Timothy Bowers

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Test 4: NE 533

1) Zrlo $T=625k$ $t=400$ days $t_c = 500\mu m$

a) $t^* = 6.62\times10^{-7}\exp\left(\frac{11949}{625}\right) = 133$ days $t^* < t$

$\delta^* = 5.1\exp\left(\frac{-550}{625}\right) = 2.115\ \mu m$

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$k_L = 7.48\times10^{6}\exp\left(\frac{-12500}{625}\right) = 1.54\times10^{-2}\ \frac{\mu m}{day}$

$\delta = \delta^* + k_L(t-t^*) = 2.115\mu m + 1.54\times10^{-2}(400-133) = \boxed{6.2268\mu m}$

b) $f=0.18$ $PBR=1.56$ $\rho_{Zr} = 6.5\frac{g}{cm^3}$ $\rho_{ZrO_2} = 5.68\frac{g}{cm^3}$ $C_H = ?$

$f^o_{ZrO_2} = \frac{32}{91+32}$, $\frac{M_H}{M_O} = \frac{1}{16}$

$t = 365$ dy

$$C_H = \frac{2f\delta\rho_{ZrO_2} f^o_{ZrO_2}\frac{M_H}{M_O}}{(t_c - \frac{\delta}{PBR})\rho_{Zr}}\times10^6 = \frac{2(0.18)(5.68)(\frac{32}{91+32})(\frac{1}{16})(6.2268)}{(500 - \frac{6.2268}{1.56})(6.5)}\times10^6 = \boxed{64.215\text{ wt ppm pickup}}$$

2) O spieces diffusion is the rate limiting step in aqueous corrosion of Zr cladding.

$H_2O \mid O^{-2} \rightarrow ZrO_2 + 2e^- \mid Zr$

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Therefore, increases in temperature increase corrosion rate since diffusion follows Arrhenius behavior.

3) The Pilling-Bedworth ratio is the ratio of oxide volume to metal volume. It tells the oxide layer stability where for PBR<1 the oxide layer provides no additional protection to the metal. For PBR>2 the oxide layer falls off and does not slow down oxidation. For 1<PBR<2, the oxide layer is passivating with parabolic decrease in corrosion rate over time.

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4) Hydrides form in cool, high stress areas of the cladding. The Soret effect, which states that more ~~hydrides~~ would ~~form~~ build up in low temperature areas, and increased crystal lattice spacing from the strain are ~~more~~ more energetically stable locations for ~~hydrides~~ to ~~form~~ amass. As a result, hydrides tend to build up in the rim ~~of~~ the cladding (~50-60 μm). They are circumferential during reactor operations and radial after dry when removed from a reactor. Hydrides cause embrittlement, decrease fracture toughness, enable delayed hydride cracking phenomena, increase corrosion rate, and increase irradiation growth.

14/14

5) A Reactivity Initiated Accident (RIA) is a design basis accident that often sets some reactor operation limits. In a PWR a Control Rod Ejection Accident (CREA)
11/14 occurs when mechanical failure of the control rod housing enables coolant pressure to eject a control rod. This ~~normally~~ could happen as fast as ~~At~~ 0.1s and is worse when the reactor is at normal operating temperature and pressure at low or zero power, but critical. In a BWR, a Control Rod Drop Accident (CRDA) occurs when the control rod blade separates from the control rod mechanism and the blade drops in free fall out of the reactor. This event also occurs quickly, and is worse when in normal operating conditions at low-to-zero power, but critical. During a RIA, a rapid insertion of reactivity (by removing negative reactivity quickly) causes a fast increase in core power. Accident outcomes vary based on the power spike magnitude and pulse, but worst case outcomes include cladding ballooning and rupture, steam pulse from pellet fragments, and potential release of fission products outside of containment.

- Wanted more description of material effects/evolution

6) A Loss of Coolant Accident (LOCA) is a design basis accident that often sets some reactor design features and operating limits. During
12/14 a LOCA some rupture to the primary system removes cooling from the reactor since it flashes to steam and leaves the loop(s). The reactor is SCRAMed, but decay heat can cause a reactor melt down if core cooling is not restored. During a LOCA increases in rod temperature cause ballooning and an resultant rod rupture releasing fission products into the primary which has a leak, defeating multiple layers of

containment. A water deluge system can restore cooling, but can induce a thermal shock on the cladding increasing rod failure probability. This is different from a LOCA because it happens over a longer time frame.

-Still wanted a bit more...

7) Burnup increases fission gas inventory, embrittles rod materials, and reduces the rod gap due to creep. The combination of these effects makes a reactor more likely to fail due to a departure from nucleate boiling event (overpower) early in life when high power exceeds thermal removal capability, and more likely to fail due to pellet cladding mechanical interaction at the end of life when overpower increases cladding stress beyond its strength and breaches the cladding.

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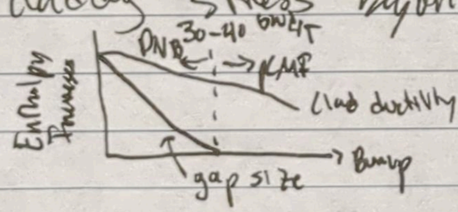

8) The four pathways to make a fuel/cladding system more accident tolerant are:

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1) Improve reaction kinetics with steam: Cladding coatings, like chromium improve high T steam performance of the reactor (not as much over 1200°C)

2) Improve cladding properties: Use a different cladding system (like FeCrAl cladding) that has better corrosion performance.

3) Improve fuel properties: Using a Urania-based fuel uses additives to improve fuel pellet thermal conductivity.

4) Enhance fission product retention: Using a fully ceramic micro-encapsulated (FCM) fuel adds another layer of containment to the system.

9) Zirconium cladding oxidizes rapidly when exposed to high temperature steam. Oxidation is linear on bare metal and parabolic on a filmed surface, however above 1000°C high temperature steam accelerates corrosion back to linear rates or worse.

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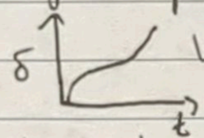

8 hours @ 1200°C oxidizes all cladding in experiments, while 8 hours at 1000°C just has a thick layer. - high T leads to phase changes

10) Fuel rod internal pressure, power to melt, and cladding oxidation and hydrogen build up influence PWR operations. Exceeding limits set by these requirements challenges cladding integrity and containment.

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11) CRUD on the cladding surface increases centerline temperature by adding another temperature layer to overcome, and increases the radioactivity of the constituents (like Co60 and Ni63). CRUD can accumulate outside of the reactor, raising the radioactivity surrounding the primary system. Personnel must not exceed dosage levels per federal regulation.

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12) Balancing Boric acid and LiOH to keep pH > 6.9 and adding zinc to the coolant improve performance. keeping pH >6.9 preferentially deposits CRUD on non-reactor surfaces. Adding zinc ~~inhibits~~ reduces stress corrosion cracking and competes with Co60 deposition, allowing more time for it to be caught in the filter.

6/6

NE533 Test 4 Crib Sheet

Timothy Bones

$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$

Corrosion reactions require oxidant + electric current, net is composite of an oxidation + reduction reaction. Oxidation takes place at an anode but reduce H else where as a cathode

Thermodynamics state if reaction will occur, kinetics set the rate I total current

Types: 1) uniform: thin layer on surface 2) nodular: small, circular oxide blisters
3) Shadow: local regions that mirror shapes of nearby noble reactor components

Formation:

$H_2O \mid Zr$

Oxidation

$Zr(s) \rightarrow Zr^{4+}(aq) + 4e^-$

$Zr(aq)^{4+} + 2H_2O(l) \rightarrow ZrO_2(s) + 4H^+(aq)$

Reduction reaction

$4e^- + 4H^+(aq) \rightarrow 2H_2$

Growth:

$H_2O \mid O^{-2}\rightarrow \; ZrO_2 \; \leftarrow e^- \mid Zr$

$2H_2O(l) \rightarrow 2O(aq)^{-2} + 4H^+(aq)$

$Zr^{4+} + 2O^{-2} \rightarrow ZrO_2 + 4e^-$

$4e^- + 4H^+(aq) \rightarrow 2H_2$

Transport of O is rate limiting, diffusion process, homo layer, no oxide loss all oxygen to oxide, no saturation of ions in oxide

$\frac{\delta^2}{2} = k^2 t \rightarrow \delta = k t^{1/2}$

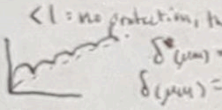
Observed kinetics slower than parabolic: additional ions, non-uniform $\vec{E}$ in oxide layer

$W = \frac{m_2 - m_1}{S}$; $\delta(\mu m) = \frac{W(mg/dm^2)}{14.7}$

Pilling-Bedworth ratio: PBR: Ratio of volume oxide to volume metal

$L_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n\, M_{metal} \cdot \rho_{oxide}}$

<1: no protection, thin + broken ; 1<PBR<2: passivating ; >2: spalling



$\delta^*(\mu m) = 5.1 \exp(\frac{-550}{T})$; $t^*(d) = 6.62 \times 10^{-7} \exp(\frac{11949}{T})$

$\delta(\mu m) = \delta^* + k_L (t - t^*)$; $k_L(\frac{\mu m}{d}) = 7.48 \times 10^6 \exp(\frac{-12500}{T})$

Temperature + Irradiation accelerate corrosion rates

Zr 22 $\frac{W}{mK}$; ZrO_2 1.7–2.7 $\frac{W}{mK}$; Brittle hydrides ; less metal

Oxide layer is micro crystalline, initially equiaxed, growing into columnar grains

Hydrogen pickup causes embrittlement, ↓ fracture toughness, DHC, ↑ corrosion, ↑ irradiation growth

Diffusion: $D_{Zr}^H = D_0^H \exp(-E_m^H / k_B T)$; $E_m^H = 0.47\,eV$; $D_0^H = 7 \times 10^{-3} \frac{cm^2}{s}$; $t = \frac{L^2}{4 D_{Zr}^H}$

$D_{Zr}^H = 7 \times 10^{-3} \exp(-0.47 / k_B (355 + 273.15)) = 1.19e{-6} \frac{cm^2}{s}$; 12 min time

Hydrogen goes to high stress, low temp areas forming hydrides

Hydride rim from Soret effect (thermal) ~ 50–60 μm

Reactor conditions cause circumferential hydrides, radial hydrides reprecipitate outside reactor from tensile stress

DHC: driving force for diffusion is stress field potential vs grad chemical potential precipitates at crack tip

$f_H = \frac{H_{absorbed}}{H_{generated}}$; $J_H = 2 f J_O$; $C_H^{clad}(wt\,ppm) = \frac{m_H}{m_{Zr}} = \frac{2 f m_O}{m_{Zr}} = \frac{2 f \delta \rho_{oxide} f_{O,ox}^{\circ} M_H/M_O}{(t - \frac{\delta}{PBR})\rho_{metal}} \times 10^6$

H pickup, diffuse quick, hydrides form ($C_{ss}(T)$), reduce ductility,

Design Basis Accident (DBA): Reactivity initiated accident (RIA); Loss of coolant accident (LOCA)

Beyond DBA: Too unlikely

Reactivity: $\delta k = k - 1/k$; $k = \varepsilon L_f p L_{th} f \eta$; ε: fast fission factor L_f: fast non-leakage ; p: resonance escape probability L_{th}: thermal non-leakage ; f: thermal fuel utilization η: reproduction factor

Ideally negative reactivity feedback

RIA: PWR = Rod ejection BWR: Rod dropped

Control Rod Ejection Accident (CREA): mech failure of CR housing, coolant pressure ejects rod 0.1 s, worst at HZP and $P_{th} = 0$ but critical

Control Rod Drop Accident (CRDA): Blade separation from mechanism, drops in free fall

Ex: 1952 NRX at Chalk River, 1961 SL-1, K-431 Ru Echo II sub '85; Chernobyl 1986

Chernobyl: light water graphite moderated (RBMK); bad feedback, test conditions

RIA

↑ fuel temp

Solid thermal expansion; expansion of fission gas

Hydrides → ↓ Ductility

gap closing → PCMI, early DNB → clad temp ↑

fuller expansion

grain boundary separation

clad cracking

Hydride assisted PCMI

clad straining, ballooning failure

Brittle failure oxidation

fission gas release, rod pressure ↑

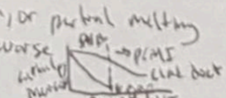
Fuel fragmentation

Fuel-water interaction

Cladding fails from PCMI, balloon/burst, severe oxidation, or partial melting

Pulse defined by total integrated energy, sharper spike worse

Pellet fragment ejection generates steam rapidly



LOCA: ΔP causes cladding ballooning, limiting cooling flow

Zr → α+β @ 850C β @ 1000C ; O content stabilizes α+β, but less ductile

Oxidation increase at high temp. Exothermic oxidation runaway w/ no cooling (TMI) excess H_2 gas in containment (Fukushima)

Quenching thermal shock may cause fragmentation

Accident tolerant fuels: ↑ coping time, ↑ time to melt, ↑ time to melt beam pray

Improve reaction kinetics w/ steam
- ↓ oxidation heat
- ↓ oxidation rate
- ↓ hydrogen production
- ↓ hydrogen embrittlement

Improve clad properties
- ↑ resistance to clad fracture
- ↑ geometry stability
- ↑ thermal shock resistance
- ↑ melt temp
- ↓ fuel-clad interaction

Improve fuel properties
- ↓ fuel op temp
- ↓ cladding internal oxidation
- ↓ fuel relocation
- ↑ melt temp

Enhance fission product retention
- retain gaseous + solid FPs

Improvements

near term: clad coating to improve high T steam; uranium-based fuel, additives ↑ thermal cond } drop in

Mid fuel + cladding: U_3Si_2 fuels, FeCrAl cladding, ~ layers out

Transformational: fully ceramic micro-encapsulated (FCM) fuel SiC/SiC composite cladding

Safety limits: Clad temp max 1204°C, local oxidation ≤ 17% wall thickness
H generated < 1% if all Zr was oxidized ; radiation dose limits

Steam oxidation: linear δ ∝ kt for some/then $\delta^2 \propto kt$ for thin, but not specified below 600°C parabolic 800°C

8 hrs @ 800C gone @1000°C cracked + breach @1200°C all oxidized

$UO_2 \rightarrow U_3O_8 \rightarrow$ U... in water

Fe-Cr-Al oxide at 1200°C, but better corrosion, SiC cladding even better

Cr coating better performance to 1000°C, no help at 1200°C

PCMI: total permanent hoop strain limited to 1%

Cladding elongation + assembly bow: fuel rod bow + potential grade assembly bow

Cladding oxidation + hydrogen pickup: H > 70–100 ppm = hydrides, t_{ox} < 10% ~ 100 μm

Cladding wear: fretting cumulative wear < 10% thickness reduction

Power to melt: T ~ 2750°C @ 50 MWd/kgU 600 W/cm needed to melt

Fuel rod internal pressure: overpressure must < 8 MPa

DNB + Normal operating limits - 1.3 DNBR set limit

Chemistry: Control pH, avoid corrosion + solutes

CRUD accumulates on Ni alloy + Stainless components, is Ni, Fe, Co: 1.060 + Ni: 0.3

Boric acid + LiOH → pH > 6.9 ↓ Crud buildup + Zinc inhibits SCC + dams to boiling

Zinc + cobalt favor tetrahedral sites in spinel structure, more pickup from

BWR use hydrogen + noble metal (Pt) to reduce SCC + Zn injection

Zn + noble metal ↑ CRUD on fuel + oxide layer spalling

1) Coupon 8 cm × 8 cm × 1 mm, m_1 = 35 g Δm = 1 g δ = ?

$W = \frac{\Delta m}{S} = \frac{1g}{0.64 dm^2} = \frac{1000 mg}{0.64 dm^2} = 1562.5 \frac{mg}{dm^2}$; $\delta = \frac{W}{14.7} = \frac{1562.5}{14.7} = 106.3 \mu m$

2) Power law: t = 300 days T = 600 K δ = ?

$t^* = 6.62 \times 10^{-7} \exp(\frac{11949}{600}) = 295$ days $t > t^*$ ✓

$\delta^* = 5.1 \exp(\frac{-550}{600}) = 2.039 \mu m$

$k_L = 7.48e6 \exp(\frac{-12500}{600}) = 6.7e{-3} \frac{\mu m}{day}$

$\delta = 2.039 + 6.7e{-3}(300 - 295) = 2.073 \mu m$

3) Hydrogen concentration from problem 2

$t_c = 0.1\,cm$ f = 0.15 $\rho_{Zr} = 6.5 \frac{g}{cm^3}$ $\rho_{ZrO_2} = 5.68 \frac{g}{cm^3}$

$C_H(wt\,ppm) = \frac{2 f \delta \rho_{ZrO_2} f_{ZrO_2}^{\circ} \frac{M_H}{M_O}}{(t_c - \frac{\delta}{PBR})\rho_{Zr}} \times 10^6$; $f_{ZrO_2}^{\circ} = \frac{32}{91+32}$, $\frac{M_H}{M_O} = \frac{1}{16}$, PBR = 1.56

$t_c = 1000 \mu m$

$C_H = \frac{2(0.15)(2.073)(5.68)(\frac{32}{91+32})(\frac{1}{16})}{(1000 - \frac{2.073}{1.56})(6.5)} \times 10^6 = 58.19$ wt ppm