



SPENT FUEL DISSOLUTION AND CLADDING PROTECTION

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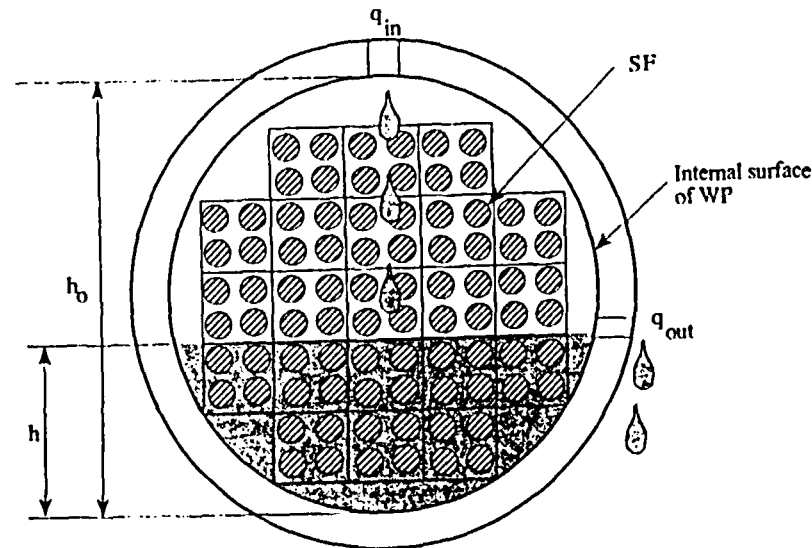
**TPA Version 3.2 External Review Group
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OUTLINE OF PRESENTATION

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- TEST METHODS**
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AND PROMPT RELEASE**
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- TPA3.2 SENSITIVITY ANALYSIS**

SCENARIOS

- Bathtub versus Drip



Schematic of bathtub model with incoming and outgoing water conduits

TEST METHODS

- immersion tests: semi-static batch with slow replenishments to simulate bathtub
- drip tests: very slow drips of groundwater onto spent-fuel surfaces without forming immersions to simulate drip
- flow-through tests: artificially high flow rate to eliminate secondary phases to determine the intrinsic dissolution rate

DISSOLUTION MODEL

Model 1: DOE model

- pure carbonate solution
- flow-through tests
- accelerated tests (or drip?)

$$\log r = 9.310 + 0.142 \log [\text{CO}_3^{2-}] - 16.7 \log (p_{\text{O}_2}) + 0.140 \log [\text{H}^+] - 2130/T + 6.81 \log (T) \log (p_{\text{O}_2})$$

r : dissolution rate [$\text{mg m}^{-2} \text{d}^{-1}$], $[\text{CO}_3^{2-}]$: total carbonate concentration [mol/L],
 (p_{O_2}) : oxygen partial pressure [atm], $[\text{H}^+]$: concentration of hydrogen ions [mol/L]
 T : temperature

Model 2: NRC base model

- oxidative
- bathtub (immersion)
- J-13 well water with Ca and Si ions

$$r = r_0 \exp[-34.3/(R T)]$$

r_0 ($\text{mg m}^{-2} \text{d}^{-1}$) from 1.4×10^4 to 5.5×10^4 , and R ($\text{kJ mol}^{-1} \text{K}^{-1}$)

- model 2 basis

(1) Activation Energies (kJ mol⁻¹ K⁻¹) are from immersion tests (Wilson, 1990)

¹³⁷ Cs	⁹⁰ Sr	⁹⁹ Tc	¹²⁹ I
18(10),16	-37 (-32), -14	33(28),26	29(33), 24

- The first for HBR fuels and the second for TP fuels
- All from PNL-7169 except the parentheses from PNL-7170 RT data

(2) Three groups of dissolution rate

- J-13 well water, synthetic groundwater, granitic groundwater, tap water, and distilled water: (2.4x10⁻⁴ ~5.4) mg m⁻² d⁻¹ at room temperature (RT)
- chloride solution: (5x10⁻³ ~5.7) mg m⁻² d⁻¹ at RT
- carbonate solution: (0.23 ~ 3.3) mg m⁻² d⁻¹ at RT

(3) Tests of particles may increase the dissolution rate by as high as a factor 10 compared with grain tests, but the difference depends on (a) test conditions such as flow-through or immersion, (b) marker representing the matrix dissolution, (c) chemistry inside waste package is not well known, (c) details of sample types such as size or oxidation state, (d) spent-fuel types such as fresh, archived, or different burnup, and (e) contribution of grain boundary inventory.

Model 3:

- user defined rate
- drip tests: (a) slow drip, (b) J-13 well water with Ca and Si ions (cations are partly depleted),
(C) high intensity of radiation
- others: W. Murphy

SURFACE AREA MODEL, DRY OXIDATION, AND PROMPT RELEASE

- grain model: $\sim 10 \mu\text{m}$ grains are exposed partially by grain boundary wetting.
- particle model: $\sim 1 \text{ mm}$ particles are exposed.
- * For a fixed volume of spent fuel, the total surface area is inversely proportional to the radius of grains or particles.
- * Uncertainties: grain boundary opening, release of grain boundary inventory, and marker of the dissolution rate
- dry oxidation:
 - (a) lower oxidation to $\text{UO}_{2.4}$ at below 250°C - diffusional oxidation leading to partial grain boundary opening
 - (b) higher oxidation to U_3O_8 at above 250°C - almost instantaneous leading to the exposure of subgrains
- prompt release: inventory of grain boundaries and gaps up to 6 %

NUMERICAL COMPARISON OF MODELS

Dissolution Rate (mg m ⁻² d ⁻¹) at 25° C	
This Base Model (NRC Model 2, Grain, Particle)	(1 ~ 5)x10 ⁻²
DOE Model (NRC Model 1, Pure Carbonate Solution, Grain, User Supplied)	~ 3 ([CO ₂]=2x10 ⁻³ M, P _{o₂} =0.2 atm, pH=8.4)
ANL Drip Test Model (NRC Model 3, Particle, User Supplied)	7 ~ 110

CLADDING PROTECTION

- Restrict reactive surface area or provide containment

Reduction of Radionuclide Releases from Perforated Cladding (Ahn, 1998)

Reduction of Radionuclide Release from Pinhole (~0.02 cm Diameter) or from Slit - (~0.015 Diameter x ~2.54 cm Length) Defected Cladding in J-13 Well Water. Ratios are Radionuclide Releases from defected-cladded Spent-Fuel to that from Bare Spent-Fuel Matrices. Data from Wilson (1990)

Radionuclide	Reduction in Release
Np-237	~ 1/70
Tc-99	~ 1/140
I-129	~ 1/(7x10 ⁵)
Sr-90	~ 1/65
Pu-(239+240)	~ 1/(7x10 ⁴)
Am-241	~ 1/(3x10 ⁵)

Data were selected for Cycle 2 and Cycle 3. The Cycle 1 data was the first semi-static immersion test and included the release of spent-fuel grains and the gap inventory. Cycle 2 tests were retests of first-cycled samples that had been placed in new leachant after removing the altered layer. In general, tests after Cycle 2 showed little gap inventory if it was not of a large amount initially. Detection limits of radionuclides were used in the calculation when hole-defected or slit-defected samples did not release detectable radionuclides.

Potential Degradation Mechanisms of Zircaloy Cladding

- **General Corrosion Rate of Zircaloy is Extremely Low Due to Protective ZrO_2 Passive Film**
- **Localized Corrosion (Pitting)**
 - **Neutral and Acidic Chloride Solutions**
 - **Above a Critical Potential, E_{rp} (Repassivation Potential)**
 - **E_{rp} can be Reached in the Presence of Oxidizing Species**
- **Stress Corrosion Cracking (SCC)**
 - **Same Environments and Potentials That Promote Pitting**
 - **Local Tensile Stresses Could Enhance Potential for SCC**

DOE has Considered the Possibility of Localized Corrosion and SCC of Zircaloy in the Presence of Oxidizing Chloride Solutions Unimportant

Cladding Degradation Mechanisms (*Continued*)

- **Diffusion-Controlled Cavity Growth (DCCG) Creep Failure Mechanism**
 - **Concern with Model Extrapolation to Lower Stresses and Temperatures**
 - **Cladding Temperature May Reach 500°C During Storage and Transportation**
 - **Corresponding Increase in Pressure**
- **Effect of Alternate EBS Design**
 - **Failure by Creep Rupture is Unlikely With No Backfill**
- **Delayed Hydride Cracking (DHC)**
 - **May not be Important Because the Operating Stress Intensity is Below the Crack Growth Threshold Stress Intensity, K_{IH}**
 - **May Need to be Reevaluated Considering Higher Stresses**

Cladding Degradation Mechanisms (*Continued*)

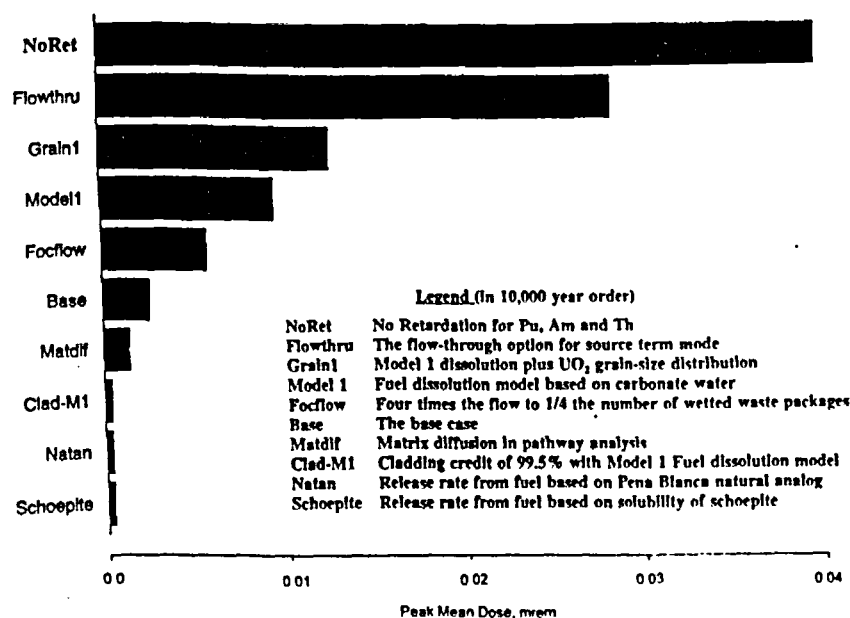
- **Hydride Embrittlement**
 - **Hydrogen Pick-up in the Repository Expected to be Small**
 - **Hydride Reorientation of Existing Circumferential Hydrides**
 - **Temperature**
 - **Stress**

Hydrogen Embrittlement May Be an Important Failure Mechanism Depending on the Cladding Temperature and Resulting Hydride Reorientation

TPA3.2 SENSITIVITY ANALYSIS (Codell, 1999)

- dissolution model
- potential colloid contribution

Peak Mean Dose for 10,000 Years



Peak Mean Dose for 50,000 Years

