U.S. Department of Energy

OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

Mass and Activity of Key Radionuclides Potentially Released From Waste Forms, Waste Packages and Drifts Over Time

Presented to:
Nuclear Waste Technical Review Board

Presented by:
David Sassani,
MTS/Golder Associates Inc.
Rob Howard,
Bechtel-SAIC Company, LLC
Contributions from J. Schreiber, Sandia National Labs

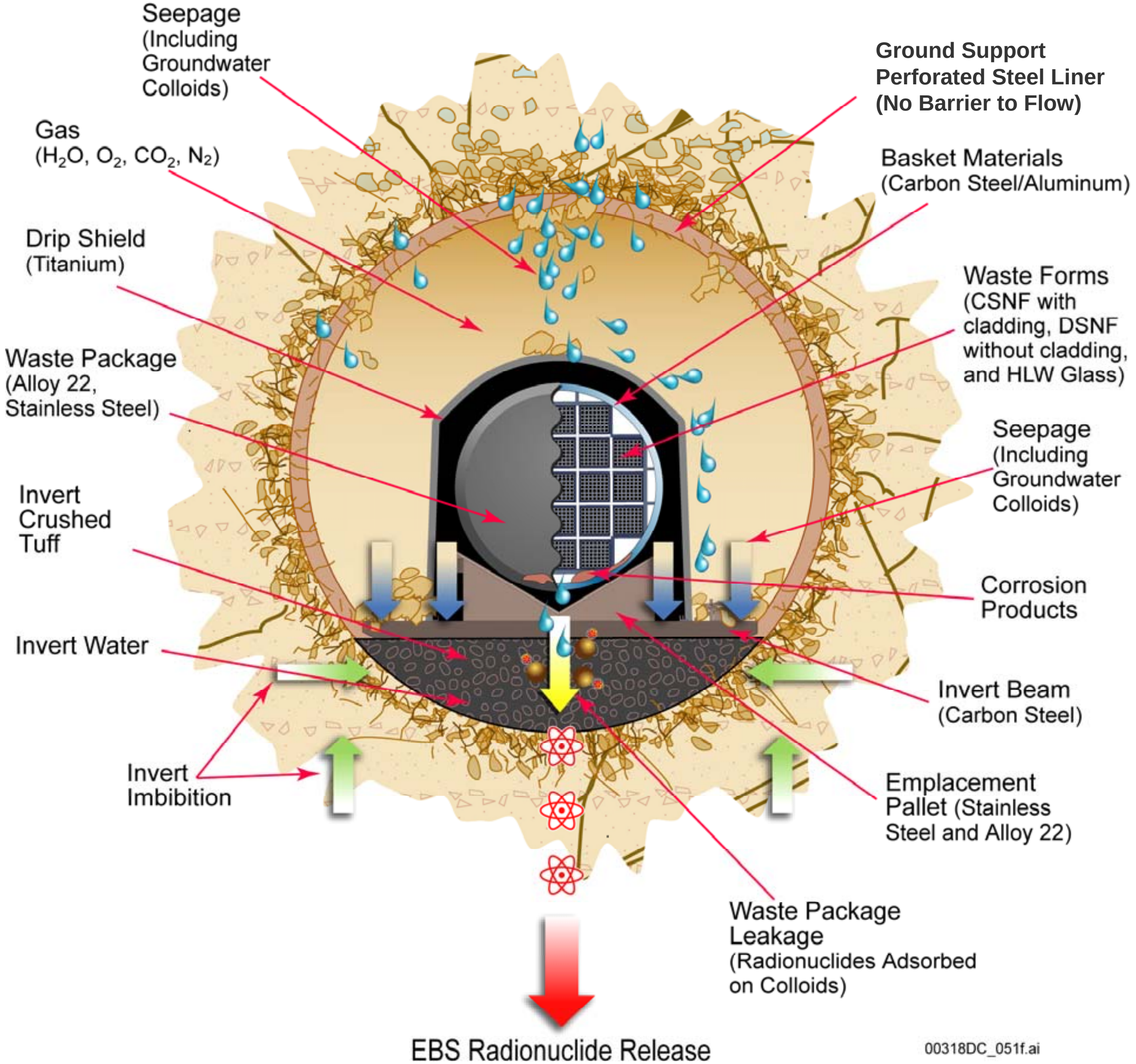
February 01, 2006
Las Vegas, Nevada

Source-Term Overview

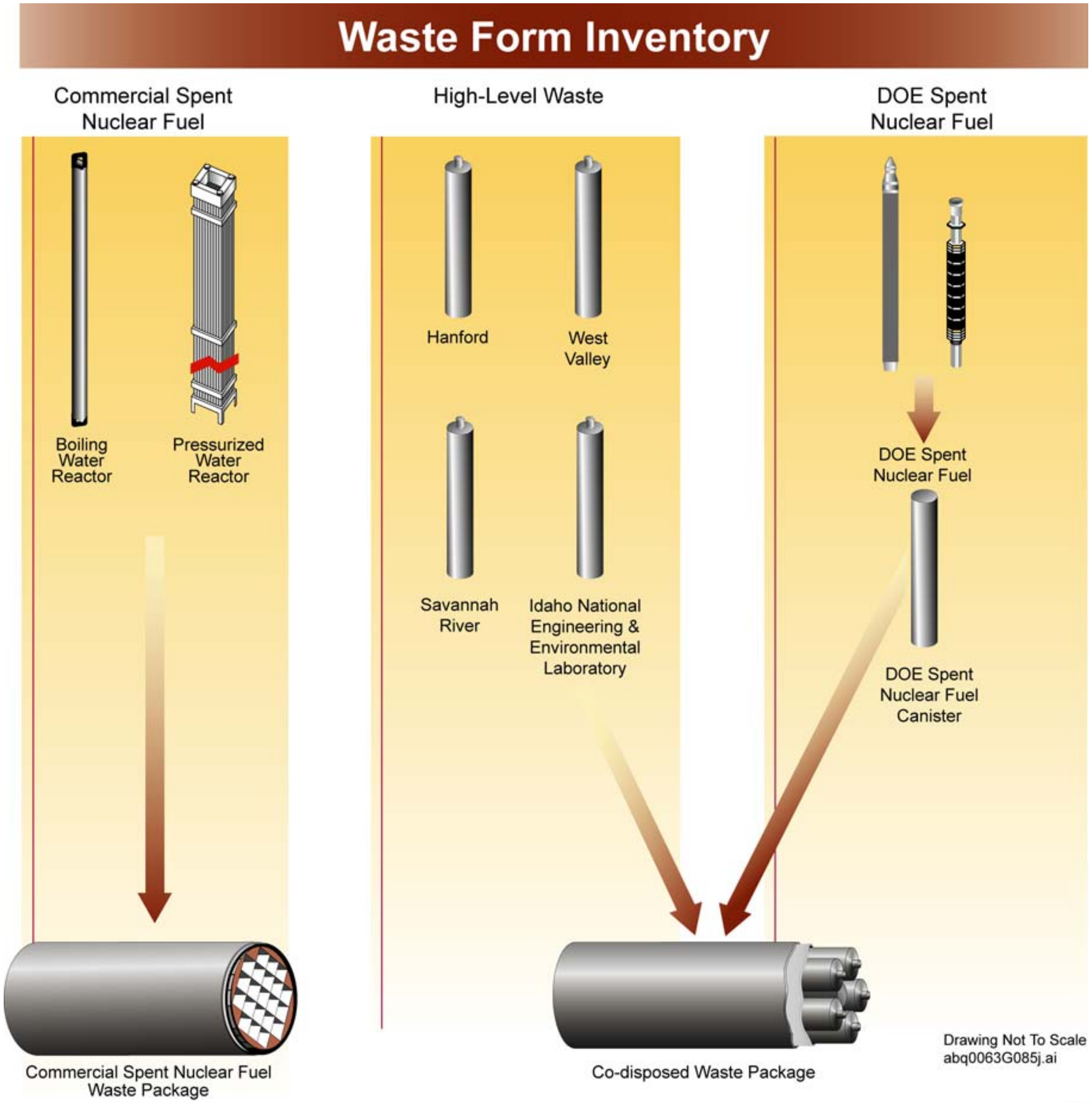
- Source-Term Model Concepts
- Source-Term Model Integration, Descriptions, and Technical Bases
  - Waste Form Degradation Models
  - Solubility-Limited Concentration Models
- Additional Studies
- Science and Technology Source-Term Targeted Thrust Projects

Source-Term Model Concepts

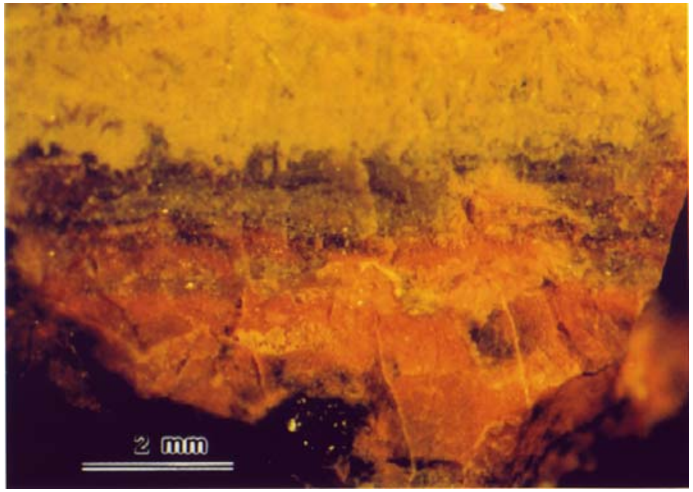
General Engineered Barrier System Design Features and Materials and Natural Processes



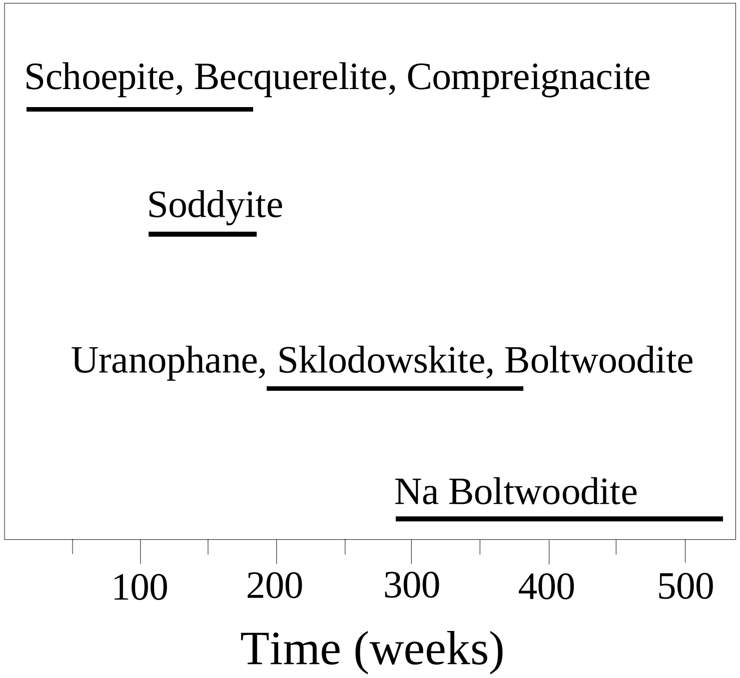
Waste Form Types



UO_{2+x} Corrosion and Uranyl Phase Paragenesis



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

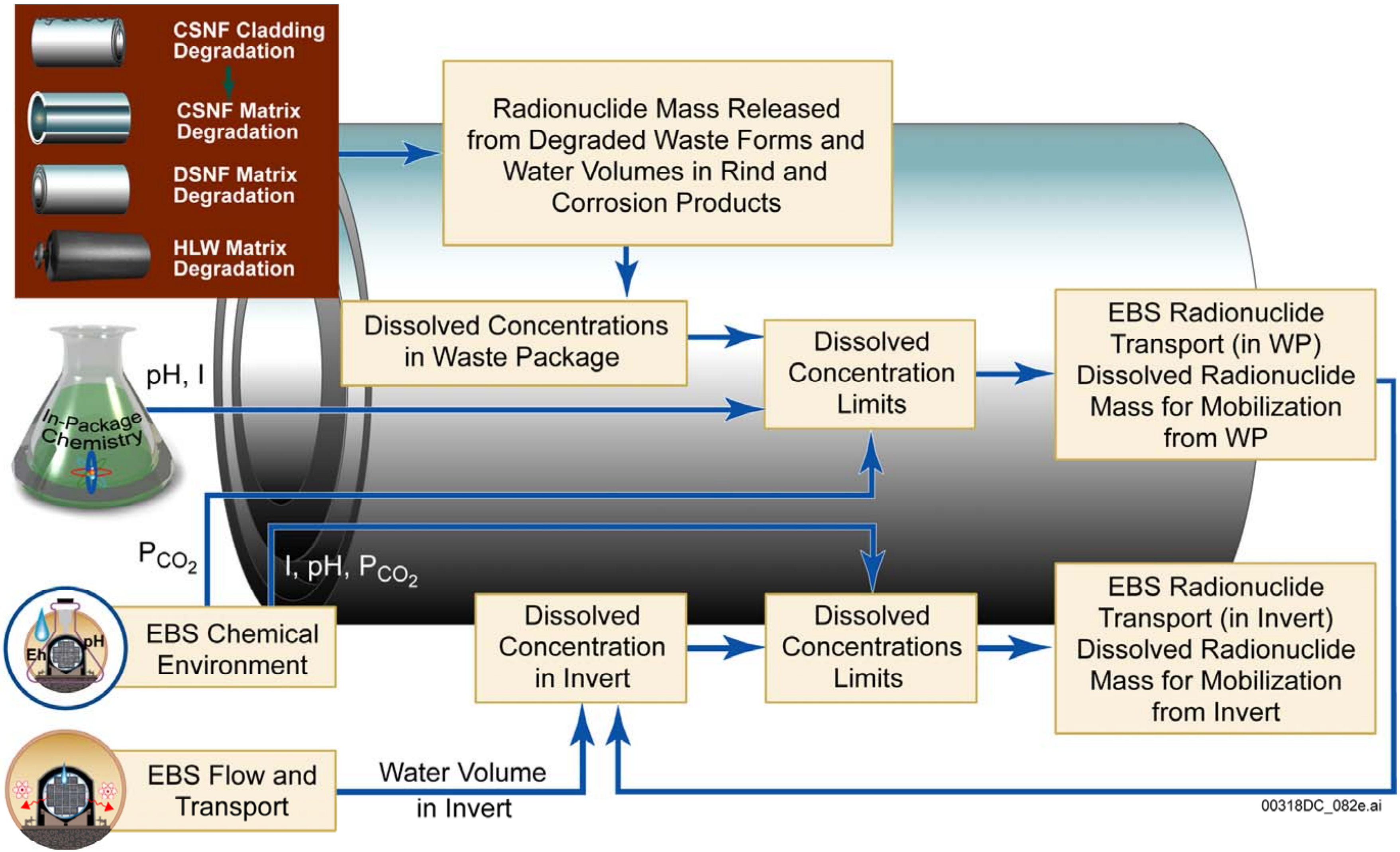


- **Natural uranyl mineral paragenesis is well defined from numerous observations of uraninite alteration in geologic systems**
- **Uranyl mineral relations observed in laboratory testing on UO_2 and spent fuel parallel observations of natural alteration**

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

Source-Term Model Integration, Descriptions, and Technical Bases

Connections within the Source-Term Model



Spent Fuel Degradation Model

- **Gap and Grain Boundary Instantaneous Release Fractions**

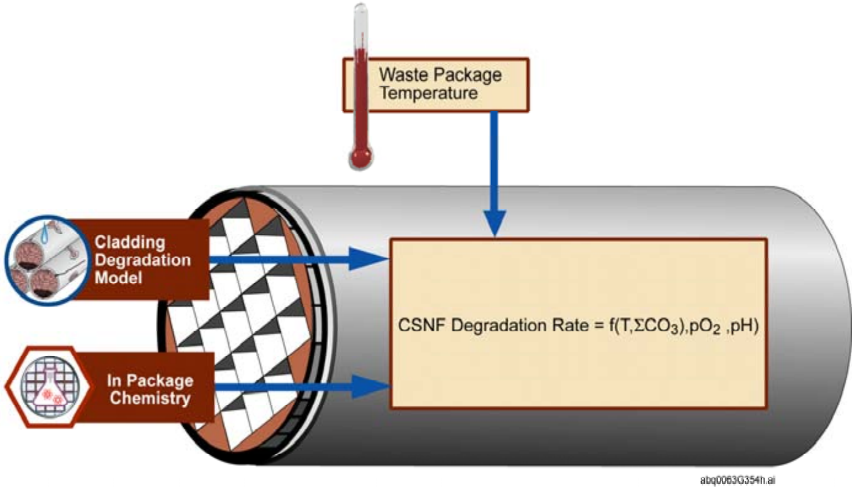
Triangular Probability Distribution Functions of Instantaneous Release Fractions

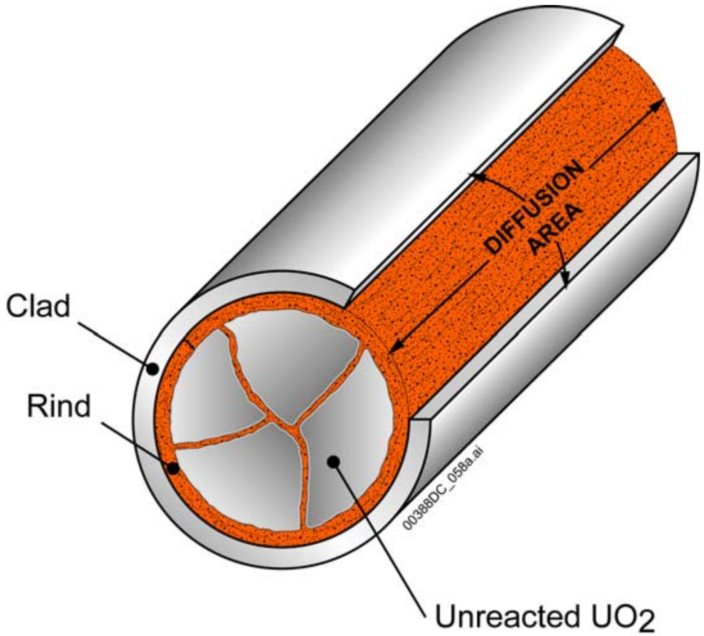
	^{137}Cs (%)	^{129}I (%)	^{99}Tc (%)	^{90}Sr (%)
Apex	3.63	11.24	0.10[a]	0.09
Minimum	0.39	2.04	0.01[b]	0.02
Maximum	11.06	26.75	0.26	0.25

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

- **Matrix Dissolution Rates Depend on Chemical Conditions and Temperature (Flow Through Tests)**

Description of Commercial Spent Nuclear Fuel (CSNF) Matrix Degradation Model





- **Mass of exposed fuel depends on cladding failure**
- **Defective clad splits instantaneously after waste package breach**
  - **Mass of fuel in split rod available**
- **Clad split area increases as fuel alters to schoepite (volume increases as rind forms)**
  - **Porosity of rind treated as uncertain (schoepite values)**
  - **Alteration rind assumed saturated**
    - **Water volume into which radionuclides dissolve**
    - **Diffusive transport path**
- **Radionuclides released via**
  - **Instantaneous gap and grain boundary**
  - **Matrix degradation**

Spent Fuel Matrix Degradation

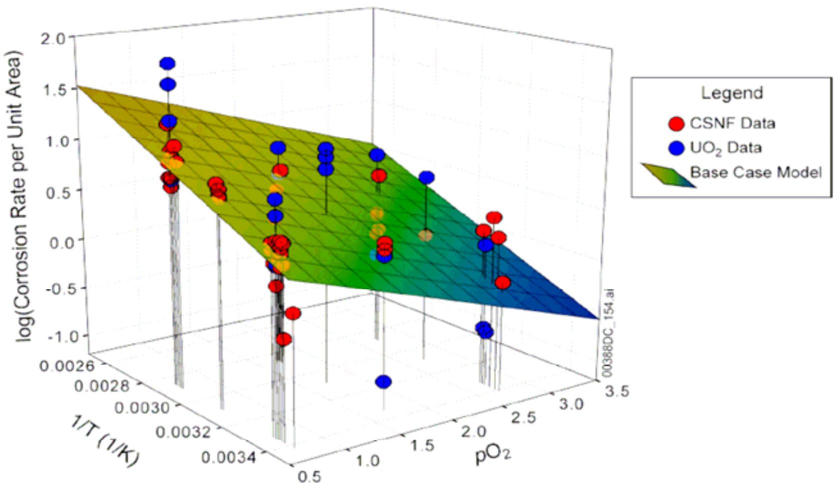
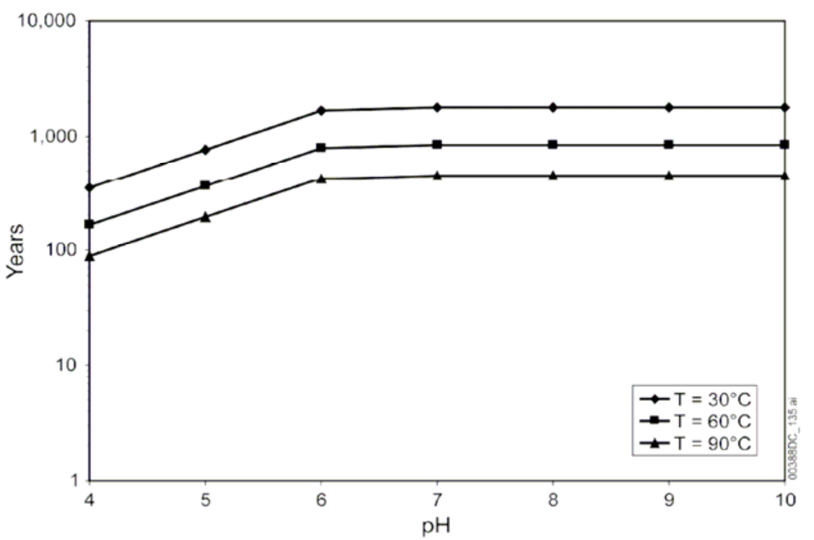


Figure 6-3. Comparison of the Base-Case Model (pCO_3 = 2.7) to the Input CSNF and UO_2 Data



- **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 with the rind water volume for comparison to limitations from solubility controls**

Np Solubility Models Considered

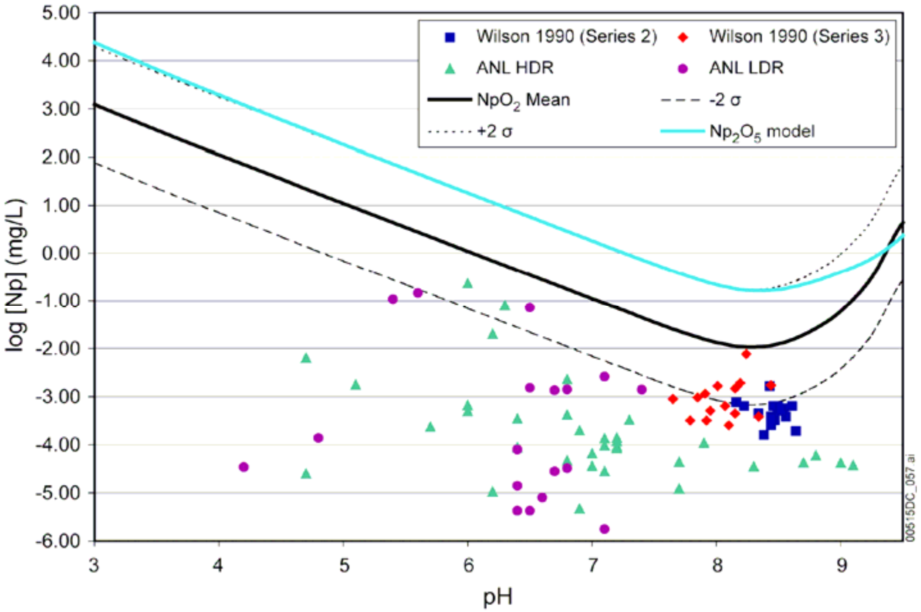
- Pure Phase Models (thermodynamic data – OECD/NEA database)
  - Np_2O_5 – metastable Np(V) oxide
  - NpO_2 – stable Np(IV) oxide
  - Solution dominated by NpO_2^+ species (reduction reaction for NpO_2)
- Secondary Phase Models
  - Coprecipitation of Np within uranyl alteration phases
  - Expected that 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
- 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*
  - Use Np_2O_5 outside the package in the Invert
    - Hedge against uncertain precipitation kinetics of NpO_2

Additional Support for NpO_2 Model

- NpO_2 Formed 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)
- Precipitation of NpO_2 from Solution (Roberts et al., 2003)
  - ~3 Months at 200°C

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

- Spent fuel observations indicate that reasonably long time (years) should be available for precipitation/formation of NpO_2
- 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

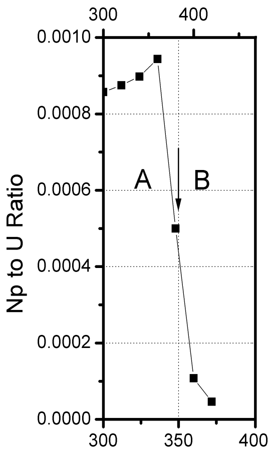


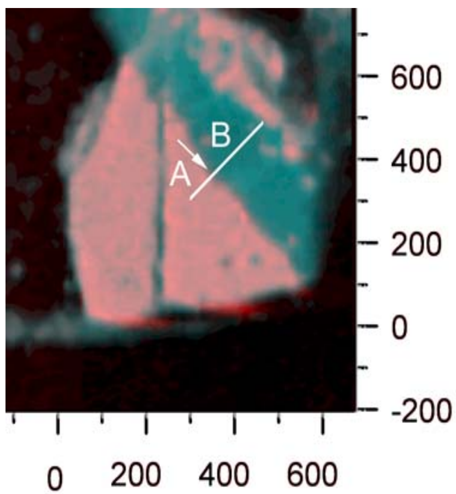
Data Source: Wilson 1990a [DIRS 100949]; Wilson 1990b [DIRS 100793] (Series 2 and Series 3 tests, respectively); and CRWMS M&O 2000 [DIRS 131861]; CRWMS M&O 2000 [DIRS 153105]; and Thomas, 2004 [DIRS 163048] for ANL high-drip and low-drip tests.

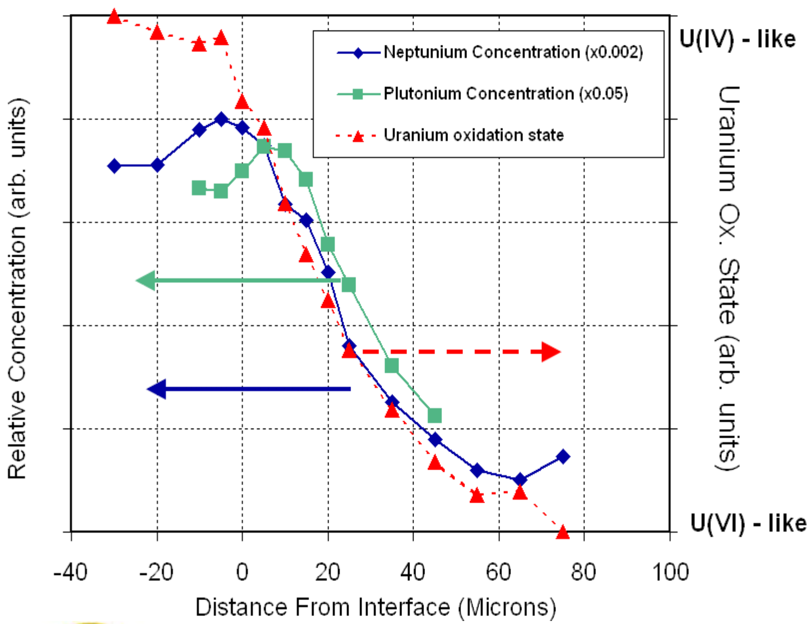
- Several recent studies indicate Np retention in uranyl solids – although mechanism is uncertain
  - Burns et al., (2004), Buck et al., (2004), Friese et al., (2004), Douglas et al., (2005)
- Additional studies on Np in CSNF and NpO_2 formation kinetics

Additional Studies

Np and Pu Across CSNF Corrosion Front

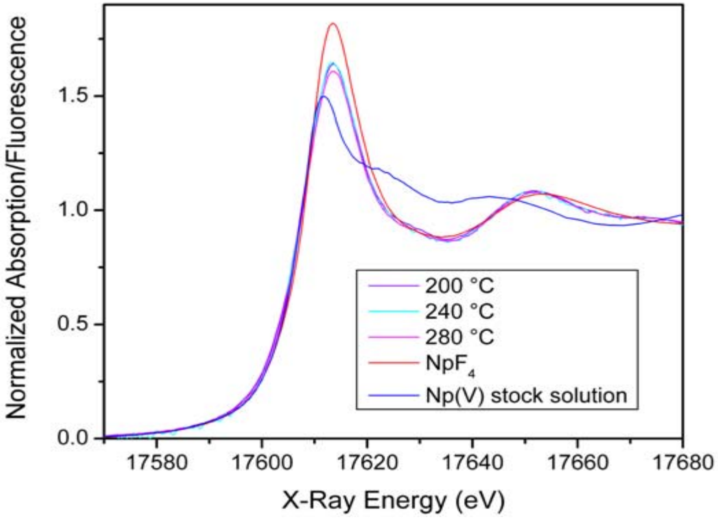


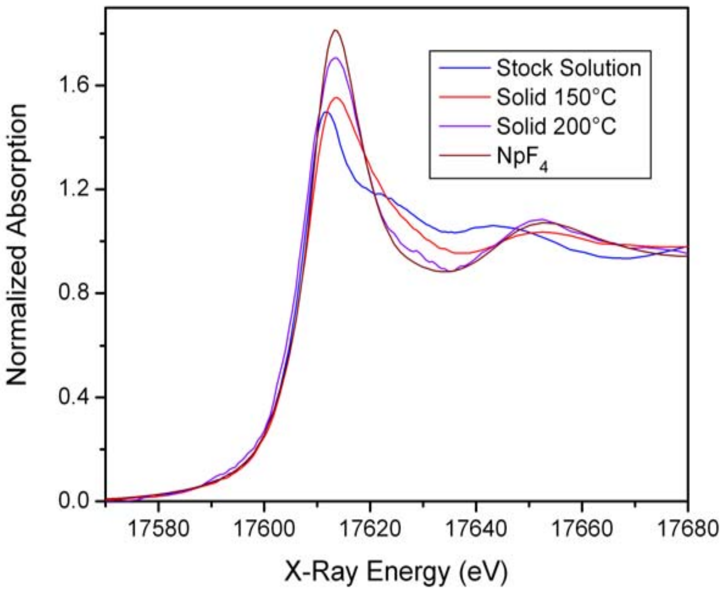




- **X-ray Absorption Spectroscopy shows Np(IV) in the fuel matrix**
- **Np/U ratio decreases in ~50µm mixed-valence U(IV)/U(VI) region adjacent to the corrosion front**
- **Np and Pu peak near the surface of the corroded spent fuel**
- **Results provide evidence that redox conditions at and near the 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 Precipitation from Np(V) Solution





- **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)**
- **Ongoing work addressing**
  - **Homogenous and heterogeneous precipitation at lower temperatures**
  - **Temperature-dependent rate for development of Np(IV) solids.**

Science and Technology Source-Term Targeted Thrust Projects

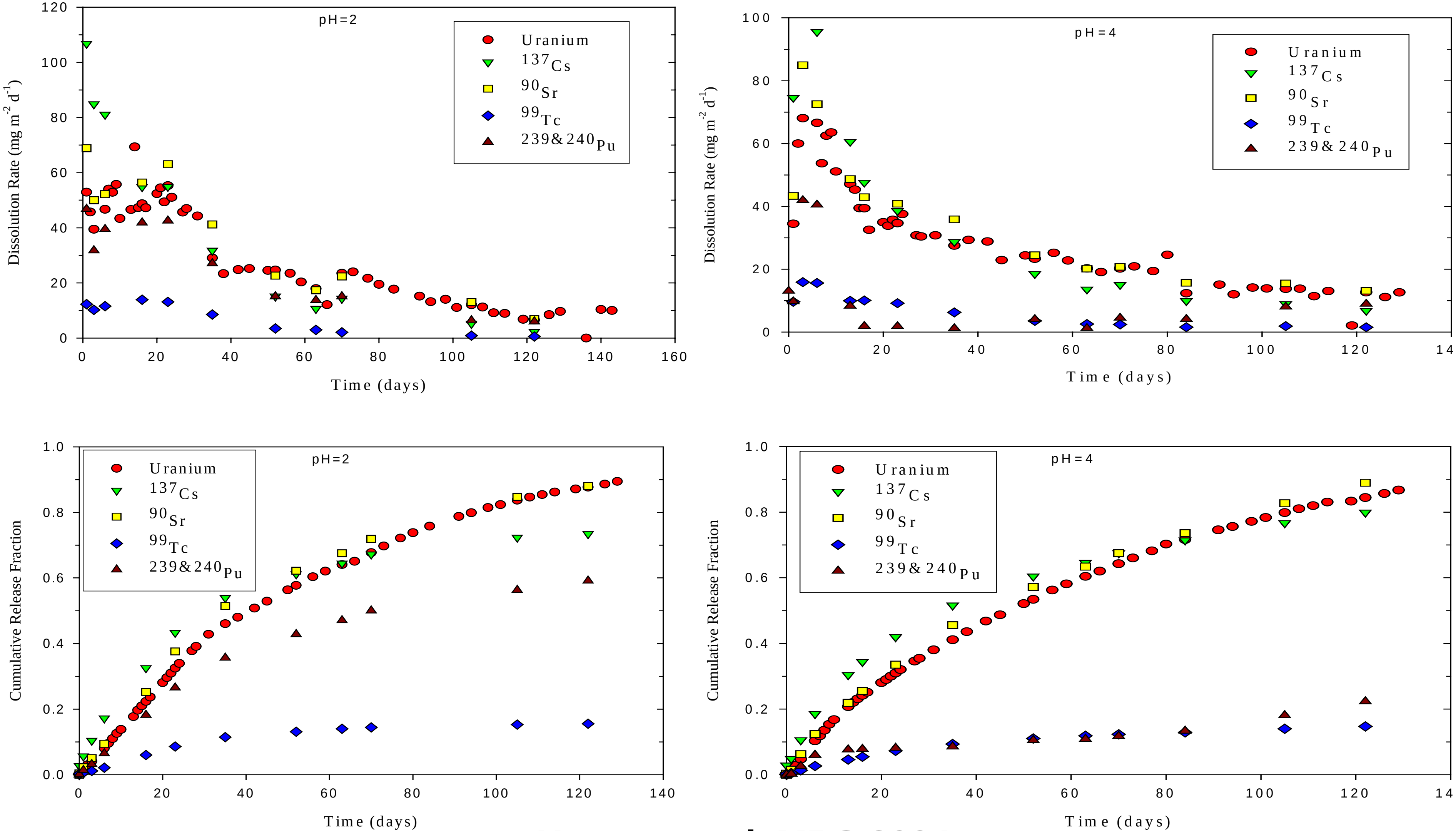
Source Term Targeted Thrust

- Research program is focused on the changing conditions over *time*, identifying the *critical processes* within each time interval, and with attention to the *radionuclides* that are the *major contributors to dose*
- Directors:
  - Rodney Ewing, University of Michigan
  - Mark Peters, Argonne National Laboratory

Selected Summary of Research Programs

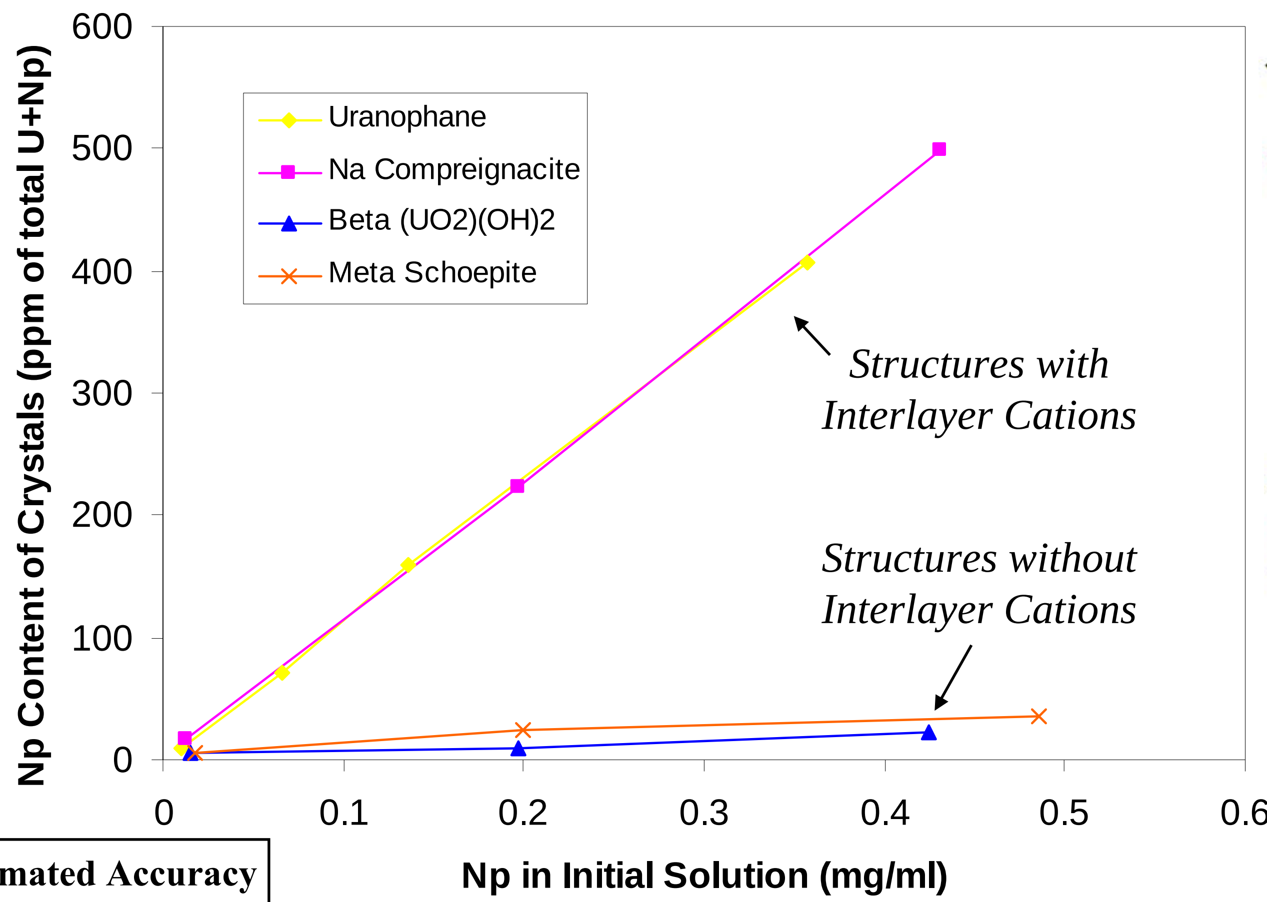
- SNF dissolution mechanisms and rates
- Formation and properties of U^{6+} secondary phases
- Waste form – waste package interactions
- Integration of in-package chemical and physical processes

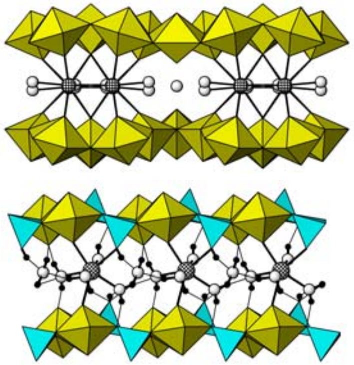
Low pH Single Pass Flow-Through (SPFT) on CSNF

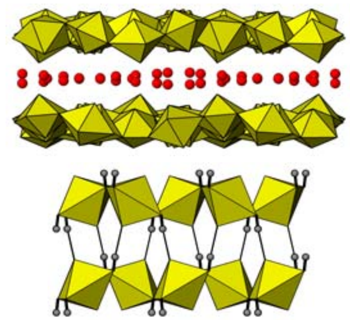


Hanson et al. MRS 2004

Np^{5+} Incorporation into Uranyl Phases







Estimated Accuracy
±10% Np

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

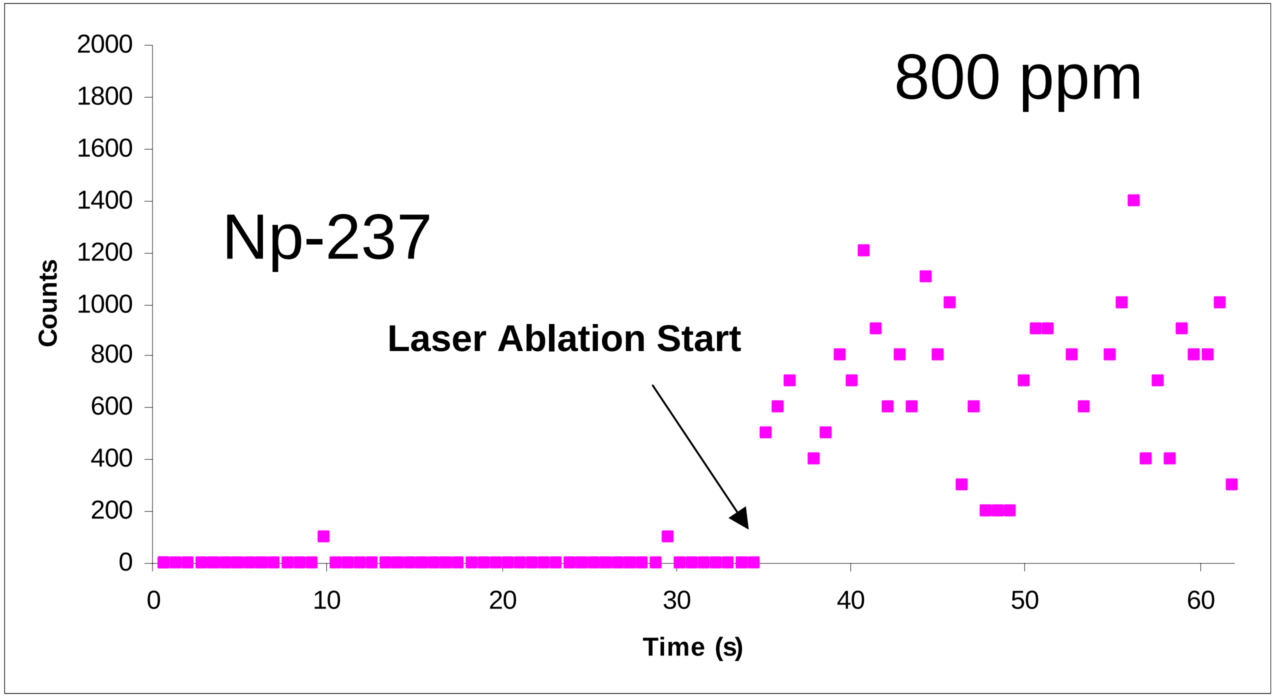
Becquerelite

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

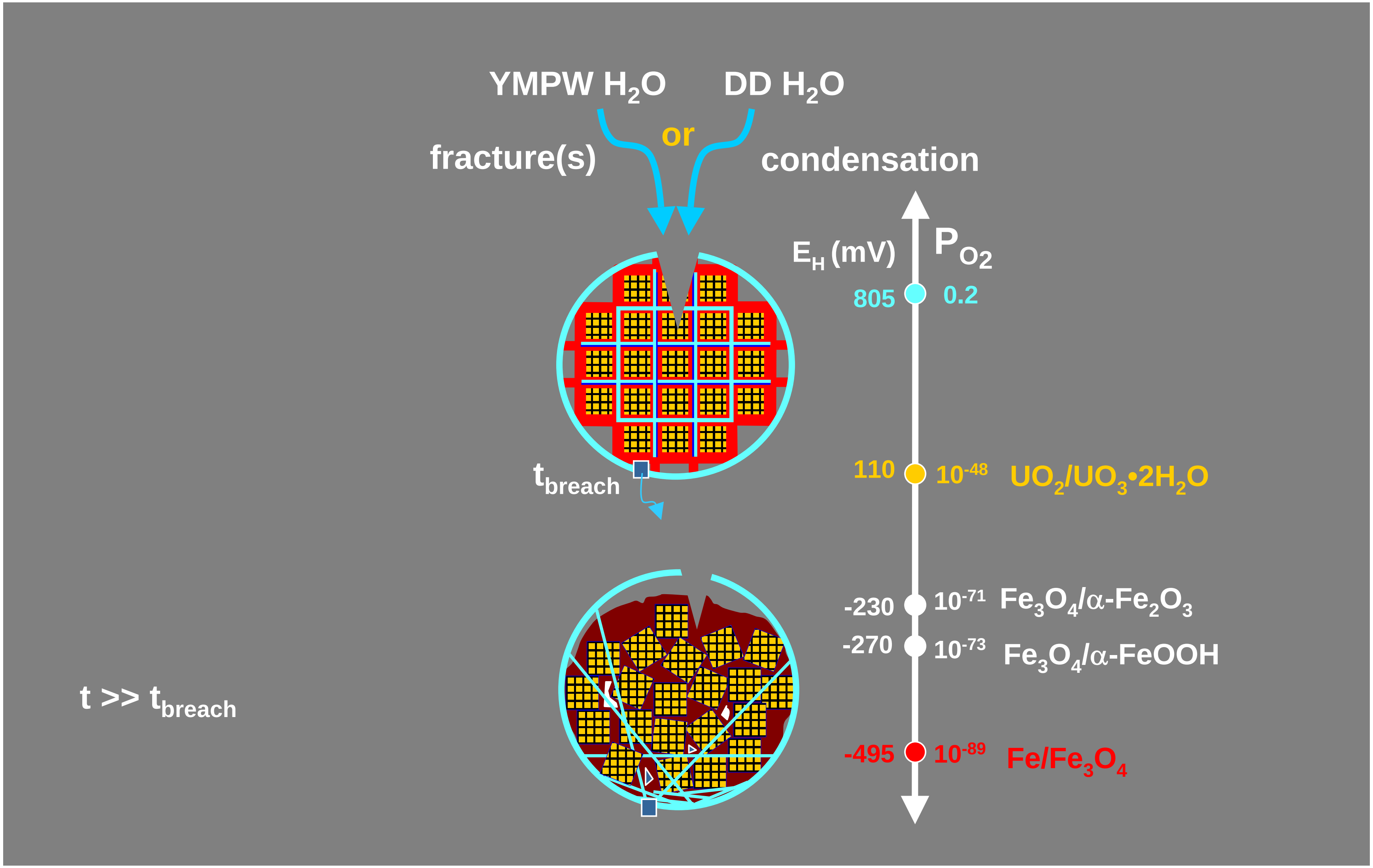
Np^{5+} in charge: 725 ppm

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

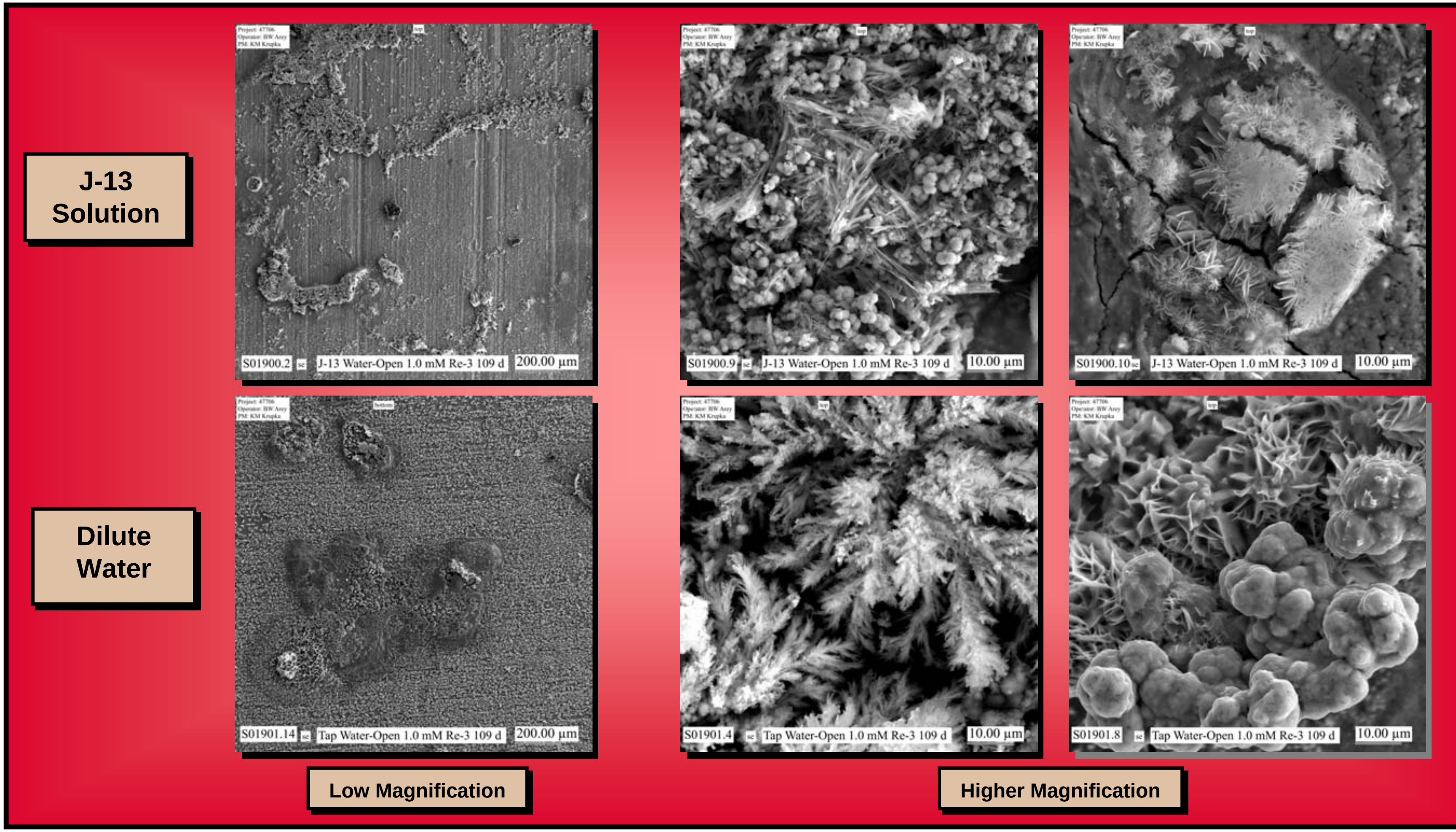
Np in crystal by count ratio: 800 ppm



In Package Geochemistry



Corrosion Products



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