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Radiolysis Effect on Wasteform Corrosion

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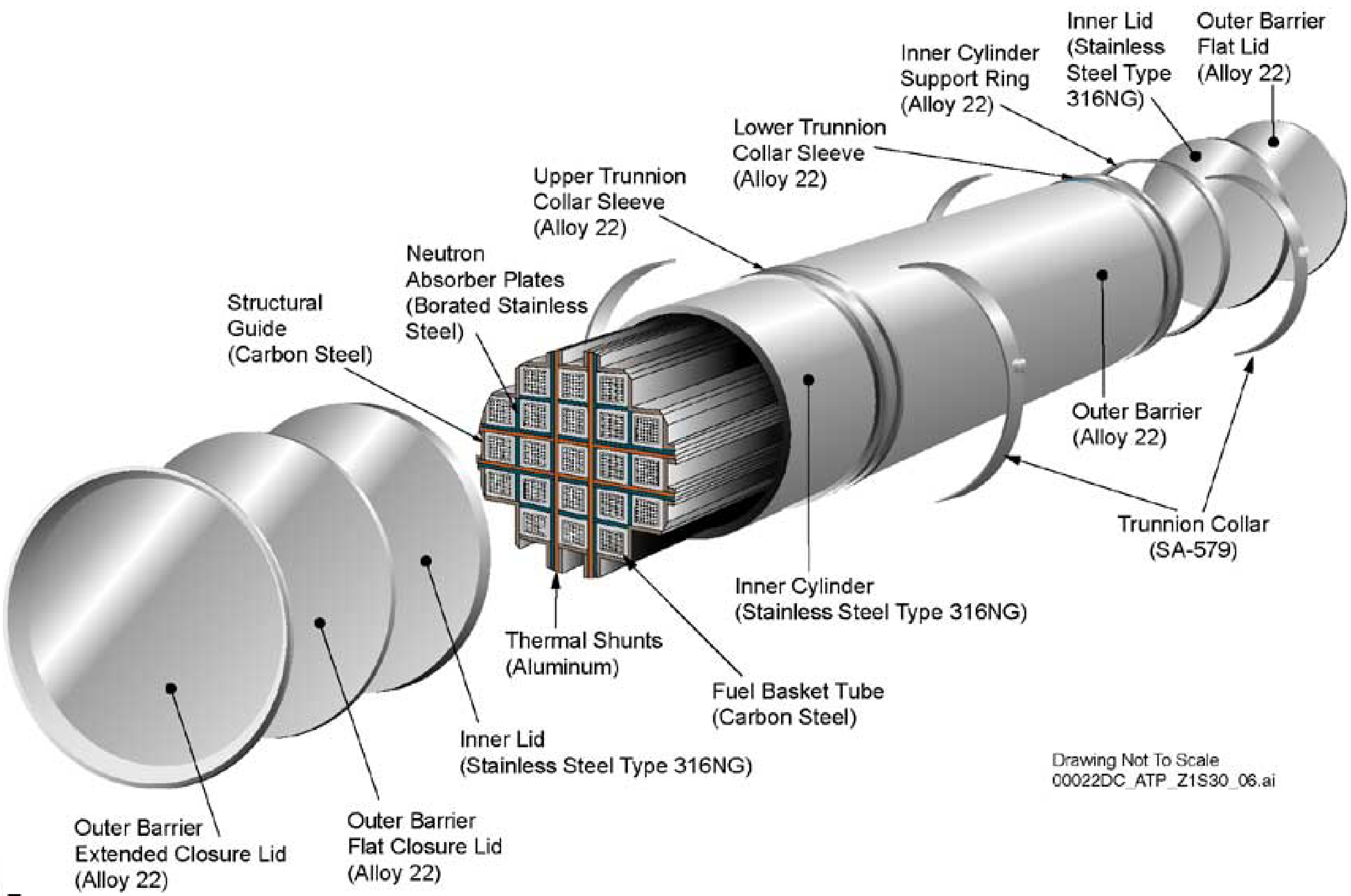
Purpose

- **Spent fuel waste packages in Yucca Mountain**
  - **Looking at what would happen if after 500+ years the waste package breached allowing water to come into contact with the fuel**

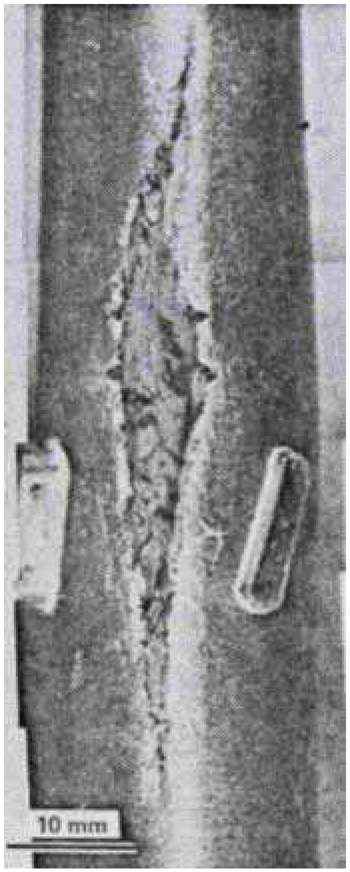


Yucca Mountain Science and Engineering Report, Rev. 1, DOE/RW-0539-1

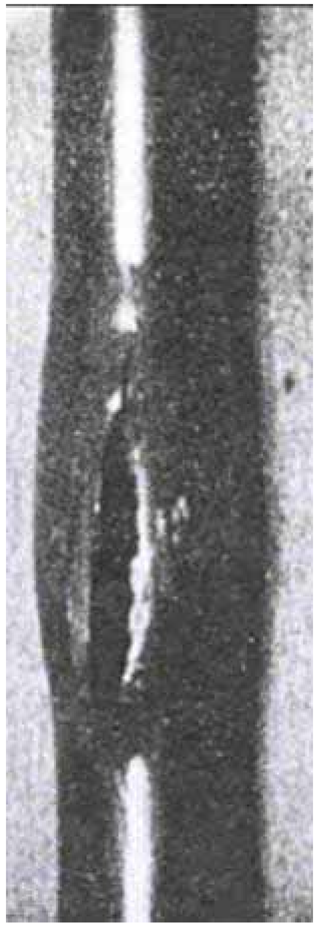
Failed Fuel Rods

- 0.1-1% of the cladding surrounding the uranium in the fuel rods fail during reactor operation. If the drip shield and waste package fail and water gets to this failed fuel rod it may result in the dissolution of spent fuel.
  - This is statistically ~6 rods per waste package
- Potential causes of cladding failure
  - Cladding initially fails within the reactor
  - Rockfall
  - Earthquake severely shakes and severs the rods
  - Igneous intrusion (annealing)

Cladding Failures



CANDU Fuel



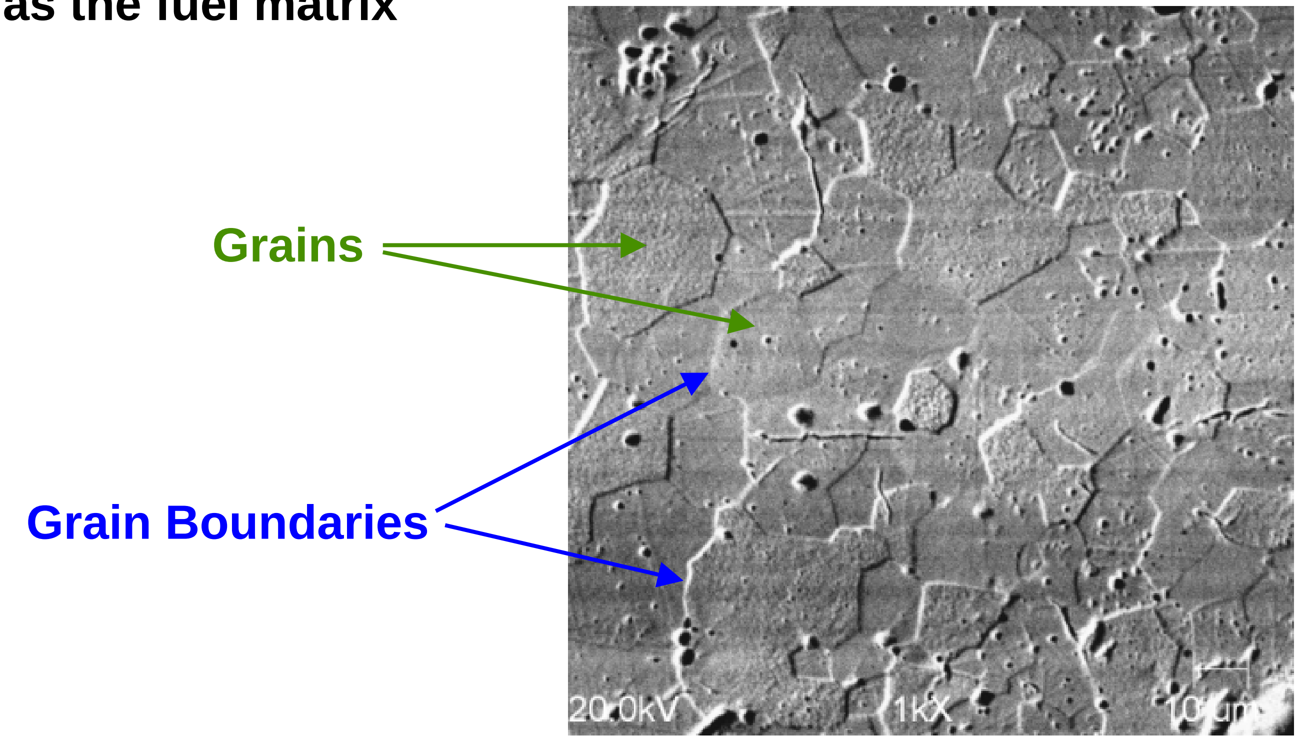
Pinhole Defect
Followed by Fuel
Oxidation

Spent Fuel from
N-Reactor at Hanford

Spent Fuel from
N-Reactor at Hanford

Release of Radionuclides

- **There are two types of releases**
  - **Fast: the inventory of radionuclides that are in the gap between the fuel pellets and the cladding (gap inventory) and the radionuclides at the grain boundaries**
  - **Slow: release as the fuel matrix degrades**

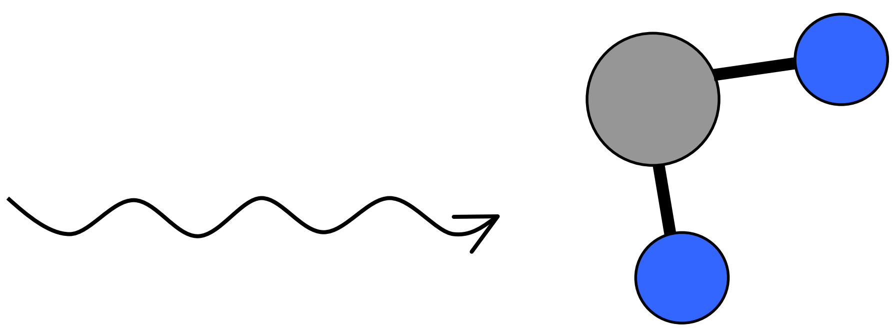


Current Models

- Current Yucca Mountain models conservatively do not account for the effects of radiolysis
  - Questions on how significant radiolysis is under oxidizing conditions
- Current models based on experimental data on 10-30 year old fuel with significant ^{90}Sr and ^{137}Cs concentrations contributing to radiolysis
- After 1,000 years there will be a 1,000-10,000 decrease in dose
- Due to this decrease in dose, we hypothesize waste form degradation rates may be much lower than the present conservative models predict

Radiolysis

- **Radiolysis: the chemical decomposition of water by use of radiation**
  - **Main radiolysis products: e^-_{aq}, H^+, OH^-, H_2, O_2, O^-, H_2O_2, H_3O^+, H_2O^+**
  - **Radiolytic products can turn a reducing or anoxic environment into an oxidizing environment increasing the solubility of UO_2**



Radiolytic Products

- **Different types of radiation result in different ratios of radiolytic products***
  - **α-Higher yields of molecules (H_2O_2 and H_2)**
  - **β/γ-Higher yields of radicals (OH, e^-_{aq}, H^+)**
- **Radicals are more effective than H_2O_2 in dissolving UO_2***
  - **So spent fuel after 500 years which will have mainly α-decay, will result in a lower rate of fuel dissolution than spent fuel after only 10 years of decay where β/γ radiolysis contributes to radical production**

***Christensen, Sunder "Current state of knowledge of water radiolysis effects on spent nuclear fuel corrosion," *Nuclear Technology*, 131 (2000) 102-123**

Different Tests

- *Individual effects of α, β, γ radiation on the dissolution
  - Dope UO_2 with each type of radiation
- *Simulation of 500+ year old spent fuel
- Chemistry effects of different isotopes in the fuel
  - Run simultaneous tests with a radioactive isotope and their corresponding nonradioactive isotope
- Effect of different water situations
  - SPFT (Single Pass Flow Through) Tests
  - Static Tests
  - Humid Air Tests

*Focus of my research

SPFT Tests

- **Unlike the static tests the SPFT tests will prevent alteration products from forming on the surface**
  - **This maintains a forward rate of reaction**
  - **The alteration products have been shown to slow down the dissolution of the uranium**
    - **It will block the fuel corrosion process**
    - **Deposits will retain radionuclides released by fuel corrosion**
  - **Therefore SPFT tests will show a worst case scenario**
    - **The effects of decrease in radiolysis over time should be even more dramatic under low flow conditions**

Radiation Effects on Dissolution

- **Isotopes we are testing to observe radiation effects**

  - **β: Sr-90 (28.79 yr $t_{1/2}$; 0.546 MeV β)/ Y-90 (64 hr $t_{1/2}$; 2.280 MeV β)**
    Cs-137 (30.07 yr $t_{1/2}$; 1.176 MeV β)

  - **α: Pu-238 (87.7yr $t_{1/2}$; 5.593 MeV α)**
    Pu-239 (24,110 yr $t_{1/2}$; 5.245 MeV α)
    Pu-240 (6,564 yr $t_{1/2}$; 5.256 MeV α)
    Np-237 (2,144,000 yr $t_{1/2}$; 4.959 MeV α)

  - **γ: Ba-133 (10.51 yr $t_{1/2}$; 0.517 MeV γ)**

RADFUEL

- **RADFUEL: Radiolytically Aged Fuel**
- **Contain all main radioactive constituents that will be present at a specific time in the future**
  - **500 years**
  - **1,000 years**
  - **5,000 years**

Pellet Production

- UO_2 powder and dopant are added together, wetted, and tumbled overnight
- UO_2/dopant slurry are vacuum filtered and then oven dried overnight

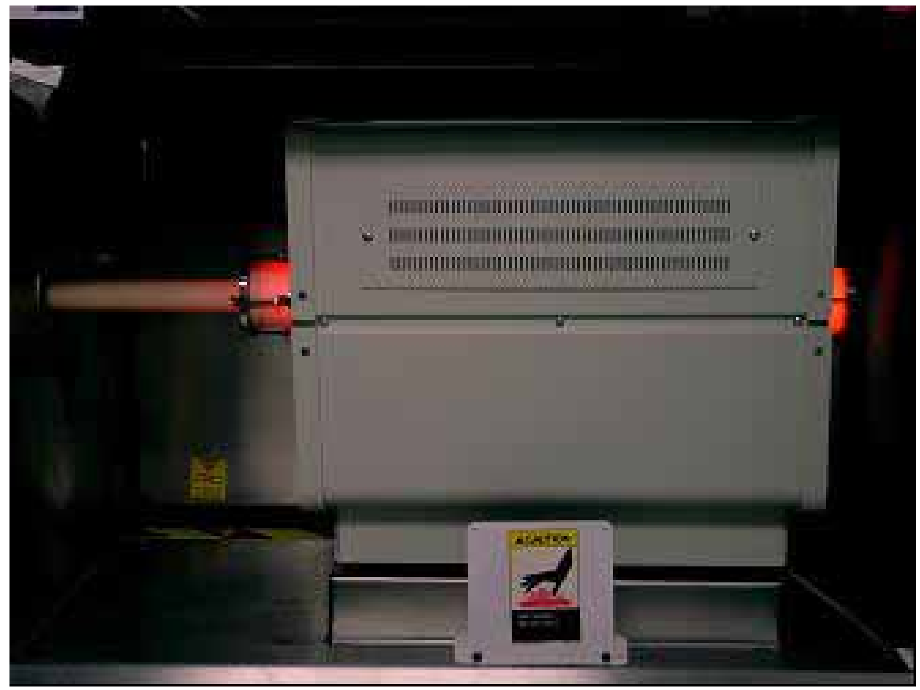
Pellet Production

- **The UO2 is crushed into a powder and pressed at ~48,600 psi into thin slices**

The slices are then crushed and the powder is pressed (at the same pressure) into a pellet

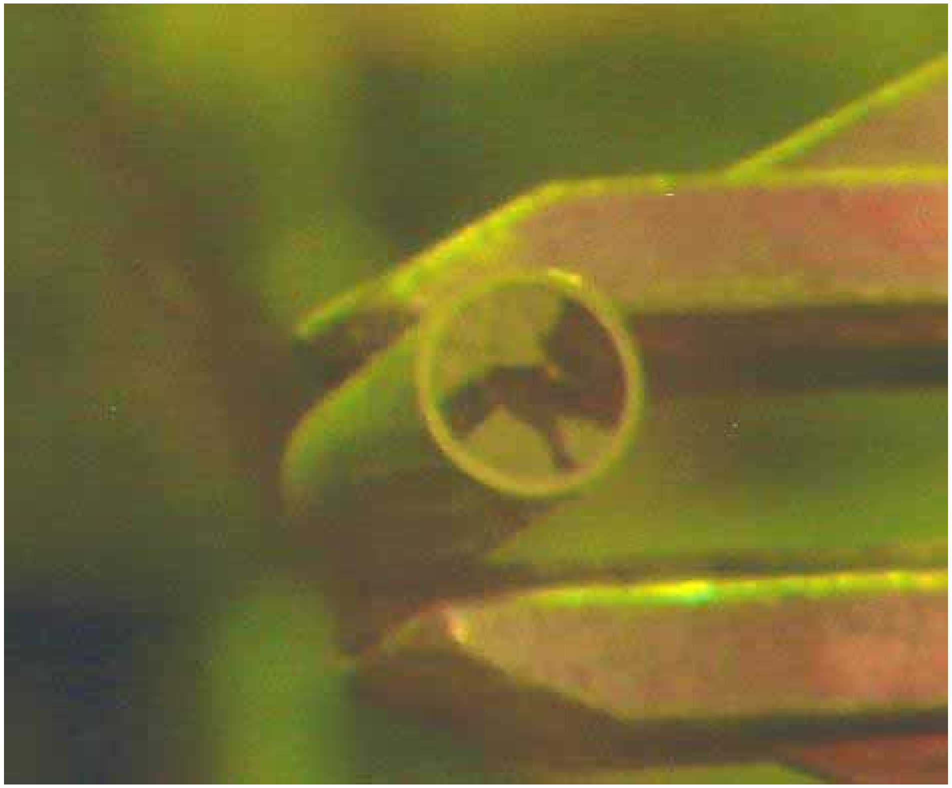
Pellet Production

- **The pellet is sintered for 24 hours at 1650 °C**



Preparation

- **The pelle is then crushed**
  - **In a spent fuel scenario the pellets are cracked due to thermal gradients during reactor operations as shown below**
  - **SPFT tests use fragments (as-received) or fuel crushed to individual grains to provide a known, maximum surface area**



SPFT Set-Up

- Single-pass Flow Through Tests
  - Flows: 0.05-0.2 ml/min of water (enough to maintain forward rate of fuel dissolution)
  - Temperatures: 50^{o}C, 75^{o}C, 90^{o}C
  - Water Composition:
    - Initial tests will be with DI water (neutral pH) sparged with air to allow equilibrium concentrations of dissolved oxygen and carbonate
      - Simulates scenario of water vapor infiltration into a failed waste package, followed by condensation
    - Subsequent tests will use a simulated pore water containing dissolved species
      - Simulates scenario of dripping groundwater into a failed waste package

Flow Set Up

- Doped UO_2 is crushed to a powder consisting of individual grains
- Powder is weighed and placed inside the Linear Flow Cells
- Water is equilibrated to desired temperature, pH, and sparged with air
- The equilibrated water is pumped into the oven, up through the cell, and out the top of the oven
- At the top is a 2-way valve where the flow can be directed to either collection vials or to a waste container

SPFT Tests

Analysis Methods

- Standard radiochemical separations and counting
- KPA (Kinetic Phosphorescence Analysis)-Uranium concentration in the water after the SPFT test
- XRD (X-ray Diffraction)-determine crystalline phases present (metallic, oxide, compound, etc.)
- XPS (X-ray Photoelectron Spectroscopy)-look at oxidation state of elements on the surface of the reacted particles
- SEM-Grain Size of UO_2 in pellet and for visual examination to look at morphology
- TEM with EELS (Electron Energy Loss Spectroscopy)-Find small quantities of radionuclides in the reacted fuel

Current Modeling

- **Using Monte Carlo techniques to determine dose of radionuclide(s) to water**
  - **Results of Sr-90/Y-90**

U/Water	Sr-90 (Avg. E = 0.196 MeV)		Y-90 (Avg. E = 0.935 MeV)		Total E Deposited in H_20 (MeV)
	Fraction of E Deposited in H_20	E Deposited in H_20 (MeV)	Fraction of E Deposited in H_20	E Deposited in H_20 (MeV)	
1:1	0.06	0.012	0.065	0.061	0.073
1:1.56	0.13	0.026	0.159	0.148	0.174
1:2.25	0.209	0.041	0.27	0.252	0.293

Water Chemistry

- **G-Values can then be used to calculate the concentration of e^-_{aq}, H^+, OH^-, H_2, O_2, O^-, H_2O_2, H_3O^+, H_2O^+**
- **G(x) Value: The number of molecules of (x) created for each 100 eV of energy absorbed**

G Values for γ and α irradiation of Neutral Water*

Species	G Value	
	Gamma	Alpha
OH	2.67	0.24
e^-_{aq}	2.66	0.06
H^+	2.76	0.30
H	0.55	0.21
H_2	0.45	1.30
H_2O_2	0.72	0.985
OH^-	0.1	0.02
H_2O	-6.87	-2.71
O_2^-	0	0.22

G Values for γ and 5 MeV α **

Species	G Value	
	Gamma	5 MeV He
OH	2.70	0.35
e^-_{aq}	2.60	0.15
H^+	3.10	0.18
H	0.66	0.10
H_2	0.45	1.20
H_2O_2	0.70	1.00
OH^-	0.50	0.03
HO_2	0.02	0.10

*Christensen, Sunder, “Current State of Knowledge of Water Radiolysis Effects on Spent Nuclear Fuel Corrosion,” *Nuclear Technology*, 131, (2000), 102-123

**Pastina, LaVerne, “Effect on Molecular Hydrogen on Hydrogen Peroxide in Water Radiolysis,” *Journal of Physical Chemistry A*, 105, (2001), 9316-9322

Uranium Concentration

- For the α-radiation, once the H_2O_2 Concentration is known, the UO_2 dissolution rate can be estimated

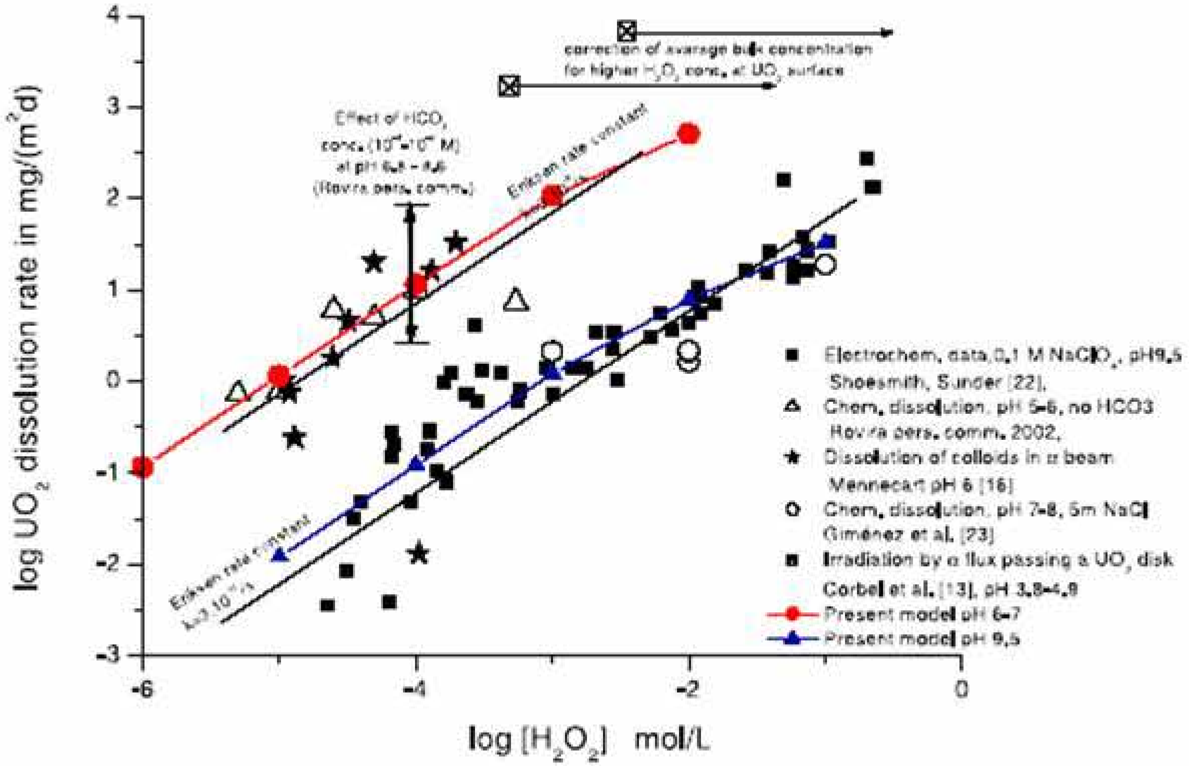


Fig. 2. Effect of the concentration of hydrogen peroxide on UO_2 and spent fuel dissolution rates. Calibration of model calculations with experimental results published in literature.

Grambow, B., et. al. "Electrochemical Aspects of Radiolytically Enhanced UO2 Dissolution," *Radiochimica Acta* 92, 603-609, 2004

Modeling for RADFUEL

- Using the Final Environmental Impact Statement*
  - Statements gives the radionuclide activity for average PWR fuel assemblies
- Set up a system of equations for isotope activity as a function of time
- Use ORIGEN 2.2 to compare isotope inventory/activity
- Base composition of RADFUEL on this information
- Predict initial radiological products from dose using Monte Carlo techniques
- Calculate resulting chemistry in the water

An Aerial View of Yucca Mountain

http://www.nei.org/images/Yucca_Mountain_Aerial_View.jpg