# DISSOLUTION KINETICS OF SPENT NUCLEAR FUELS IN THE POTENTIAL YUCCA MOUNTAIN REPOSITORY ENVIRONMENT

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# OBJECTIVES

- **Survey literature to develop models for spent nuclear fuel (SNF) dissolution**
- **Develop models for SNF dissolution**
- **Develop technical support for the models for an independent analysis of a potential High-Level Waste (HLW) repository at Yucca Mountain (YM)**
- **Investigate the impact of developed models on repository performance using the Total-system Performance Assessment (TPA) Code jointly developed by the U. S. Nuclear Regulatory Commission (NRC) and Center for Nuclear Waste Regulatory Analyses (CNWRA)**

# BACKGROUND

- **Three Key Areas Controlling the Release Rate from the Engineered System in which SNF is Disposed:**

**(1) groundwater contact modes of SNF from component failure of waste package and drip shields**
**- drip vs. immersion conditions, drip rate effect, partial cladding protection**

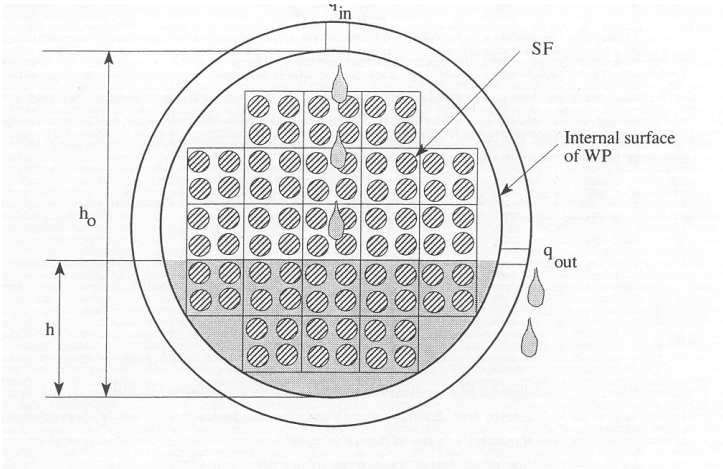
**(2) in-package environments**
**- availability of cations, carbonate concentration, pH, oxygen and iron concentration,**
**- temperature**

**(3) SNF conditions prior to aqueous dissolution**
**- oxidation, hydration, grain boundary radionuclide inventory**

# GROUNDWATER CONTACT MODES

**Perforations/Cracks on Waste Package**

- **uniform corrosion: uniform with dust deposits or seepage water; random patch penetration**
- **localized corrosion: random from salt deposits**
- **stress corrosion cracking: random vertically in closure welds**




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

- **ANL Drip Rates per Unit Surface Area of SNF:**

**1.3 x ($10^{-3}$ - $10^{-2}$) mL/cm$^2$-day [5.1x($10^{-4}$ – $10^{-3}$) in$^3$ / in$^2$–day]**

**(0.75 to 0.075 mL [4.6x($10^{-3}$ – $10^{-2}$) in$^3$] for 3.5 days, over about 10 SNF fragments, with each fragment 7.0 – 8.5 g [1.5 – 1.9, x$10^{-2}$ lb]) (Finn et al., 1998)**

- **Repository Seepage Rate per Unit Surface Area of SNF:**

**~ 1.7 x $10^{-4}$ mL/cm$^2$-day [6.7x$10^{-5}$ in$^3$ / in$^2$-day]**

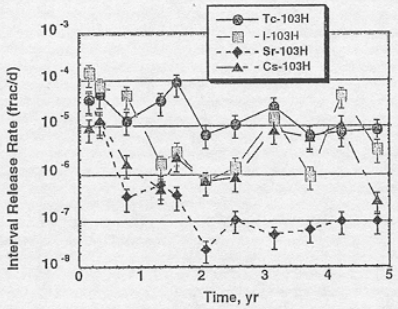
**groundwater seepage rate: (1.5 – 150) L/year [9.2x(10 – $10^3$ in$^3$/year]; focused seepage 1.5 x $10^4$ L/year [9.8x$10^3$ in$^3$/year]**

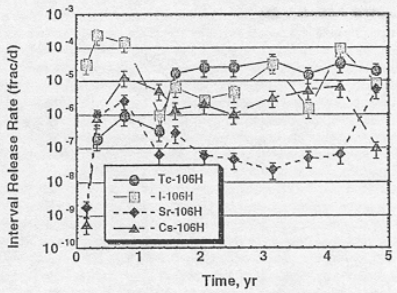
**SNF: 21 PWR assemblies with 264 rods (of ~0.2x0.2x0.2, cm,[0.08x0.08x0.08, in] pellets) per assembly**

# GROUNDWATER CONTACT MODES

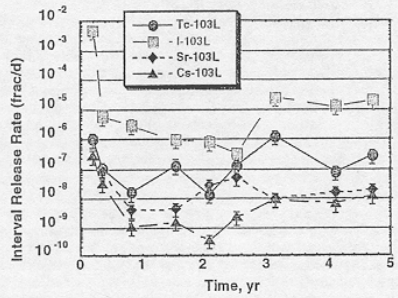
**SNF Drip Test Results of ANL with J-13 Well at 90°C (194°F) (high-drip-rate: 0.75 mL [4.6x10$^{-2}$ in$^3$ ], low-drip-rate: 0.075 mL [4.6x10$^{-3}$ in$^3$ , for 3.5 days, Cunnane, 1999)**

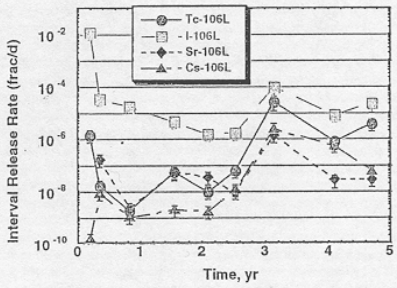
High-Drip-Rate




Low-Drip-Rate



# GROUNDWATER CONTACT MODES

## Relevant SNF Dissolution Rates in the Potential YM Repository

| Dissolution Rate ($mg/m^2$-d) | Sample | Solution | pH | T (°C) | Test Method | Reference |
|---|---|---|---|---|---|---|
| 0.2 - 1.0* | SNF | J-13 | 8.4 | 25 | I | Wilson, 1990 |
| 0.2 | Archived SNF | J-13 | 8.4 | 22 | FT | Gray and Wilson, 1995 |
| 0.07 | SNF | Allard Synthetic Ground Water | 8.1 | 20 - 25 | I | Forsyth, 1997 |
| X 5 | | | 3.2 | | | Forsyth and Wermer, 1985 |
| 0.023 - 0.165 | SIMFUEL | Allard and Granite Grounwater | near neutral | 25 | ** | Oversby and VMO Konsult, 1999 |
| 0.19 - 0.57 | SNF | Clay, Granite Groundwater | near neutral | 25 | I | Grambow et al., 2000 |
| 4.2 - 8.0 | SNF | J-13 | 8.4 | 90 | Drip | Finn et al., 2002 |
| 3 x ($10^{-2}$ - 1) | $UO_2$ | $NaHCO_3$ +$CaCl_2$ +Silicic Acid | 8.4 | 25 | FT | Gray and Wilson, 1995 |
| (0.8 - 2.5) x $10^{-2}$ | $UO_2$ | Silicate Solution | Near Neutral | 25 | FT | Tait and Luht, 1997 |
| 25 | SNF | 2 x $10^{-2}$ M total carbonate | 8 | 25 | FT | Gray, 1997 |
| 0.2 - 9.0 | SNF, $UO_2$ | 5 x ($10^{-4}$ - $10^{-2}$) M total carbonate | 8 - 10 | 25 | FT | TRW Environmental Safety Systems Inc., 2000 |
| x (10 - 20) | $UO_2$ | Dilute KCl or KOH $NaClO_4$ | ~ 3 w.r.t neutral | 25 | FT | Torrero et al., 1997 |
| | | | ~ 3 w.r.t neutral | 20 - 30 | I | Thomas and Till, 1984 |

*(~ x 1/140, partially cladded); ** static tests, increase ~ x2.5 in flow-through tests
I= Immersion, FT= Flow-through; SNF=Spent Nuclear Fuel
- Tc (Sr if Tc is unavailable) was used as a marker; all under oxidizing conditions otherwise specified

**mg/m2-d =1.42x10-9 lb/in2-d, 20 (68) , 22(71.6), 25 (77), 90 (194)° C(F)**

# GROUNDWATER CONTACT MODES
## *Partial Cladding Protection*

- **Slit (~0.015 cm [5.9x10$^{-3}$ in] dial. x ~2.54 cm [1 in] length)- or Hole (~ 0.02 cm [7.9 x 10 $^{-3}$ in] dial.)- Defected SNF Immersion Tests in J-13 Well Water at 85 °C (185 °F) (Wilson, 1990)**

  **- release decreased by a factor of ~ 140 for Tc-99, ~7 x 10$^{5}$ for I-129 and ~65 for Sr-90**

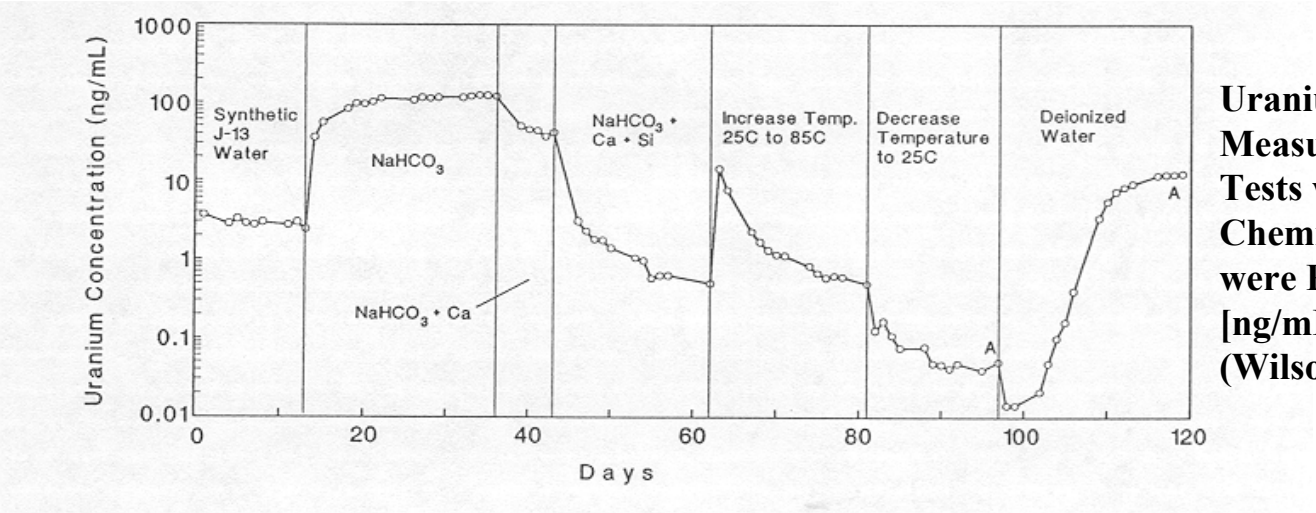
- **Drip Tests of Partial Clad Rod Segments (Goldberg, 2003)**

  **- Tc-99 release, 2.6 x 10$^{-8}$ fad (~ 0.04 mg/m$^{2}$-d [ 5.7x10 $^{-11}$ lb/in $^{3}$-d])**

- **No release decrease with half SNF surface area exposed in immersion tests (Forsyth, 1997; Forsyth and Wermer, 1985; Stroes-Gascoyne, 1985)**

- **Cladding Unzipping at 175 °C (347 °F) after ~1.5 years (Cunnane et al., 2003)**
  **- Under repository conditions it is of low probability, because (1) uniform corrosion rates are low and (2) low pH (less than 3 to cause localized corrosion) is of low probability.**

# ENVIRONMENTAL IN-PACKAGE CHEMISTRY
## *Cation Effects*



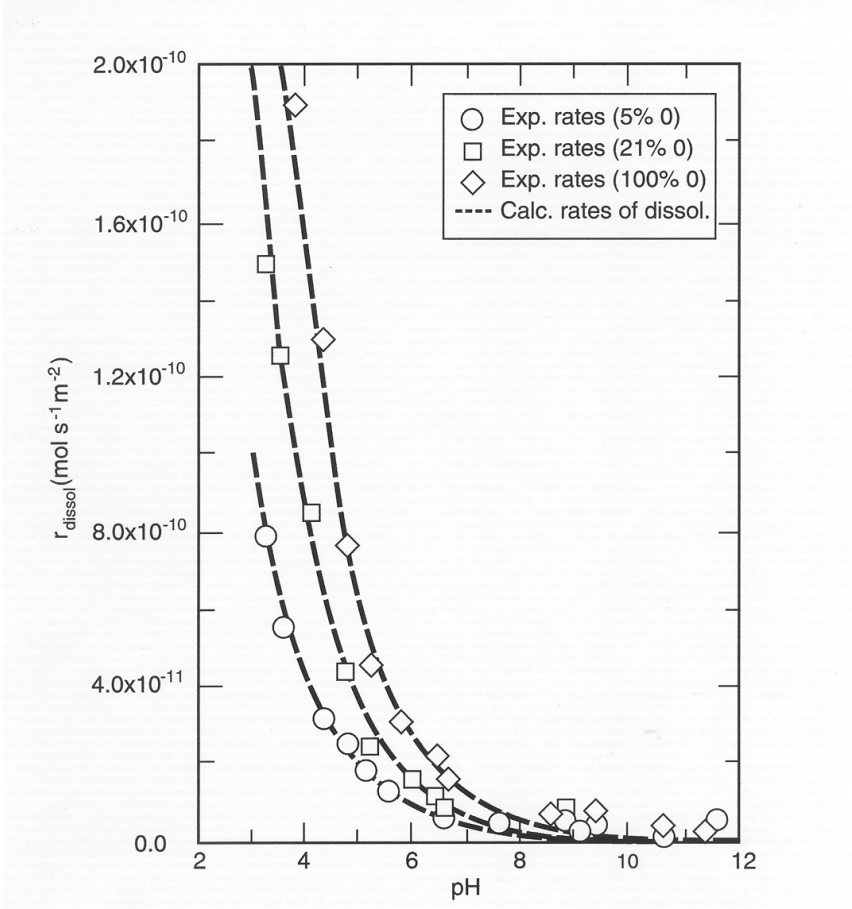

**Uranium Concentration Measured in a Flow-Through Tests with $UO_2$ where Water Chemistry and Temperature were Periodically Adjusted [ng/mL: $3.6 \times 10^{-11}$ lb/in$^3$] (Wilson and Gray, 1990)**

- **Ca and Si ($Ca^{2+}$ and $SiO_4^{4-}$) tend to decrease SNF dissolution rates by as much as or more than two orders of magnitude at 25 °C (77 °F) compared with those in carbonate solutions of ($2 \times 10^{-4}$ - $2 \times 10^{-2}$ M).**

- **Carbonates and low pH ease the inhibition effects of these cations. However, repository relevant solutions did not show the effects (Table).**

- **These ions may be depleted in drip tests. However, Schoepite formed instead could impede the oxygen transport to the bare SNF resulting in the decrease of the dissolution rates.**

# ENVIRONMENTAL IN-PACKAGE CHEMISTRY
## *pH Effects*




**Rates of $UO_2$ Dissolution as a Function of pH and Oxygen Concentration [mol/s-$m^2$ : $6.5x10^{-4}$ mol/s-$in^2$ ] (Torrero et al., 1997)**

- **Data under Oxidizing Conditions (Torrero et al., 1997, and Thomas and Till, 1984)**

  **- SNF dissolution rates increase by a factor of 10 – 20 at pH ~ 3, as the pH decreases below ~ 5.**

- **Metallic ions such as Cr ions from the proposed Department of Energy (DOE)'s WP and internal structure are responsible for low pH.**

- **Expected dilution of cation effects at low pH was not observed in Swedish tests in Allard Synthetic Ground Waster (Table)**

## ENVIRONMENTAL IN-PACKAGE CHEMISTRY

*Effects of Oxygen and Iron Concentration*

**- In the presence of steel components, local oxygen concentration may decrease.**

**- Decrease in SNF dissolution rates by more than an order of magnitude in SIMFUEL tests in NaCl solution at ambient temperature (Quiñones et al., 2001)**

**- The oxygen in the potential air-buffered YM repository environment is considered to be abundant to mask the radiolysis effects. Therefore, if iron effects would be significant to minimize air-buffered oxygen effects, the counter-balanced radiolysis effects would be minimal too.**

## ENVIRONMENTAL IN-PACKAGE CHEMISTRY

*Temperature Effects*

- **The activation energy varies depending on test conditions (Shoesmith, 2000): (29–34) kJ/mol (6.9 – 8.1 kcal/mol) in non-complexing neutral solutions; 47 kJ/mol (11.2 kcal/mol) in aerated carbonate solutions; 20 kJ/mol in distilled water; (26-31) kJ/mol (6.2 – 7.4 kcal/mol) in a borate-buffered granite groundwater;**
  **negative with mineral deposits; No activation at low pH**
- **(24 -33) kJ/mol (5.7 – 7.9 kcal/mol) for Tc-99 and I-129 from SNF immersion tests (Wilson, 1990)**

# CONDITIONS OF SNF PRIOR TO WASTE CONTACT
## *Oxidation/Hydration*

- **$UO_{2.4}$, $U_3O_8$, or $UO_3$ $xH_2O$ (x = 0.8, 2) dissolves similarly with unoxidized matrices.**

- **$UO_{2.4}$ tends to open up more grain boundaries increasing the dissolution rates by a factor of ~ 10 in $2x10^{-3}$ M of total carbonate, pH = 9, and temperature of 50 °C (122 °F) (Gray, 1997). $UO_{2.4}$ is likely to form during the early period in the initially failed WP at RH less than ~ 50. Grain boundary openings would be masked with alteration products in drip or immersion tests.**

- **$U_3O_8$, or $UO_3$ $xH_2O$ tends to become sub-grain sized powder, increasing exposed surface area by as much as two to three orders of magnitude. The drift could collapse, which could lead to higher temperatures of DOE's proposed WP above 250 °C (482 °F) (Manepally et al., 2003) necessary to form $U_3O_8$.**

- **In addition to $UO_3$ $xH_2O$ formation, vapor hydration or aqueous dissolution may weaken grain boundaries and any type of impact would result in powdering of the matrices into grains. High magnitude seismic events would occur at low but finite probabilities, leading to SNF powdering**

- **Sensitivity of dose to SNF powdering to grain level was evaluated using TPA Codes.**

# CONDITIONS OF SNF PRIOR TO WASTE CONTACT

## *Effects of Grain Boundary Inventory*

- **In the current DOE or NRC performance assessment models, the RN release from the inventory at grain boundaries is instantaneous. Therefore, it is necessary to determine the true matrix dissolution rates to determine the release rates of Tc-99 or I-129.**

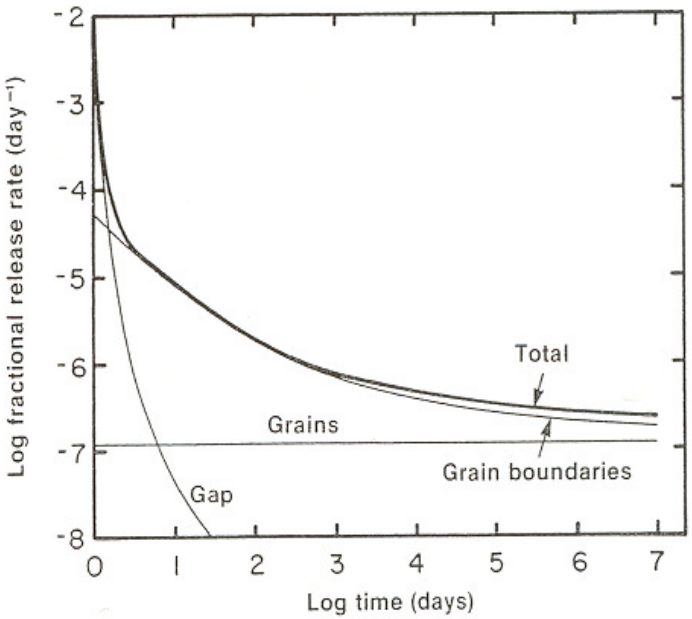
- **Whereas tests of SNF grains excluded the grain boundary inventories by pre-washing, tests with fragments under all conditions of immersion, drip or flow-through tests appear to measure a substantial amount of grain boundary inventory in the apparent matrix dissolution rates based on the release of Tc-99, I-129, Cs-137, or Sr-90.**

- **A significant portion of the released RN is from grain boundaries and the real matrix dissolution could be lower as indicated in the flow-through tests with addition of Ca/Si ions.**

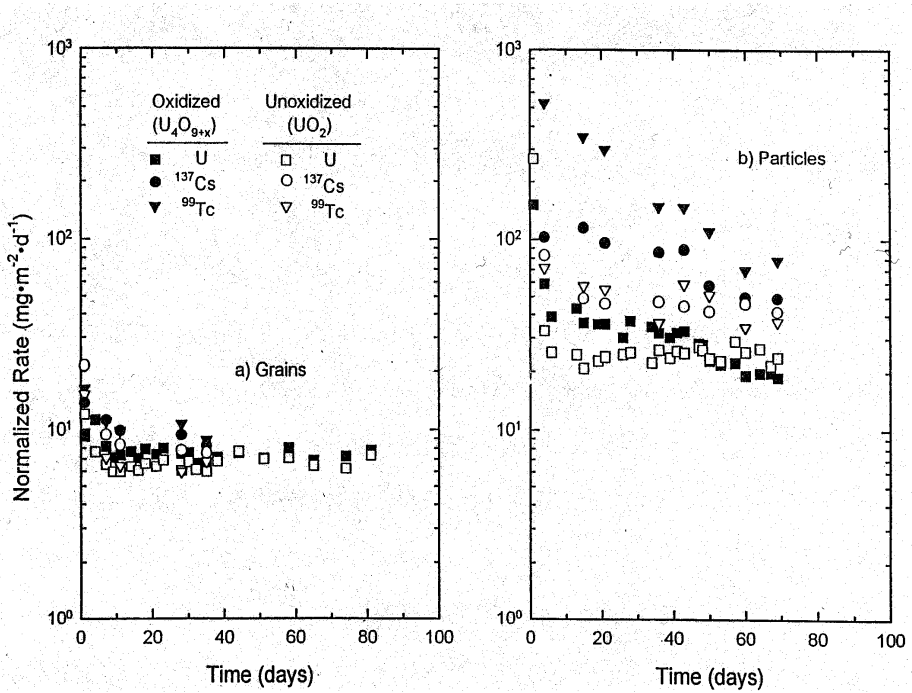
- **Base Calculations: an average 5 grain penetration, a grain boundary RN inventory ~ 2%, $10^{-6}$ /d release**

# CONDITIONS OF SNF PRIOR TO WASTE CONTACT

## *Effects of Grain Boundary Inventory*




**Schematic of Three Stages in Fission Product Release from Used Fuel (Johnson et al., 1985)**




**Dissolution Rates of ATM-105 Spent Fuel in 2 x $10^{-3}$ M $NaHCO_3/Na_2CO_3$, pH = 9, $O_2$ = 0.2 atm, 50°C (122 °F) (Gray and Wilson, 1995)**

# REPOSITORY SYSTEM-LEVEL SENSITIVITY STUDIES

- **Base Case SNF dissolution rate, r ($mg/m^2$-d):**

$$r = r_o \exp [ - E_o/RT]$$

**- $E_o$: activation energy, 29 kJ/mol, from immersion tests,**
**- $r_o$: pre-exponential coefficients and varies between 1.2 x ($10^3$ - $10^6$) $mg/m^2$-d [1.7x($10^{-6}$ – $10^{-3}$) $lb/in^2$-d ], selected to simulate the dissolution rates in the range 0.01 – 10 $mg/m^2$-d [1.42 x ($10^{-11}$ - $10^{-8}$) $lb/in^2$-d] at room temperatures and in mineral waters extending to low pH.**
**- extracted from Table considering *low drip rates, partial cladding protection, cation effects, low pH effects, iron effects, and the effects of grain boundary inventory*.**
**- In TPA, $r_o$ values are distributed in log-normal and sampled randomly.**

- **The dose from the base case above is 0.021 mrem/year in the year of ~10,000.**

**- first accelerated case: upper part of the base case, 3.6 $mg/m^2$-d [tot. carbonate: 0.002 M; oxygen: 0.2 atm; pH, 8; and 25 °C; Gray and Wilson, 1995; Mohanty et al., 2002], 0.047 mrem/year in year of ~10,000.**
**- second (plus first) accelerated case: powdering to grains, 0.0479 mrem/year in year of ~10,000.**

# CONCLUSIONS

- **Both immersion and drips would be groundwater contact modes with SNF at the potential YM repository.**
- **Current drip tests were conducted at drip rates much higher than the repository conditions where the SNF dissolution rates could be lower more than an order of magnitude.**
- **Partial cladding protection would decrease the SNF dissolution rates more than 50 times.**
- **Ca and Si ions could decrease the SNF dissolution rates more than an order of magnitude.**
- **Low pH (near 3) would increase the SNF dissolution rates as much as a factor of 20.**
- **Iron component could form reducing environments reducing the SNF dissolution rates more than an order of magnitude.**
- **Dry oxidation and hydration would occur in the early period for the initially failed DOE's proposed WPs at finite probabilities. This process would increase the effective surface area by a factor of (10 - 1000).**
- **The release from the grain boundary/gap inventory is substantial (2 – 10 times the matrix dissolution rates) in apparent releases.**
- **The base case model for TPA results in 0.021 mrem/year and the sensitivity studies of accelerated SNF dissolution rates result in 0.0472 and 0.0479 (powdering) mrem/year, peaks occurring at ~ 10,000 year.**

**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 is also an independent product of the Center for Nuclear Regulatory Analyses and does not necessarily reflect the view or regulatory position of the NRC.**

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