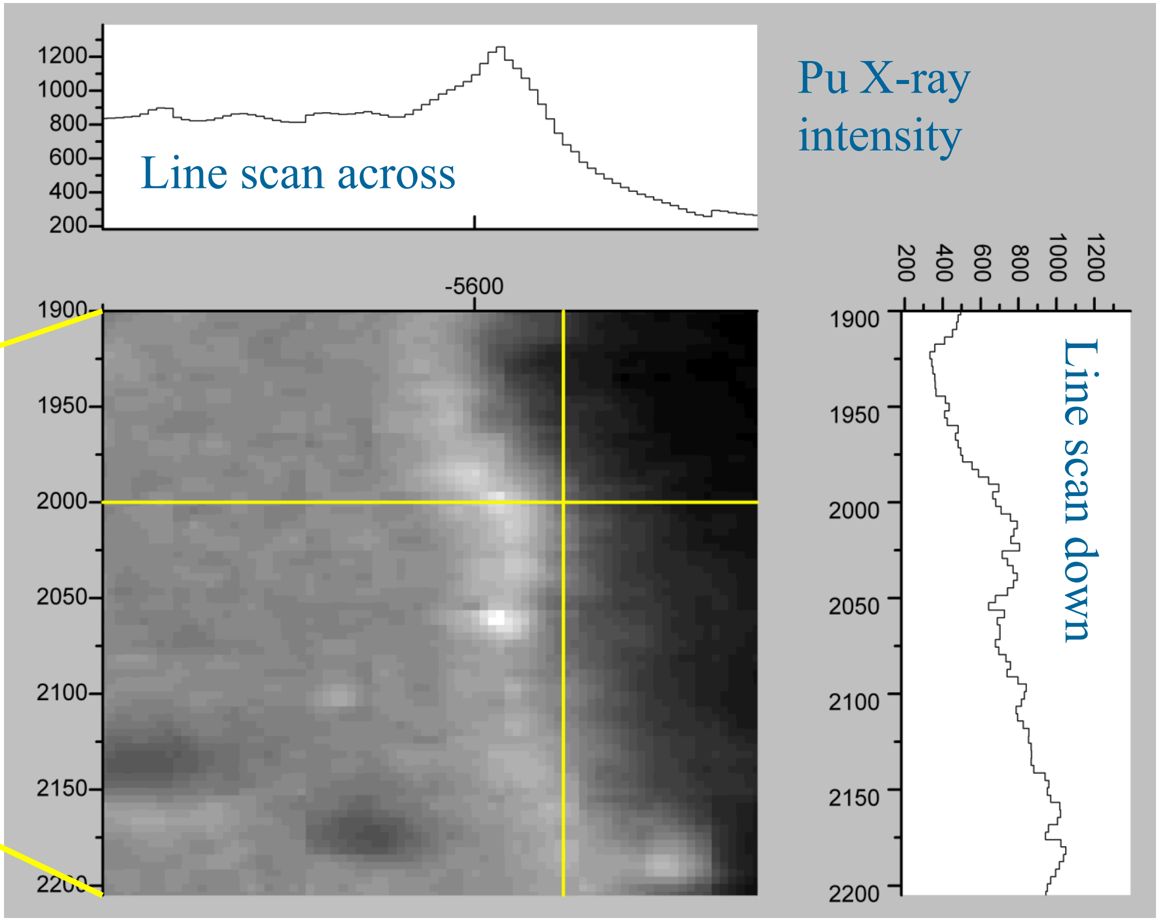


- Mass of exposed fuel depends on clad failure
- Defective clad splits instantaneously after waste package breach
  - Full Mass of fuel in split rod available
- For additional clad failure
  - Split area increases as fuel alters to schoepite
    - (volume increases as rind forms)
    - (Diffusion area increases as split opens)
  - Porosity of rind treated as uncertain
    - (schoepite values)
  - Alteration rind assumed saturated
    - Water volume into which radionuclides dissolve
    - Diffusive transport path
- Radionuclides available to be released
  - Instantaneous gap and grain boundary
  - Matrix degradation UO_2 => schoepite

YM XAS Results Across CSNF Corrosion Front

Scanning Electron Image (SEM) of corroded CSNF





- **Plutonium enrichment shown near CSNF corrosion front (Np also enriched) – (ANL)**

Direct Np-phase Precipitation from Np(V) Solution YM Procedure (ANL)

- Np(V) solution (pH 6.5) was added to Parr vessels.
- Vessels were heated in the ovens at 150, 200, 240 and 280ºC
- The vessels were cooled down and solutions sampled after selected times
- The solution samples were filtered
    - The filtrates were analyzed for dissolved Np concentration and pH
    - The isolated solid phases were analyzed using XAS, SEM, and TEM

OSTI Source Term Targeted Thrust (STTT)

- OCRWM Office of Science and Technology and International (OSTI) Studies for YM
- Critical Processes
  - Kinetics of waste form corrosion
  - Formation of secondary, alteration phases
  - Sorption/reduction on the surfaces of near-field materials
  - Formation and mobility of colloids

OSTI Source Term Targeted Thrust (STTT)

- Four Major Research Areas
  - SNF dissolution mechanisms and rates
  - Formation and properties of U^{6+} secondary phases
  - Waste form - waste package interactions
  - Integration of in-package chemical and physical processes

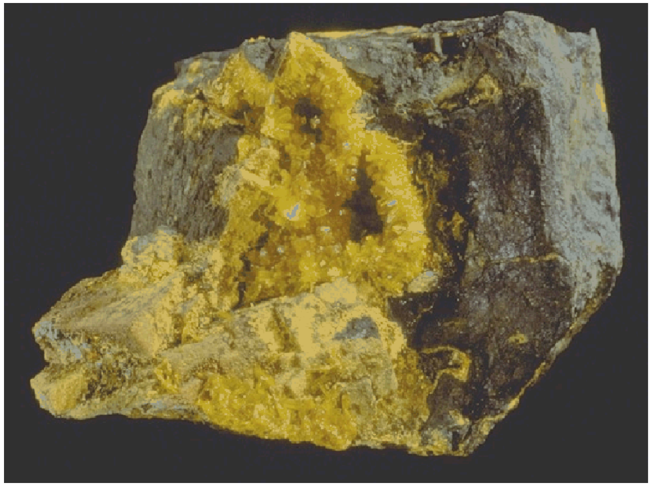
OSTI Source Term Targeted Thrust (STTT)

- Formation and properties of U6+ secondary phases
  - Peter Burns and Jeremy Fine (Notre Dame)
  - Alex Navrotsky (UC - Davis)
  - Rod Ewing and Satoshi Utsunomiya (Un. of Michigan)
  - Udo Becker (Un. of Michigan)
  - Jeff Fortner, Jeremy Kropf and James Cunnane (ANL)
  - Thomas Albrecht-Schmitt (Auburn) & Iain May (Manchester University)

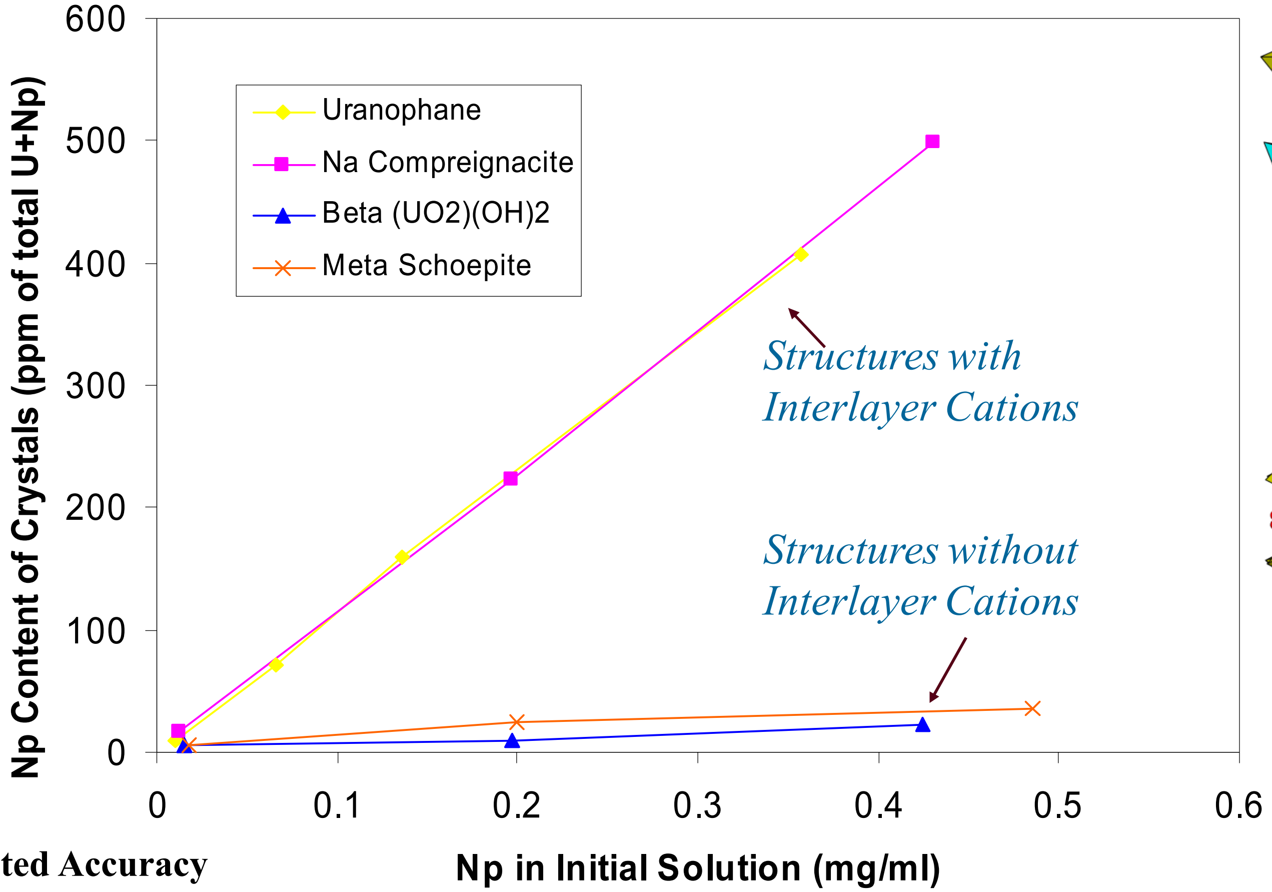
OSTI Incorporation of Np^{5+} in Single Crystals

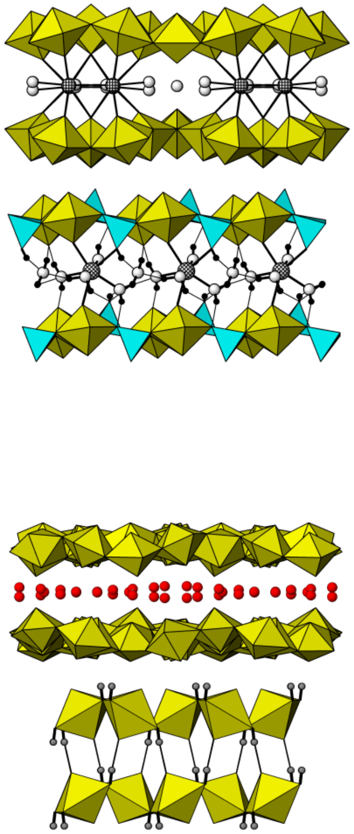
Is Np^{5+} *really* incorporated in uranyl phases?

Challenges: Synthesis of single crystals of uranyl phases
Quantification of ppm Np in uranyl phases



OSTI Np^{5+} Incorporation into Uranyl Phases





Estimated Accuracy

±10% Np

Burns et al. (2004): Radiochimica Acta 92, 151-159

OSTI Single Crystal - Becquerelite

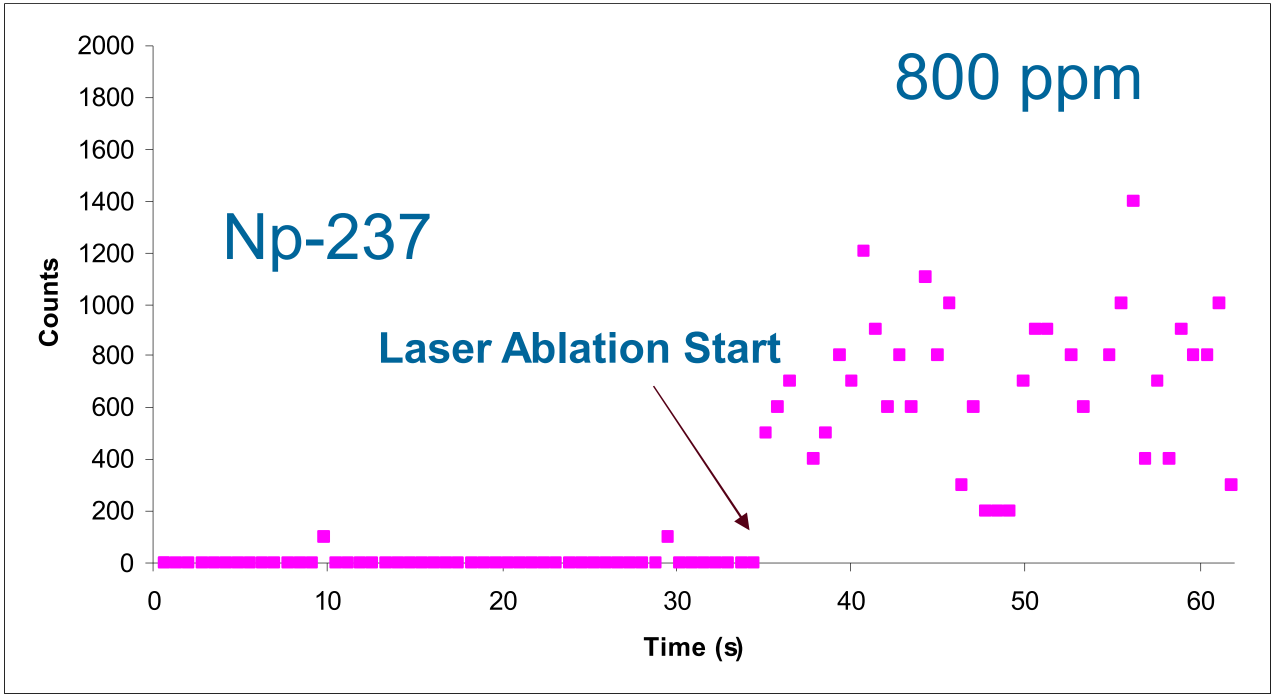
Synthesis: 0.0825 g UO_3, 0.125 g $CaCO_3$, 2.07 g H_2O, 0.0016 g Np^{5+}

Np^{5+} in charge: 725 ppm

Np/U ratio: 0.0016 g/0.0687 g = 0.023

Np in crystal by count ratio: 800 ppm

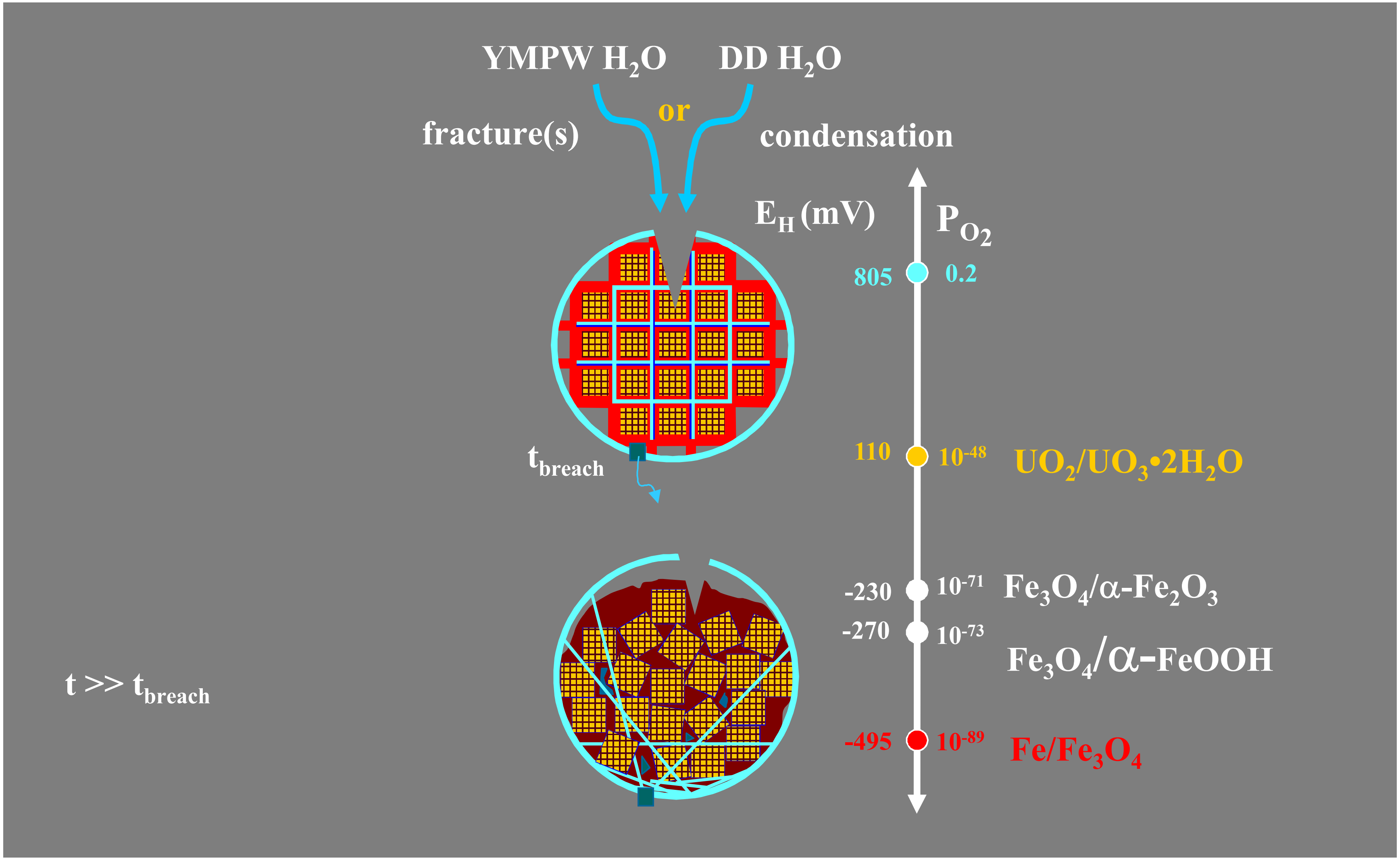
(see Burns and Klingensmith, *Elements*, 2006)



OSTI Source Term Targeted Thrust (STTT)

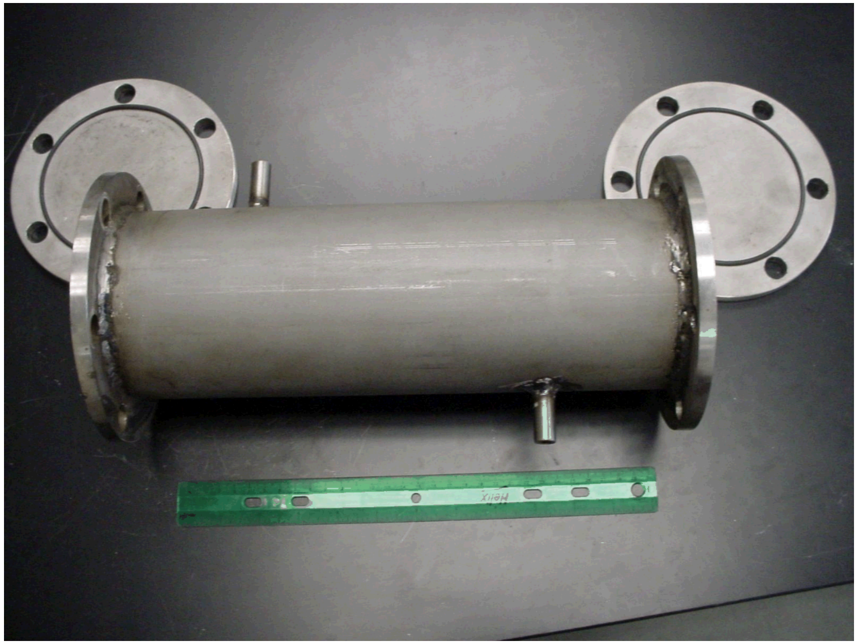
- Waste form – waste package interactions
  Pat Brady and Kate Helean (SNL)
  Sue Clark (WSU); Lawrence Hull (INL)
  David Wesolowski and Donald Palmer (ORNL))
  Udo Becker (Un.of Michigan)
  Jonathan Icenhower, Edgar Buck, Eric Pierce (PNNL)
  Jim Jerden (ANL)
  Ken Krupka and Chris Brown (PNNL)

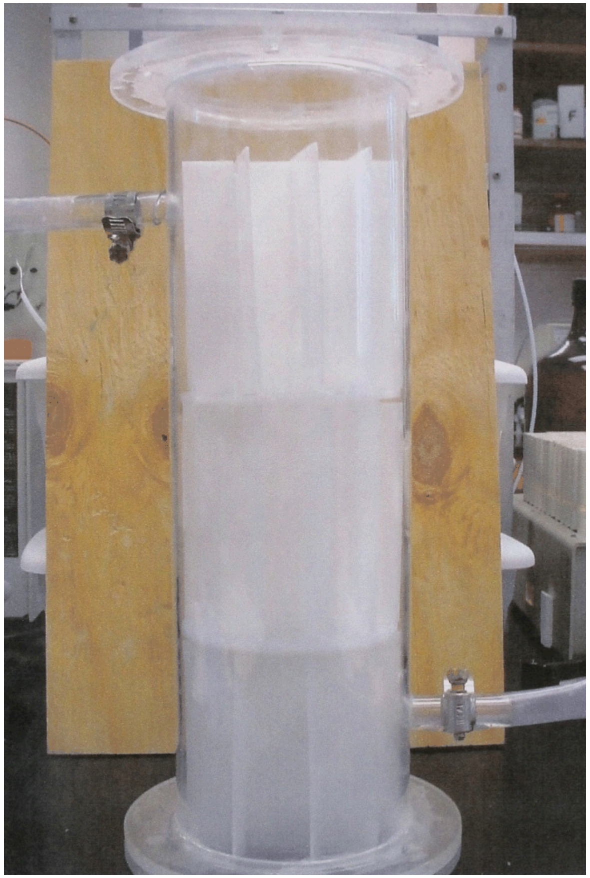
OSTI In-Package Geochemistry



The OSTI Mock-ups

- 1:20 scale mockups at NMT





The OSTI Mock-ups (continued)

- 1:40 scale mockups at SNL and U Mich

- **Constructed using 316SS shell**
- **A516 carbon steel internal components**

- **RT, >90% RH, periodic fluid injections.**

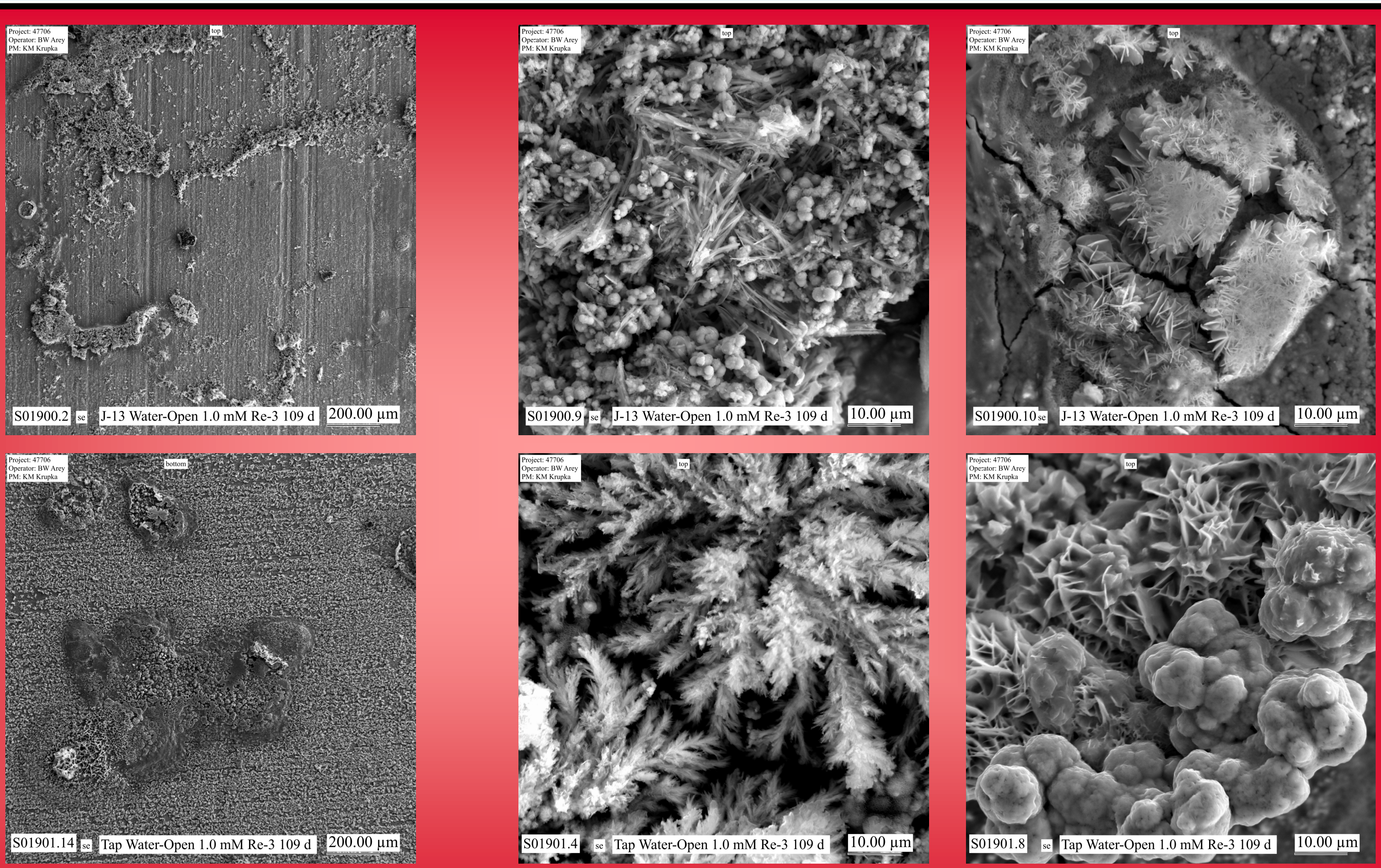
- **Operating mode: “open” and “closed”**

- **U Mich studies: UO_2**

OSTI Corrosion Products

J-13 Solution

Dilute Water

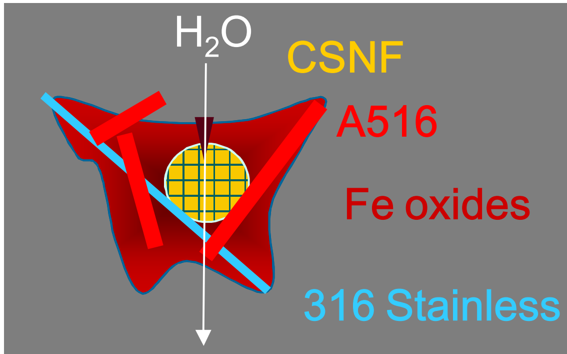


Low Magnification

Higher Magnification

Typical SEM Micrographs Showing Complex Assemblage of Corrosion Products that Formed on A-516 Carbon Steel Coupons Reacted in J-13 Synthetic Groundwater after 109 Days

OSTI Integrated In-Package and Near-Field Chemistry Model



INTEGRATED MODEL

PHREEQC 1-dimensional transport
YMPW input $Ca/HCO_3/Si$ water
Kinetic inputs - R_{A516}
SCM inputs - $Fe(OH)_3$ equilibria
Zone 2 mineralogies and fO_2
Zone 2 Tc uptake/release controls
Zone 3 Np uptake/release controls

'Most likely' RN release mechanisms and rates

zone	mineralogy	P_{O_2}	Major Process
1	UO_2	0.2	Oxidation
2	Magnetite/Green rust /Fe(III)-oxides/Steel	$< 10^{-71}$	Reduction
3	Fe(III)-oxides	0.2	Sorption