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Dissolution Processes for Commercial Spent Nuclear Fuels in Repository Conditions

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- In-Package Water Chemistry
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- Groundwater Contact Modes for CSNF
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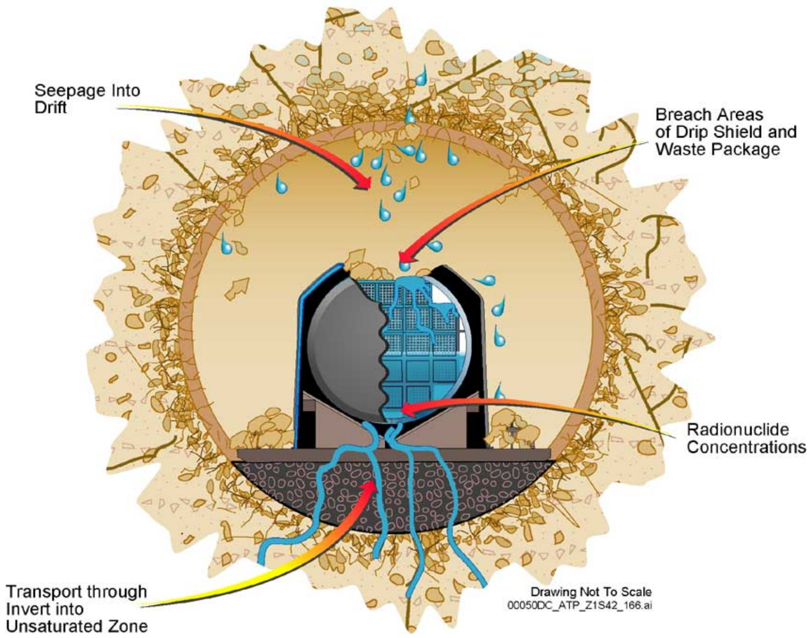
Purpose

- Present an overview of key processes for the dissolution of commercial spent nuclear fuels at conditions representative of the potential Yucca Mountain (YM) repository

- Discuss the significance of uncertainties in important processes that affect CSNF dissolution models
  - In-package water chemistry
  - CSNF characteristics
  - Groundwater contact modes

CSNF Dissolution

Matrix (i.e., irradiated UO_2) Dissolution – congruent release of Tc-99 and I-129



(DOE, 2002)

Principal Factors for Matrix Dissolution

Reaction products of UO_2 with H_2O depend on electrochemical conditions of UO_2 for dissolution and hydrolysis of dissolved species.

(1) In-Package Water Chemistry

- **Concentrations of carbonate/bicarbonate ions, oxygen, iron and other cations**
- **pH**
- **Temperature**

(2) Condition of CSNF before Water Contact

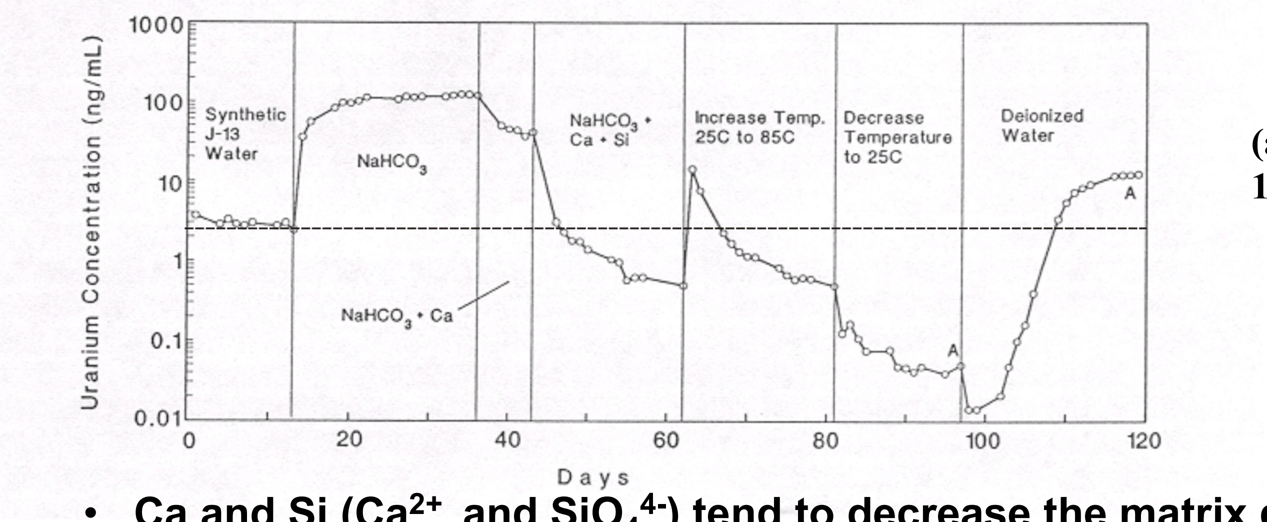
- **Extent of pre-oxidation/hydration**
- **Grain-boundary characteristics**

(3) Groundwater Contact Modes for CSNF

- **Seepage rate**
- **Immersion versus drip**
- **Extent of cladding protection**

In-Package Water Chemistry

Cation Effects

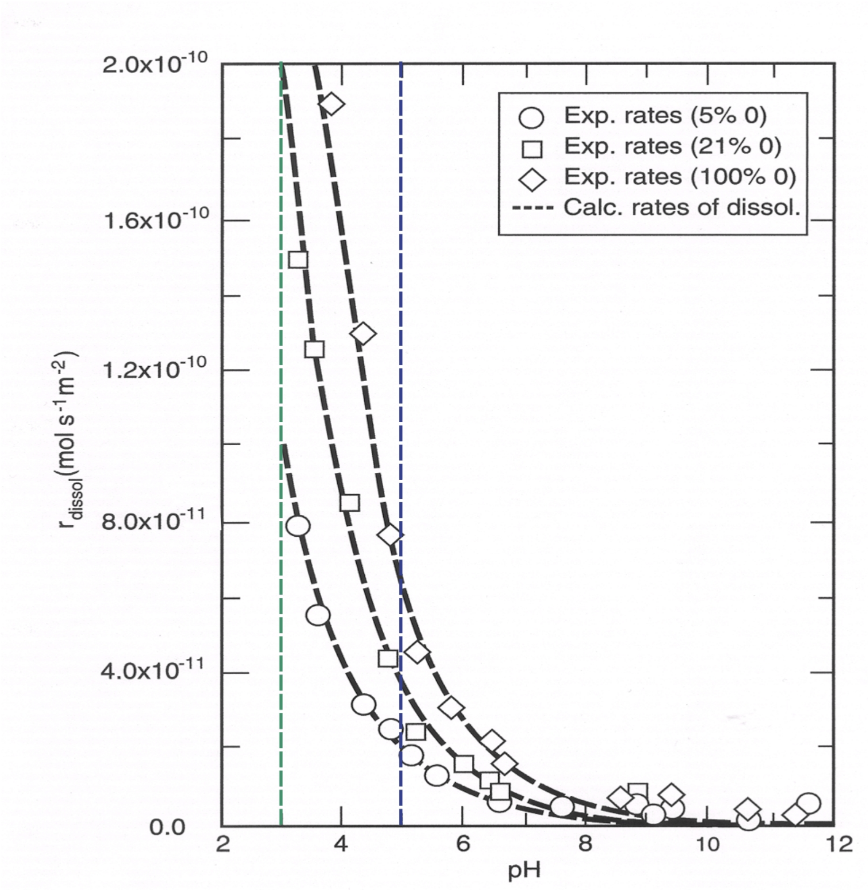


(after Wilson and Gray, 1990)

- Ca and Si (Ca^{2+} and SiO_4^{4-}) tend to decrease the matrix dissolution rates by two orders of magnitude or more at 25 °C (77 °F) compared to those in carbonate solutions of $2x10^{-4}$ – $2x10^{-2}$ M.
- Primary uncertainties
  - Competing effects of cations and low pH
  - Rates of cation depletion
  - Formation of Schoepite inhibiting dissolution

In-Package Water Chemistry *(Contd.)*

pH Effects



Rates of UO_2 dissolution as a function of pH and oxygen concentration [mol/s-m^2 : 6.5x10^{-4} mol/s-in^2] (after Torrero et al., 1997)

- **Data under oxidizing conditions (Torrero, et al., 1997)**
  - **Matrix dissolution rates increase by a factor of 4 – >10 at pH ~ 3, compared to pH below ~ 5.**
- **Metallic cations (e.g., Cr) from corrosion of waste package internals can lower pH in seepage water.**
- **Primary uncertainty is magnitude of pH variability.**

In-Package Water Chemistry *(Contd.)*

Effects of Oxygen and Iron Concentration

- **Corroding steel components may decrease local oxygen concentration.**
  - **Decrease in the matrix dissolution rates by more than 10x in SIMFUEL tests in NaCl solution at ambient temperature (Quiñones, et al., 2001)**

- **Oxygen in an air-buffered repository environment is sufficiently abundant to offset the production of oxidants by radiolysis.**

Effects of Temperature

- **CSNF dissolution rate is most sensitive to variations in temperature.**
- **The activation energy for dissolution varies depending on test conditions (Shoesmith, 2000): 0 – 47 kJ/mol (11.2 kcal/mol).**
- **Activation energy of 24 – 33 kJ/mol (5.7 – 7.9 kcal/mol) for Tc-99 and I-129 from CSNF immersion tests (Wilson, 1990)**

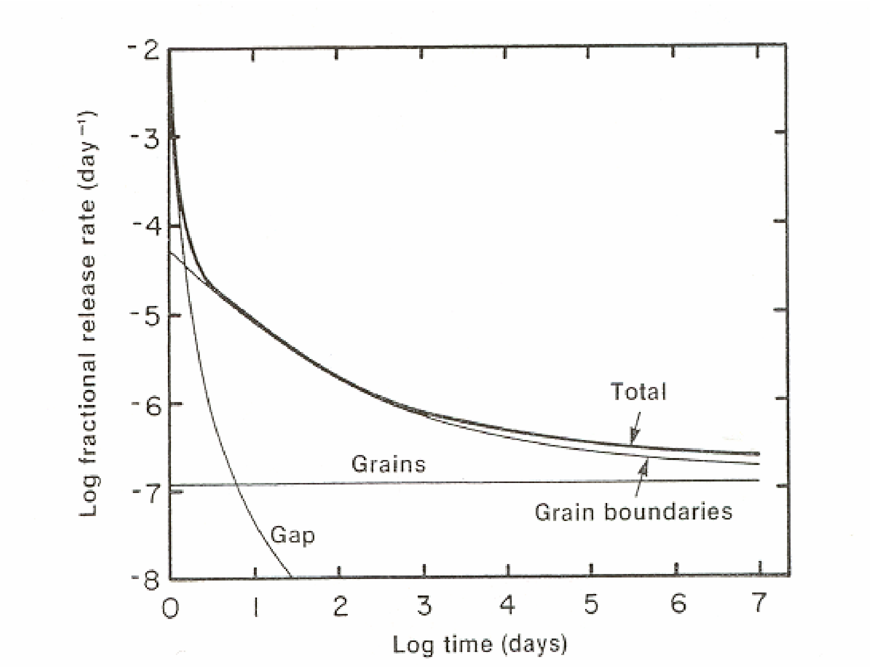
Condition of CSNF before Water Contact

Pre-oxidation/Hydration

Uncertainties in the timing and extent of pre-oxidation and hydration processes:

- **$UO_{2.4}$ or U_3O_8 dissolves similarly with unoxidized UO_2. However, UO_3 xH_2O (x = 0.8, 2) dissolves 10 – 20 times faster than unhydrated oxides.**
- **Oxidation to $UO_{2.4}$ tends to open up more grain boundaries, potentially increasing exposed surface area.**
  - **(i) Dissolution rates may increase for CSNF in initially failed WP if relative humidity is less than ~50 percent (Gray, 1997) for the oxidation during the early period in the initially failed WP.**
  - **(ii) Grain boundary openings would be, however, masked with alteration (i.e., precipitated) products of dissolved uranium.**
- **Oxidation to U_3O_8, or UO_3 xH_2O creates inter- or trans-granular fractures that increase exposed surface area by as much as 2 – 3 orders of magnitude - temperatures above 250 °C (482 °F) are necessary to form U_3O_8.**
- **Vapor hydration or aqueous dissolution may further weaken deeper grain boundaries. Mechanical impacts (e.g., seismicity) can result in additional grain breakage.**

Condition of CSNF before Water Contact *(Contd.)* *Grain Boundary Inventory*



Schematic of three stages in fission product release from used CSNF (Johnson et al., 1985)

- **Radionuclide (RN) releases from grain boundaries and matrix dissolution.**
- **Tests with fragments (i.e., particles) under dripping, flow-through or immersion that show substantial amounts of grain-boundary RN in the results were used to determine matrix dissolution rates (Tc-99, I-129, Cs-137, or Sr-90) (OCRWM, 2003).**
- **Uncertainties in the magnitude and extent of long-term RN release from grain boundaries, relative to matrix**

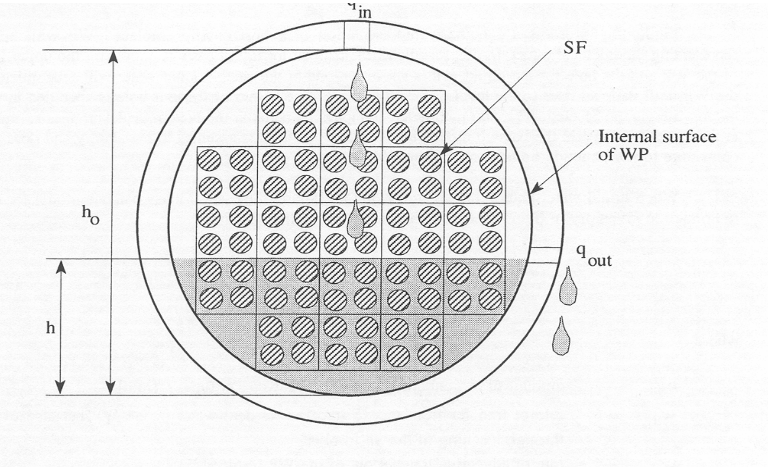
Groundwater Contact Modes for CSNF

Perforations/Cracks on Waste Package

- uniform corrosion

- localized corrosion

- stress corrosion cracking



Schematic of bathtub model with incoming and outgoing water conduits (Mohanty et al., 2002)

- **Increasing drip rates by 10x resulted in an increase in CSNF dissolution rate by at least 10x (Cunnane, 1999).**
- **Drip rates may be more than 10x lower than modeled repository seepage rate.**
- **Uncertainties in extrapolating tests to repository conditions (e.g., drip rate)**

Groundwater Contact Modes for CSNF *(Contd.)*

Failed Cladding Protection

- Immersion tests for slit (~0.015 cm [0.006 in] diameter x ~2.54 cm [1 in] length)- or hole (~ 0.02 cm [0.008 in] diameter)- CSNF cladding defects on release rate in J-13 Well Water at 85 ºC (185 ºF) (Wilson, 1990)

  - Relative to unclad CSNF, release decreased by a factor of ~ 140 for Tc-99, ~700,000 for I-129, and ~65 for Sr-90

- Drip tests of partial clad rod segments (OCRWM, 2003)

  - Tc-99 release, 2.6×10^{-8} fraction per day

- No decrease observed in release with 50 percent CSNF surface area exposed in immersion tests (Forsyth, 1997; Forsyth and Wermer, 1985; Stroes-Gascoyne, 1985)

- Significant uncertainties in the times and extent of cladding defects

Summary

- Dissolution rates are most sensitive to variations in temperatures.
- Ca and Si ions could decrease CSNF dissolution rates more than an order of magnitude.
- Release from the grain boundary/gap inventory is substantial component of effective release rates, by a factor of 2 – 10 of the long-term matrix dissolution rates.
- Other factors that potentially decrease dissolution or release rates are low drip-rates of seepage water, small opening in cladding, and presence of iron compounds.
- Other factors that potentially increase dissolution rates are low pH, and pre-oxidation and hydration of CSNF before water contact.
- A range of information in analog, primarily from laboratory experiments, to support staff review of CNSF dissolution models.

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Disclaimer

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of a license application for a geological repository at Yucca Mountain. This presentation describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the NRC under contract number NRC-02-02-012. The activities reported here were performed on behalf of the NRC office of Nuclear Material Safety and Safeguards, Division of High Level Waste Repository Safety. This presentation is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

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