



*United States  
Nuclear Regulatory Commission*

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CLADDING CREDIT

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## **CONTENT OF PRESENTATION ON CLADDING CREDIT**

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- **Effectiveness of Cladding Protection**
- **Relevant Environments in the Repository**
- **Failure Modes**
  - **Localized Corrosion**
  - **Creep**
  - **Delayed Hydride Cracking (DHC)**
  - **Hydrogen Embrittlement (HE)**
  - **Mechanical Failure**
  - **Pellet Cladding Interaction (PCI) and Stress Corrosion Cracking (SCC)**
  - **Galvanic Corrosion and Microbial Corrosion**
  - **Volume Expansion and Splitting**
- **Radionuclide Release through Perforations**
- **Summary**

## EFFECTIVENESS OF CLADDING PROTECTION

- **Intact: oxidation kinetics in water (the same in air) is slow (Ahn, 1994, 1996).**

Thicknesses of Cladding Subjected to Oxidation and Transition Time From Pre-Transition Oxide to Post-Transition Oxide

Temperature (°C)	Transition Time (years)	Thickness Oxidized (cm for 10,000 years)		
		Pre-Transition and Post-Transition	Post-Transition Only	Cyclic Pre-Transition
100	$1.6 \times 10^5$	$2.9 \times 10^{-5}$	$4.6 \times 10^{-6}$	$2.9 \times 10^{-5}$
150	3,600	$2.4 \times 10^{-4}$	$2.4 \times 10^{-4}$	$2.4 \times 10^{-4}$
200	180	$5.6 \times 10^{-3}$	$5.6 \times 10^{-3}$	$5.6 \times 10^{-3}$

From the summaries made by Rothman (59) and Clayton and Fischer (60), the oxidation kinetics at 232 to approximately 400°C are: Pre-Transition  $\Delta W^3 = 6.36 \times 10^{11} \exp(-13,636/T) t$ , Post-Transition  $\Delta W = 75.3 \exp(-556/T) + 1.12 \times 10^8 \exp(-12,529/T) (t - t_p)$ , and  $t_p = 6.73 \times 10^4 \exp(11,975/T)$ , where " $\Delta W$ " is weight gain (mg/dm<sup>2</sup>), " $t$ " is time (day), and " $t_p$ " is time to transition (days). Zircaloy density is 6.56 (90) and radiation effects are assumed insignificant after fission products decay.

- **Nonintact (Perforated)**
  - Limited Water Intrusion through Pits and Cracks in Cladding
  - Limited Radionuclide Release through Pits and Cracks in Cladding

## RELEVANT ENVIRONMENTS IN THE REPOSITORY

- **Temperature (Siegmann, 1997)**
  - below maximum 330 C in center pin before 1000 yrs
  - below maximum 140 C in center pin after 1000 yrs
- **Relative Humidity (Buscheck, 1997)**
  - above 70 % after 2000 yrs
- **Stress (Siegmann, 1997)**
  - stress: (60 ~ 100) MPa for (40 ~ 60) MWd/kgU
  - stress intensity:
    - (0.28 ~ 0.40) MPa·m<sup>1/2</sup> for median crack for surviving reactor operation
    - (1.39 ~ 2.00) MPa·m<sup>1/2</sup> with probability  $6.8 \times 10^{-5}$  for the largest crack for surviving reactor operation

## LOCALIZED CORROSION

- Excellent Resistance to Crevice and Pitting Corrosion in Chloride Solutions at near neutral pH
- However, Can be Susceptible to Pitting Corrosion with
  - stable oxidizing species in chloride solutions at any pH (Maguire, 1984)

*Effect of ferric ion on  $E_{cor}$  and  $E_{sp}$  (volts versus SCE).*

HCl. M	Fe <sup>3+</sup> ppm	Temperature. °C	$E_{cor}$	$E_{sp}$
0.05	0	100	-0.13	0.21
	200	100	0.07	0.20
	1000	100	0.20	0.20
1	0	30	-0.05	0.10
	200	30	0.05	0.10
	1000	30	0.12	0.10
6	0	100	-0.34	-0.01
	200	100	-0.02	-0.03
	1000	100	0.00	-0.01
12	0	30	-0.66	-0.18
	500	30	-0.17	-0.17
	0	50	-0.64	-0.22
	500	50	-0.19	-0.19

For instance, ferric ion (Fe<sup>3+</sup>) is a soluble species at pH < ~4.5

- halide ions (Maguire, 1984)

HCl	$E_{sp} = 0.10 - 0.08 \log [Cl^-]$	$(0.005 < [Cl^-] < 3)$
KCl	$E_{sp} = 0.14 - 0.08 \log [Cl^-]$	$(0.005 < [Cl^-] < 1)$
HBr	$E_{sp} = 0.42 - 0.08 \log [Br^-]$	$(0.009 < [Br^-] < 0.6)$
KBr	$E_{sp} = 0.38 - 0.08 \log [Br^-]$	$(0.009 < [Br^-] < 2.6)$
HI	$E_{sp} = 0.62 - 0.13 \log [I^-]$	$(0.08 < [I^-] < 0.8)$
KI	$E_{sp} = 0.67 - 0.14 \log [I^-]$	$(0.3 < [I^-] < 3)$
$E_{sp}$ = repassivation potential in volts versus SCE		
[ ] = molar concentration of the respective halide ion		

- Gamma Radiolysis on the Cladding Surface
  - strength of gamma ray: a few tens of rads/hr within 5000 yrs (McCoy, 1997)
  - strong penetration at ~ 50 rads/hr
  - fixation of nitrogen: using Burns' formula (Burns, et al., 1982), water film is likely to become acidic, for time intervals of water drip, (1 year and 3.5 days), 4 µm film thickness, ~50 rads/hr, and G = 1.9 (Burns, et al., 1982). The role of cement in the acidification is speculative; there are other opinions that gamma ray is not strong enough to acidify the solution.
- Crevice environments are not known.

## CREEP

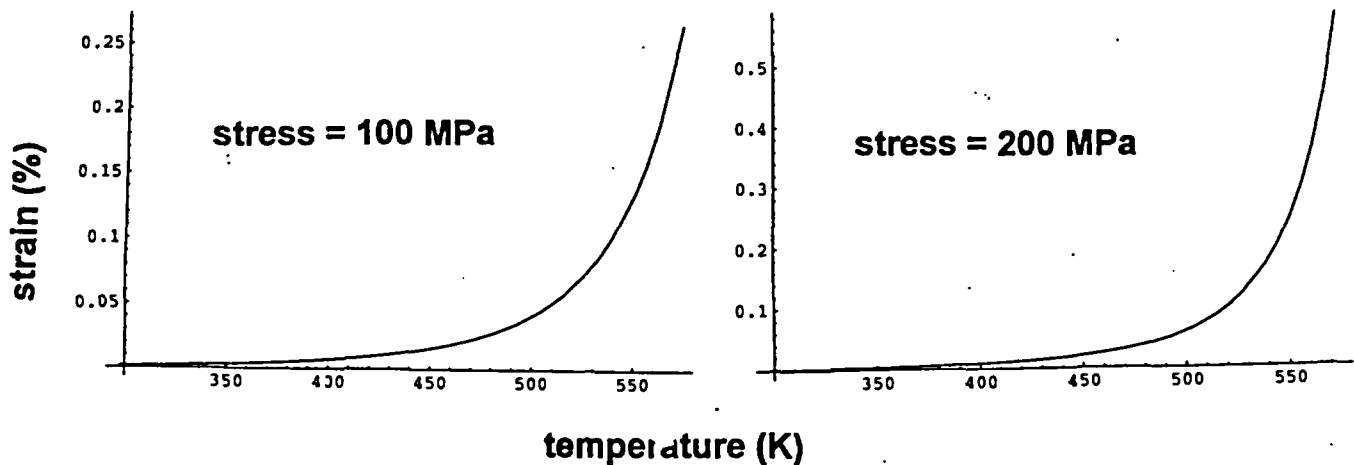
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- **Models**

- Mayuzumi, et al. (1989, 1991)
- Peehs (1985); and Romeiser (1979)
- Matsuo (1985, 1989)
- Chin, et al. (1988)

- **Evaluations using Peehs' Model**

- no failure, implying no perforation with less than 1 % strain

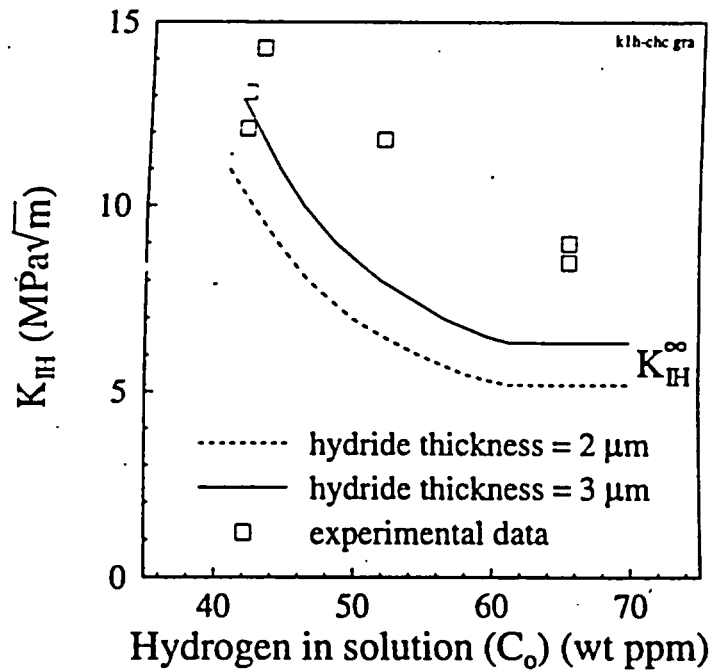


- However, Chin's model includes significant uncertainties associated with various parameters involved.
- Diffusion-controlled Cavity Growth (DCGG) (NRC, ongoing work) has not been proven and is likely to be a conservative assumption.

## DELAYED HYDRIDE CRACKING (DHC)

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- Hydride Precipitation at Crack Tip (Shi and Puls, 1994)



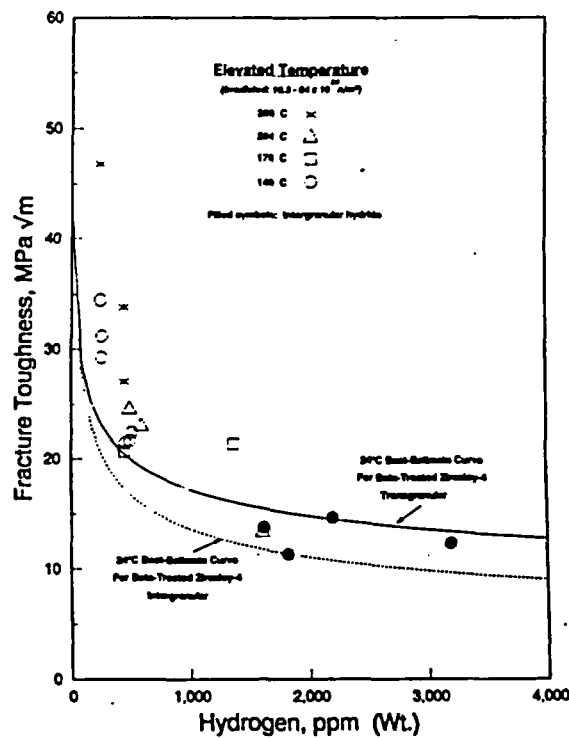
- Hydrogen Absorption:
  - Kinetics follows oxidation kinetics in aqueous environments.
 
$$\text{Zr} + \text{H}_2\text{O} \rightarrow \text{ZrO}_2 + \text{H}$$

$$\text{H} \rightarrow x\text{H}_{ab} \quad 0 < x < 1 \text{ (degree of H pick-up)}$$
  - If waste package (WP) lasts over 100 years, absorption will not be significant; Juvenile WP failure may have ~1300 ppm because of fast oxidation at elevated temperatures ( $K_{IH} \sim 12 \text{ MPa} \cdot \text{m}^{1/2}$ ) (Siegmann, 1998)
  - Radiolysis effects are not known.

## HYDROGEN EMBRITTLEMENT (HE)

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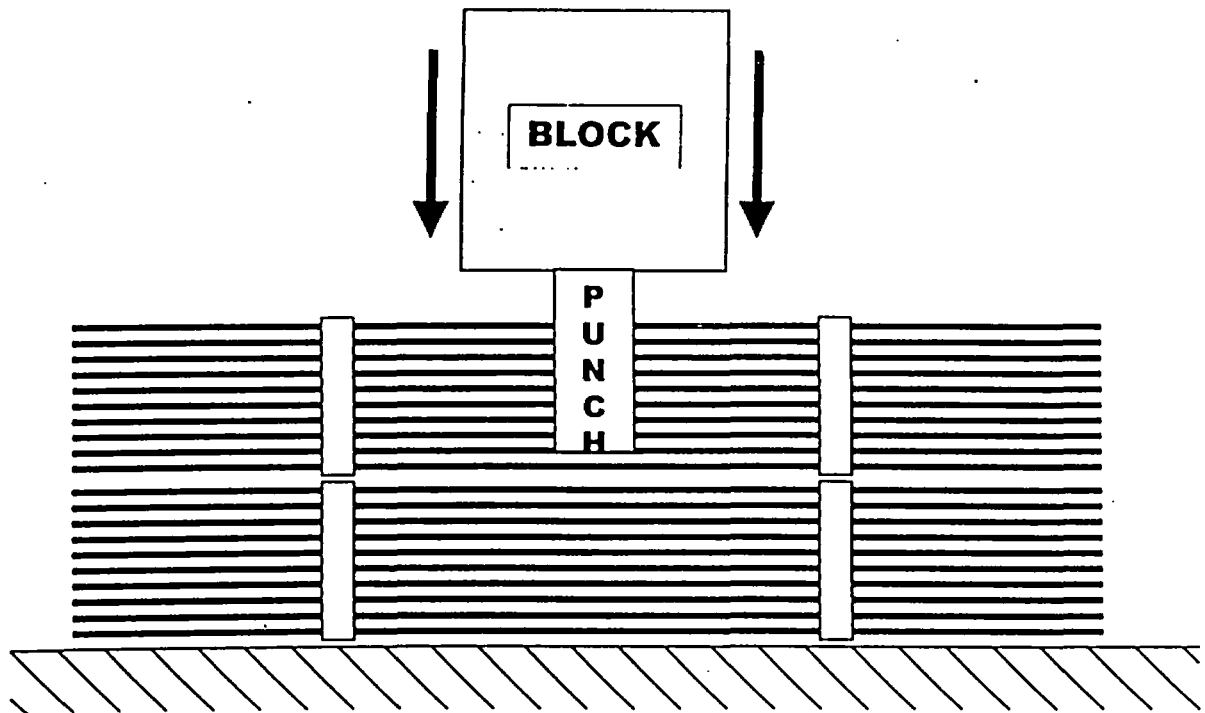
- **Hydride Reorientation**
  - Hydride dissolution at  $\sim 400$  C and  $\sim 95$  MPa (Chan, 1996)
  - More difficult reorientation (tabulation, Siegmann, 1997)
- **Toughness**
  - $K_{IH}$  :  $\sim 20 \text{ MPa}\cdot\text{m}^{1/2}$  to  $\sim 2 \text{ MPa}\cdot\text{m}^{1/2}$   
with 76 ppm hydrogen (Chan, 1996).
  - Toughness Data by Kreyns, et al. (1996)



## MECHANICAL FAILURE

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- **Rockfall Model (McCoy, 1997)**



- **Surface Area Exposure: (0.5 ~ 2.2) %**



## **PELLET CLADDING INTERACTION (PCI) AND STRESS CORROSION CRACKING (SCC)**

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- **PCI:** no evidence for iodine-induced SCC; the PCI failure is likely to be related to hydrogen or oxygen effects; and dynamic toughness for PCI is  $(5 \sim 10) \text{ MPa}\cdot\text{m}^{1/2}$  (Chung, 1997)
- **SCC:** likely to occur under conditions promoting localized corrosion in the presence of large hoop stress. SCC occurs above  $E_{cp}$  in chloride solutions (Cox, 1973; Cragnolino, 1975)

## **GALVANIC CORROSION AND MICROBIAL CORROSION**

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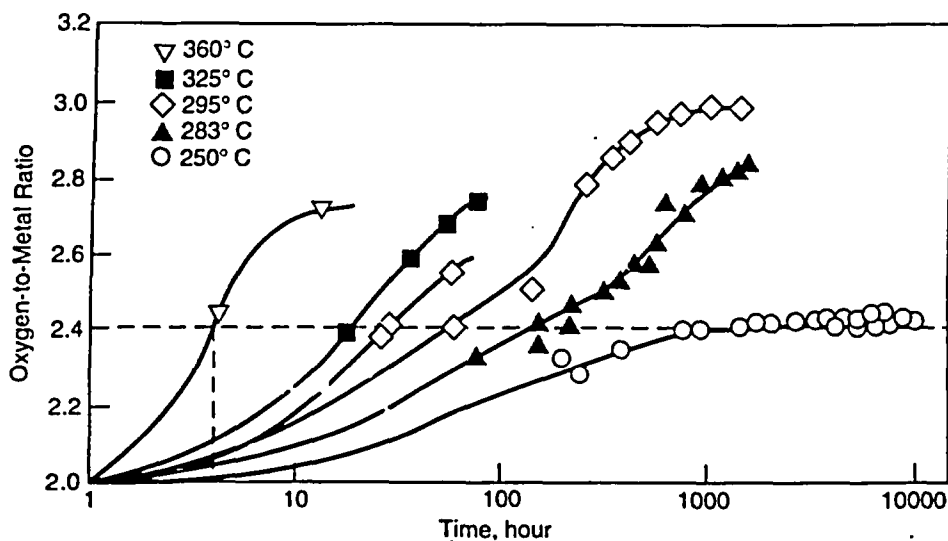
- **Galvanic Corrosion:** likely to be cathodic to spent fuel and carbon steel, and comparable to high-nickel alloys
- **Microbial Corrosion:** minimal if Zircaloy behaves like Titanium which apparently exhibits immunity to microbial corrosion.

## VOLUME EXPANSION AND SPLITTING

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- **Volume Expansion:**

- fraction of 1.36 for  $U_3O_8$  from  $UO_2$
- fraction of (2.67 ~ 5.55) for secondary minerals from uraninite (tabulation, Lichtner, 1994)
- based on linear elasticity, the stress associated with volume expansion (Ahn, 1996) exceeds the cladding strength.
- kinetics of  $U_3O_8$  formation (Einziger et al., 1992; Ahn, 1996)



- The altered phase is likely to be powdery and may not push adjacent rods at ~0.5 cm distance.
- It is considered that dissolved uranium may diffuse (or drip) out of cladding prior to secondary mineral formation. Even in the humid environment, Argonne National Laboratory (ANL) reports that water still condenses and drips.

## RADIONUCLIDE RELEASE THROUGH PERFORATIONS

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- **Decrease of Surface Area**
  - slit and pinhole defects:  $10^{-3} \sim 10^{-3}$  (Wilson, 1990)
  - with an asymptotic pit density  $\sim 6/\text{inch}^2$  for through-wall pits (Sridhar, 1998) and pit size ( $10^{-4} \sim 10^{-1}$ ) cm (Ahn, 1994):  $2 \times (10^{-3} \sim 10^{-3})$
  - DHC or creep rupture:  $4 \times 10^{-6}$  (Johnson, 1998)
- **Limited Release through Perforations (Zwahlen, et al., 1990)**
  - limited radionuclide release controlled by perforation size and effective diffusivity that is modified by density (or porosity) and sorption inside perforations; detailed multi-component analyses are required.
  - perforations are effective in decreasing gaseous release (Ahn, 1994).
- **The Stability of Perforations (e.g., Pits) are not Known.**

Reduction of Radionuclide Releases from Pinhole ( $\sim 0.02$  cm Diameter) or from Slit ( $\sim 0.015$  Diameter  $\times$   $\sim 2.54$  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	$\sim 1/70$
Tc-99	$\sim 1/460$
I-129	$\sim 1/(7 \times 10^5)$
Sr-90	$\sim 1/65$
Pu-(239+240)	$\sim 1/(7 \times 10^4)$
Am-241	$\sim 1/(3 \times 10^5)$

\*: 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.

- **TPA Exercises: (R. Codell presentation) radionuclide releases could be reduced significantly, if only  $\sim 0.5$  % spent-fuel surface is exposed.**

## **SUMMARY**

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- **Rockfall could damage cladding after substantial decrease in the wall thickness of outer steel container (estimated to occur after long time, i.e., greater than 5,000 years).**
- **Radionuclide releases could be reduced significantly, if only ~ 0.5 % spent- fuel surface is exposed.**
- **There are uncertainties associated with cladding failure by crevice and pitting corrosion, SCC, HE, and splitting by the formation of secondary minerals, although these processes appear to be of secondary importance to radionuclide release.**
- **Cladding failure by creep, DHC, and PCI are also likely to be insignificant in terms of release.**
- **Water intrusion through cladding perforations and wetting characteristics of bare spent-fuel are not well understood.**