SCIENTIFIC NOTEBOOK # 1093E

Evaluation of Drying Adequacy for Extended Spent Fuel Dry Storage

Project Number: 20.14010.01.002

ISSUED TO **Hundal (Andy) Jung**

ON **September 29, 2011**

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Table of Contents

Initial Entries

Title: Evaluation of drying adequacy for extended spent fuel dry storage - cladding and fuel oxidation and amount of residual water

Investigators: Hundal (Andy) Jung (HJ) Division 20.

Objectives: (i) To evaluate effects of cladding oxidation of the zirconium alloy cladding and spent fuel oxidation at the breached area due to incomplete drying on the integrity of cladding materials during the extended dry storage period and (ii) to estimate amount of residual water after drying process

Software used: MS Excel 2007

Entry start date: 9/29/2011

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Entry date: 9/29/2011

Evaluation of Issue on Cladding Oxidation

Issue Description:

In the presence of residual water and/or oxygen in the dry storage canister, additional oxidation in humid air or aqueous corrosion of cladding is possible during the extended storage period. Continuous growth of zirconium oxide or hydroxide can degrade the integrity of passive film formed on the intact cladding surface and subsequent volume expansion associated with oxidation and/or hydration of cladding may crack or unzip the initially defective cladding (assuming 1% defective cladding). From the 1.5 years long term test of cladding tested in humid air at 175 °C conducted by Argonne National Laboratory, splitting/unzipping of cladding was observed due to hoop stress generated by corrosion product accumulation in the gap and the cladding matrix (Cunnane, et al., 2003). Together with fuel pellet swelling due to internal gas pressure increase and more oxidation/hydration of spent fuel, cladding can further damage.

Technical approach and plan:

Because cladding damage is closely related to the thickness of oxide/hydroxide layer and microstructure on the cladding surface, analysis with numerical calculation to estimate the thickness will be conducted by utilizing known kinetic growth models and mass balance reaction equation. Literature information on oxidation and corrosion rates in the presence of water radiolysis will be also extensively used in calculation. The estimation will consider several factors including temperature, storage time, and relative humidity in a range of residual water volume (1 to 55 moles). High burnup effect on cladding oxidation will be also evaluated in terms of oxide thickness and potential changes of oxide microstructure. Integration with cladding hydrogen absorption, fuel swelling and oxidation will be also considered. Cladding materials evaluated will include traditional zircaloy and advance zirconium-based alloys such as Zirlo™, M5® in particular, for high burnup effect.

Expected outcome:

The thickness of oxide layer on the cladding and wall thinning will be estimated with storage time. With integration of cladding hydrogen absorption, fuel swelling and oxidation, determination will be made on whether not the integrity of cladding will be adversely affected by additional oxidation during the extended storage period.

Assumption**:** The dry storage system is a closed system without ingress or egress with environment outside of the cask.

Cunnane, J., W. Ebert, M. Goldberg, R. Finch, and C. Mertz, “Yucca Mountain Project Report, Waste Form Testing Work” Argonne National Laboratory, Chemical Technology Division, 2003.

Fuel Oxidation when Cladding Breaches Are present

Issue Description:

When cladding breaches are present, irradiated UO_2 fuel can react with O_2 from water radiolysis and/or water vapor from evaporation of residual water to form more oxidized forms such as $UO_{2.4}$, U_3O_8, or $UO_3.xH_2O$. Especially, with oxidation to U_3O_8, volume expansion will be approximately 38 %, leading to fuel swelling. If there is enough oxidation on the fuel surface, unzipping of cladding at the defected area (cracks) could occur. Also oxidation can take place preferentially along grain boundaries because the grain boundaries are opened up by most of the fission gas bubbles and tunnels formed from the in-reactor irradiation process. U_3O_8 formed by oxidation of the fuel is a fine powder that spalls from the fuel surface. As fuel continues to oxidize, it swells forming grain-sized particulates, leading to cladding rupture and fission gas release. This can affect cladding integrity and fuel irretrievability.

Technical approach and plan:

Fuel will be oxidized to $UO_{2.4}$, U_3O_8 or $UO_3.xH_2O$ depending on temperature and relative humidity. For simplicity, it is categorized into three groups:

Category	U oxide phase	Rate equation
1 (T > 230 °C when RH < 40 %)	U_3O_8	$w = (2kt)^{0.5}$
2 (150 < T < 230 °C when RH < 40 %) (150 < T < 230 °C when RH > 40 %)	$UO_{2.4}$ U_3O_8	$w = (2kt)^{0.5}$
3 (T < 150 °C)	$UO_{2.4}$ (when RH < 40%) Or $UO_3.xH_2O$ (only for zone 5 when RH > 40%)	$w = (2kt)^{0.5}$ for $UO_{2.4}$ Or Rate (mg/m^2/day): 0.01 (lower), 6.85 (upper)

The exposed fuel surface area will be 9.5 cm in length and 1 mm in width at the breached area based on the average crack length 3.5 cm and 1 mm width. Oxidants (O2 and water vapor) will diffuse to only axial direction by ±3 cm in length. A reference case of breach will be 1%, gives 50 rods defected out of 5000 fuel rods in 7000 liter cavity volume of canister.

Expected outcome:

Spent fuel oxidation depth and diametrical increase due to volume expansion at the breached area. The potential to rupture (split) cladding will be assessed.

Assumption: The dry storage system is a closed system without ingress or egress with environment outside of the cask.

Entry date: 10/7/2011

Topic1: Estimate of residual water volume and type identification

Water Sources and Types Concerned In Drying Process

- Unbound water
  - trapped water, ice formation, capillaries, thin wetted water
  - Ice formation can prevent by using inert gas backfill
- Physisorbed water
  - Weakly bound water on all surfaces for SNF, container metals, and corrosion products
  - May difficult to evaporate when cracks/pores present
- Chemisorbed water
  - Can exit as a hydroxide or hydrates in the native oxides or corrosion products
  - Can be decomposed to produce water
    - $UO_2(OH)_2 \cdot H_2O$ -> $UO_2(OH)_2 + H_2O$ at <150 °C
    - $Al(OH)_3$ -> $AlO(OH) + H_2O$ at 120 – 300 °C
    - $ZrO_2 \cdot xH_2O$, $ZrO(OH)_4$, $ZrO(OH)_2$ -> $ZrO_2 + H_2O$ at > 150 °C (Powers and Gray, 1973)

Powers and Gray, Characterization of the Thermal Dehydration of Zirconium Oxide Halide Octahydrate. Inorganic Chemistry, Vol.12, No.11 (1973) pp.2721-2726 (above 150 oC, tends to dehydrate to produce water and ZrO2, but, the material studied contains halides , Cl- or Br-)

Hydration of U-oxides and Metal Hydroxides
From ASTM C1553-08

Information on page 6, Table A1.1 contains information from ASTM C1553-08 “Standard Guide for Drying Behavior of Spent Nuclear Fuel.” ASTM International 2008 that is copyright information and therefore is not include in this notebook

Information on page 7, Table A1.2 & A1.3 contains information from ASTM C1553-08 “Standard Guide for Drying Behavior of Spent Nuclear Fuel.” ASTM International 2008 that is copyright information and therefore is not include in this notebook

Amount of Unbound Water

- Unbound water and physisorbed water can be removed or significantly reduced (relatively) easily by proper drying processes
- However, ASTM C1553-08 stated “Most of the chemisorbed water will still be present after standard drying process”
- Residual gas pressure measurement - currently is being used to show compliance to dryness requirement
- Based on the requirement of maintaining 3 torr (4×10^{-4} Mpa=0.004 atm) pressure for 30 minutes during evacuation in vacuum
- It gives about 1.12 mol (21.6 g) of water vapor for the 7 m^3 cask volume at 27 °C according to an ideal gas law as folloes:

$$PV = nRT$$

Where, P is pressure (Torr), V is the volume (liter), n is the number of water mole (m), R is the molar gas constant (8.31 X 10 ergs deg^{-1} $mole^{-1}$ = 62.36 Torr-liter deg^{-1}), and T is the temperature (K)

- Active reactive gas (water vapor and/or oxygen) can have ~0.6 mol with the concentration of 0.2 vol.%
- Kolhi et al (1985) data: 5 to 10 g of water from one breached rod. This gives max 0.5 liter water in 7,000 liter cavity volume of canister based on 1 % breached cladding. A total 50 rods are breached out of 5,000 rods based on 1 % breach.
- From the acceptance criteria for aluminum SNF
  - 200 °C cladding temperature limit during drying

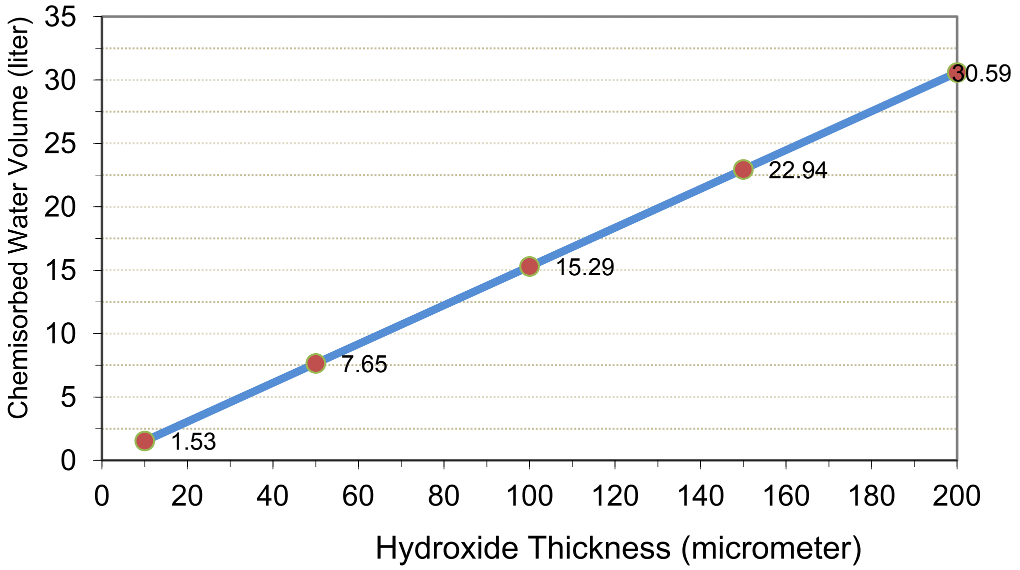
  - No more than 1 milliliter of free water (unbound water) per 0.1 m^2 of cladding surface (gives 6 L of free water for 600 m^2)

Amount of Chemisorbed Water

- Remind that the amounts of 1.2 mol of vaporized water or 6L of free water based on criteria are from the unbound water and physisorbed water, unlikely from the chemisorbed type water
- Need to estimate the volume of chemisorbed water produced by decomposition of hydroxides or hydrates
- Based on surveys of the average ATR spent fuel plates, the amount of chemisorbed water in the form of Boehmite, γ-AlO(OH) is approximately 1.7 L, assuming hydroxide thickness of 0.0034 cm (34 μm), density of 3.01 g/cm^3 for a total surface area of 108 m^2 (ASTM C1553-08)
-

Amount of Chemisorbed Water

- $ZrO(OH)_2$ for 600 m^2 cladding surface area assuming 100% decomposition (dehydration) and a density of 2 g/cm^3
  e.g., $ZrO(OH)_2 \rightarrow ZrO_2 + H_2O$ above 150 °C



- Depending on a decompostion fraction of $ZrO(OH)_2$ at the initial thickness of 10 or 100 μm

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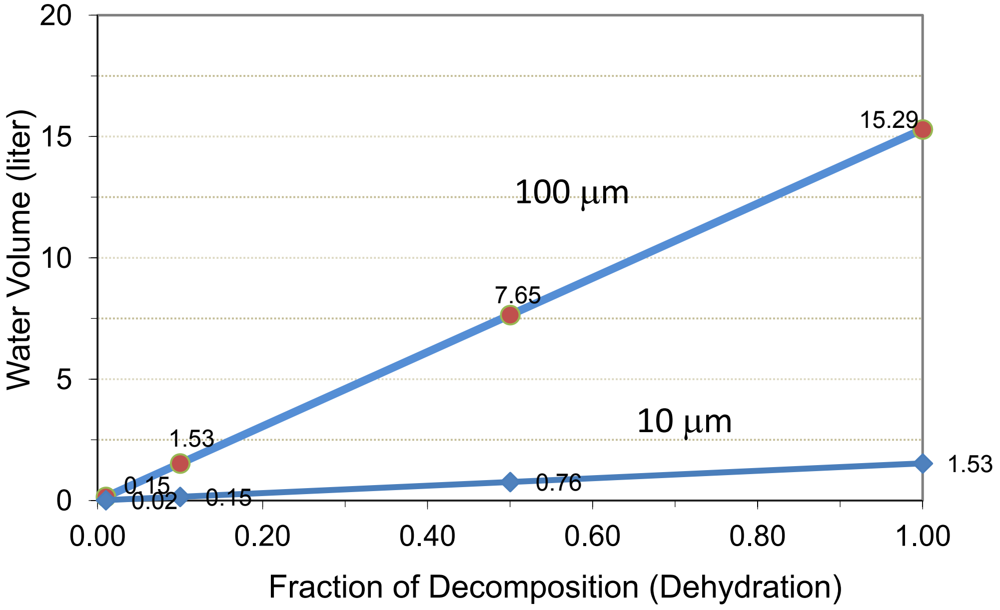

Oxide Vs. Hydroxide or Hydrate on Zr Cladding Surface

- Exposed to wet air with and without radiolysis at different water partial pressure (6 and 50 mbar) for 12 and 24 h duration (Guipponi et al., 2011)
- Oxygen signal was mainly from OH^- or H_2O not O^{2-} when radiolysis present in the form of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$

Information on page 9, Figure 3 is copyright information and therefore is not include in this notebook.

Fig. 3. Oxygen signal after experiment at (a) 6 mbar and (b) 50 mbar without and with irradiation, during 12 and 24 h.

Guipponu et al., Modification of oxidized Zircalloy-4 surface in contact with radiolysed wet air. Nuclear Instruments and Methods in Physics Research ~~B (2011) in-press~~ B272. Pp. 222-226. 2012. (with radiation, oxygen species (1s signal from XPS) on Zr surface tends to H2O or OH- not O2-)

Summary

- Unbound water can be relatively easily removed and the volume can range 0.6 to maximum 1.2 mol based on 3 torr pressure requirement for 7 m^3 canister volume or 6 L for 600 m^2 surface area for Al-cladding
- Most reliable data from the experiments by Kohli et al (1985) can be used as a reference case: max 0.5 liter of residual unbound water in 7,000 liter cavity volume of canister based on 1 % breached cladding.
- More significant contribution on residual water amount in dry storage could be from chemisorbed water as existed in hydroxides or hydrates of mostly on U and cladding surface (not from other metals in container because will be dry)
- A range of the amount of chemisorbed water on $ZrO(OH)_2$
  - 0.02 to 1.53 L with 1 to 100% decomposition at 10 mm thick
  - 1.53 to 15.3 L with 1 to 100% decomposition at 100 mm thick
- Uncertainties in estimating amount of chemisorbed water are
  - Initial amounts and distribution of Zr-hydroxides or its hydrates through the fuel assembly surface after drying before storing
  - Decomposition fraction and amounts as a function of temperature and time
  - Geometrical effects on amount and distribution of hydroxide or hydrates (e.g., cracks, pinholes, hottest zone)
- Very limited data on stability of Zr-oxide and hydroxide/hydrates at the storage conditions

Entry date: 11/7/2011

Topic 2: Cladding oxidation

Reactions $Zr + O_2 = ZrO_2$; for dry air

$Zr + 2H_2O = ZrO_2 + 2H_2$; for water or humid air (e.g., steam)

The reaction kinetics of cladding oxidation was strongly dependent on the temperature and described by the following expression

$\Delta W = A \times t \times \exp(-Q/RT)$

where ΔW - specimen weight gain in mg/dm^2, A - pre-exponential constant in mg/dm^2/day, t - time in days, Q - activation energy in cal/mol, R - gas constant in cal/mol/K, T - absolute temperature in K.

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Table 2-1. Values of A and Q/R in Eq. (4-1) From Models of Different Investigators for Zircaloy Oxidation

Model No.	Investigators	A ($mg/dm^2/day$)	Q/R (K)
1	Hillner (1977)*	1.12E+08	12,529
2	Van der Linde (1965)†	2.30E+09	14,451
3	Dyce (1964)‡	6.53E+09	15,109
4	Daalgard (1976)§	1.84E+07	11,222
5	Billot, et al. (1989)‖	1.13E+08	12,567
6	Garzaolli, et al. (1982)¶	1.18E+09	13,815
7	Stehle, et al. (1975)#	2.21E+09	14,242
8	Peters (1984)**	8.12E+08	13,512
9	Hillner, et al. (1994)††	2.46E+08	12,877

*Hillner, E. “Corrosion of Zirconium-Base Alloys: An Overview.” Presented at the Zirconium in the Nuclear Industry—3rd International Symposium. A.L. Lowe, Jr. and G.W. Parry, eds. ASTM STP 633. Philadelphia, Pennsylvania: ASTM International. pp. 211–235. 1977.

†Van der Linde, A. “Calculation of the Safe Life Time Expectancy of Zirconium Alloy Canning in the Fuel Elements of the NERO Reaction.” RCN Report 41. Petten, The Netherlands: Reactor Centrum. 1965.

‡Dyce, I.H. “Corrosion of Zircaloy Fuel Cladding: The Influence of High Heat Fluxes.” Nuclear Engineering. Vol. 9, No. 98. pp. 253–255. 1964.

§Daalgard, S.B. “Long-Term Corrosion and Hydriding of Zircaloy-4 Fuel Clad in Commercial Pressurized Water Reactors With Forced Convective Heat Transfer.” Extended Abstracts of the Electrochemical Society. Vol. 76-1, No. 31. p.82. 1976.

‖Billot, P., P. Beslu, A. Giodano, and J. Thomazel. “Development of a Mechanistic Model to Assess the External Corrosion of the Zircaloy Claddings in PWRs.” Presented at the Zirconium in the Nuclear Industry: 8th International Symposium. L.F.P. Van Swam and C.M. Eucken, eds. ASTM STP 1023. Philadelphia, Pennsylvania: ASTM International. pp. 165–184. 1989.

¶Garzarolli, F., W. Jung, H. Schoenfeld, A.M. Garde, G.W. Parry, and P.G. Smerd. “Waterside Corrosion of Zircaloy Fuel Rods.” EPRI NP–2789. Palo Alto, California: Electric Power Research Institute. 1982.

#Stehle, H., W. Kaden, and R. Manzel. “External Corrosion of Cladding in PWRS.” Nuclear Engineering and Design. Vol. 33. pp. 155–169. 1975.

**Peters, H.R. “Improved Characterization of Aqueous Corrosion Kinetics of Zircaloy-4.” Presented at the Zirconium in the Nuclear Industry: 6th International Symposium. D.G. Franklin and R.B. Adamson, eds. ASTM STP 824. Philadelphia, Pennsylvania: ASTM International. pp. 507–518. 1984.

††Hillner, E., D.G. Franklin, and J.D. Smee. *The Corrosion of Zircaloy-Clad Fuel Assemblies in a Geological Repository Environment.* WAPD–3173. West Miffin, Pennsylvania: Bettis Atomic Power Laboratory. 1994.

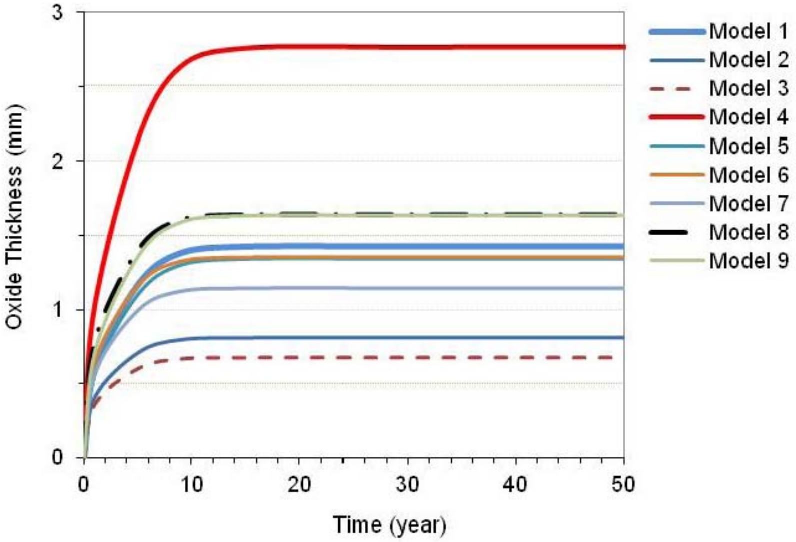

Figure 2-1: Calculated Additional Oxide Thickness on Cladding Surface During the Dry Storage Period According to the Models From Different Investigators

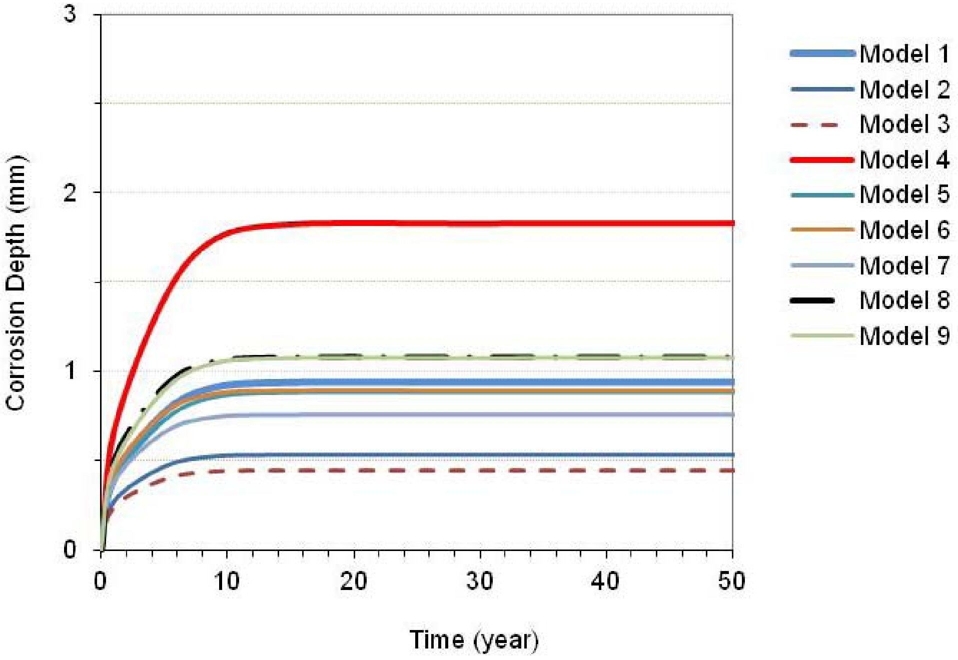

Figure 2-2. Calculated Additional Cladding Thinning During the Dry Storage Period

Note that 15 mg/dm^2 of weight gain corresponded approximately to 1μm of oxide and 0.66 μm of metal consumed by the corrosion reaction.

The temperature profiles used in this calculation are the zone 1 (hottest) and the average temperature of the lower and upper bound conditions for the low-end temperature as follows:

$$T(t) = (575 - 309)\frac{[\exp(-0.023t)+\exp(-0.064t)]}{2} + 309$$

Entry date: 11/8/2011

Topic 3: Fuel oxidation and hydration

Two-step reaction in dry air as $UO_2 \rightarrow U_4O_9 \rightarrow U_3O_8$

The time for complete conversion of UO_2 grains into $UO_{2.4}$

$$t_{2.4}(\mathrm{yr}) = 2.97\times10^{-13}\exp\left(\frac{26.6\ \mathrm{kcal}}{RT}\right)$$

Where

R — ideal gas constant
T — is the temperature (K)

The growth kinetics of the oxidized width is

$$w\ (\mu m) = (2kt)^{0.5}$$

where

t — oxidation time (hour)
k — rate constant

The rate constant measured in the temperature range of 175 to 195 °C [347 to 383 °F]

$$k\left(\frac{\mu m^2}{hr}\right) = 1.04\times10^{8}\exp\left(\frac{-24.0\ \mathrm{kcal}}{RT}\right)$$

where

R — gas constant
T — temperature (K)

The incubation time can be estimated by the following equation

$$t_{U3O8}(\mathrm{yr}) = 1.56\times10^{-19}\exp\left(\frac{44.1\ \mathrm{kcal}}{RT}\right)$$

where

R — gas constant
T — temperature (k)

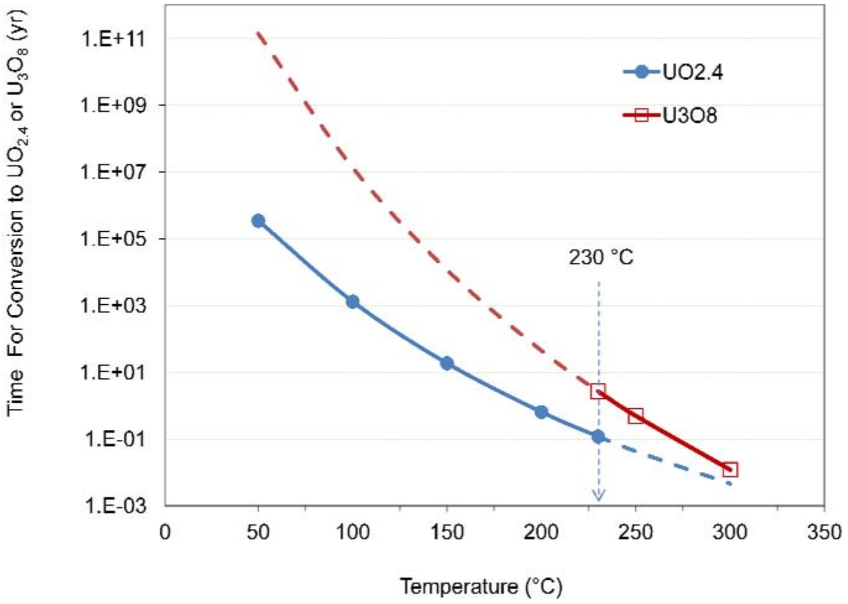

Figure 3-1. Time for Conversion From UO_2 to $UO_{2.4}$ and UO_2 to U_3O_8 As a Function of Temperature

Table 3-1. Summary of the Calculated Times for Conversion to $UO_{2.4}$ or U_3O_8 As a

T (°C)	$t_{2.4}$ (yr)	t_{U3O8} (yr)
50	3.46E+05	1.40E+11
100	1.31E+03	1.35E+07
150	1.86E+01	1.16E+04
200	6.46E-01	4.44E+01
230	1.19E-01	2.67E+00
250	4.27E-02	4.92E-01
300	4.54E-03	1.20E-02

Assuming a spherical shape grain and isotropic dimensional change, an increase of the grain radius can be estimated depending on the volume conversion fraction to U_3O_8.

As the volume (V) of a sphere shape of grain is proportional to the cube of grain radius (r) (i.e., $V = 4/3\ \pi \times r^3$), a ratio of the grain radius when there is an increase from r_1 to r_2 can be expressed as

$$\text{ratio of grain radius} = r_2/r_1 = (V_2/V_1)^{1/3}$$

where

r_1 and r_2 — grain radius before and after volume increase with U_3O_8 formation, respectively
V_1 and V_2 — volume before and after volume increase with U_3O_8 formation, respectively

Assuming a linear increase in the volume with the U_3O_8 conversion fraction of δ based on 36 percent increase when UO_2 to U_3O_8 conversion is 100 percent, the volume increase ($\Delta V = V_2 - V_1$) in percent can be calculated using the following equation

$$\Delta V = \delta \times 0.36 \times 100$$

Thus, a radius increase in percent is

$$\Delta r = (\Delta V^{1/3} - 1) \times 100$$

Table 3-2. Volume and Radius Increases In a Grain As a Function of Conversion Fraction to U_3O_8

Conversion Fraction to U_3O_8 δ (no unit)	Volume Increase ΔV (%)	Radius Increase Δr (%)
1.00	36.0	10.8
0.86	31.0	9.4
0.58	20.9	6.5
0.50	18.0	5.7
0.25	9.0	2.9
0.20	7.2	2.3
0.15	5.4	1.8

Adopting the Arrhenius type equation for crack propagation, the crack propagation by the oxide formation front velocity, can be expressed

$$V\ (\text{cm/min}) = V_o(\text{cm/min}) \times \exp\left(\frac{104.8\ \text{kJ}}{RT}\right)$$

where

V_o — coefficient {4.98×10^6 cm/min [1.96×10^6 in/min]}
R — gas constant
T — temperature (K)

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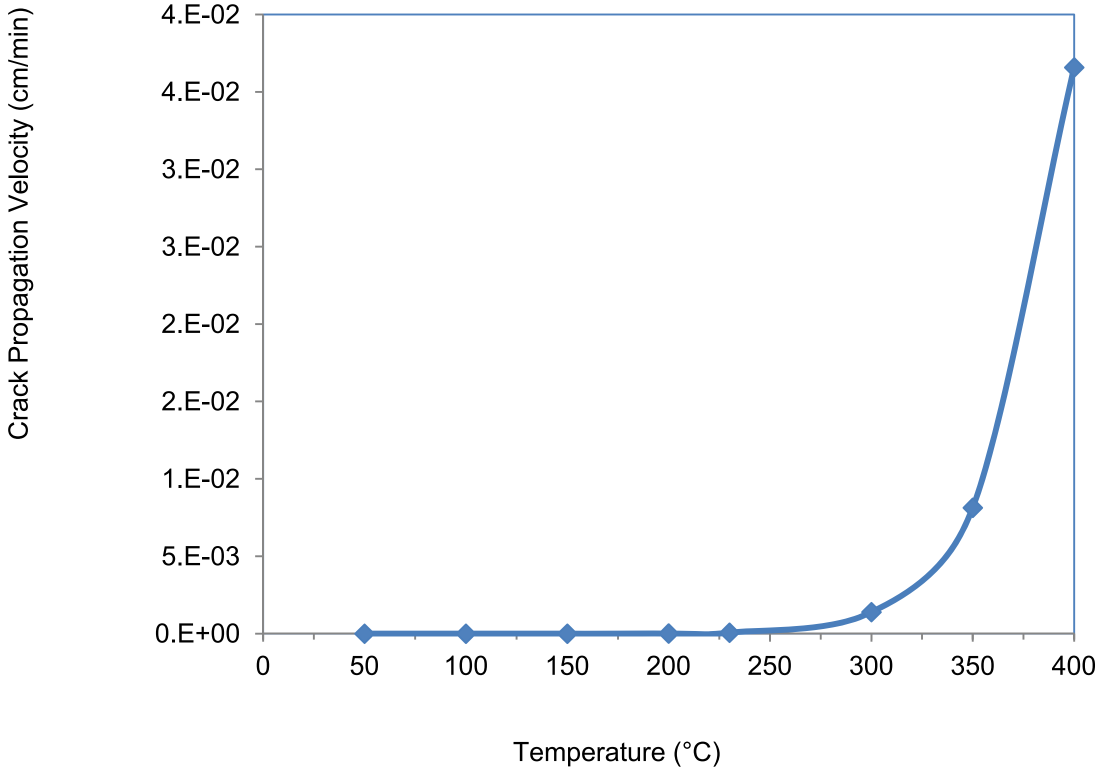

Figure 3-2. Crack Propagation Velocity as a Function of Time for Light Water Reactor Fuel

Entry date: 1/8/2012

Topic 2a: recalculation of the oxide thickness and metal loss

The oxide thickness is revaluated by dividing the time step of 0.01 years to approximate more accurate accumulated thickness. The cal caution in Figure 2a-1 results lead to thicker oxide compared to Figure 2-1 based on 5-year time step. Except the finer time step of 0.01 years compared to 5-year time step in Figure 2-1, the other conditions are same in calculation.

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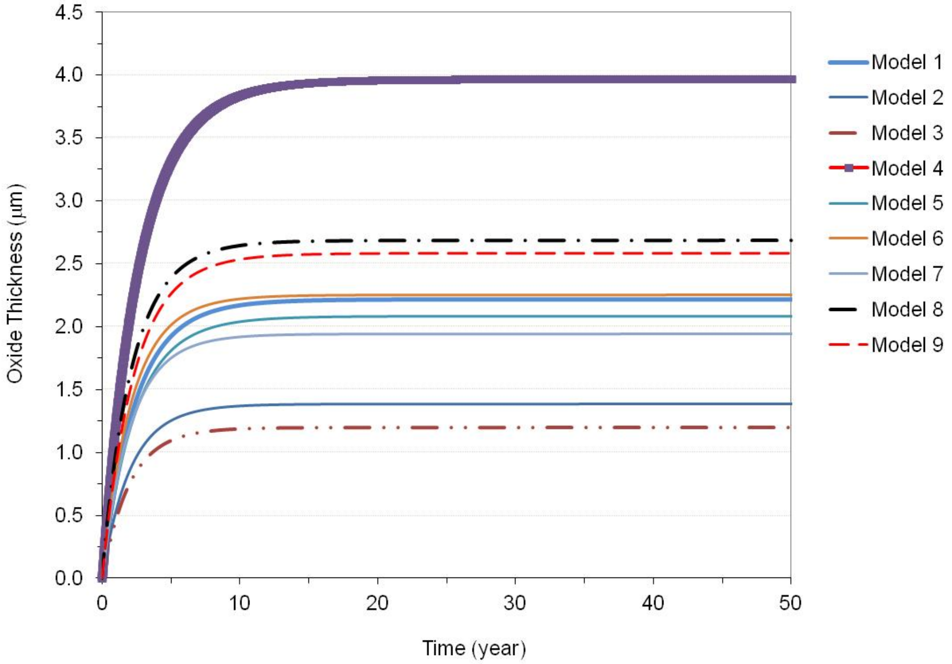

Figure 2a-1: Recalculated Additional Oxide Thickness on Cladding Surface During the Dry Storage Period According to the Models From Different Investigators

The corresponded metal loss is presented in Figure 2a-2.

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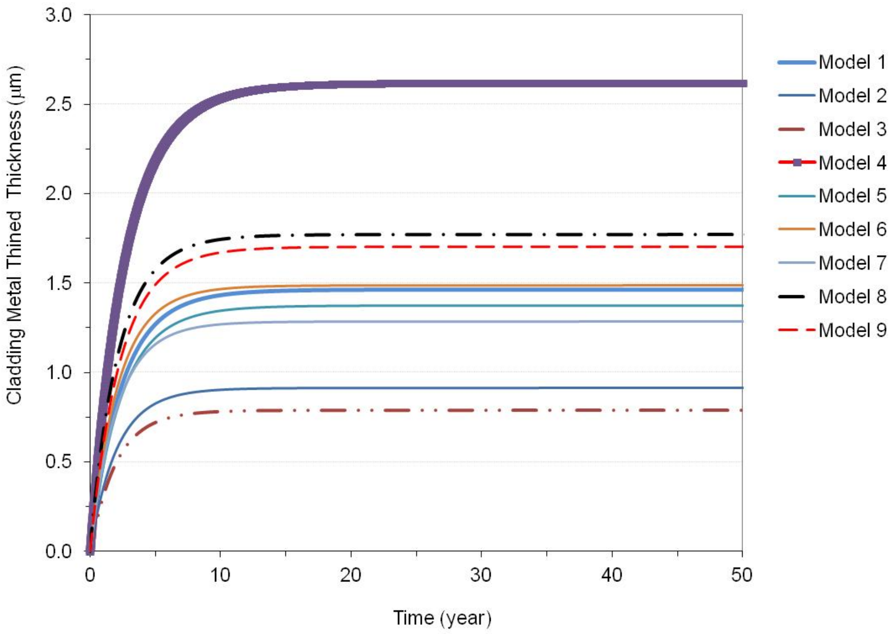

Figure 2a-2. Calculated Additional Cladding Thinning During the Dry Storage Period

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GEOSCIENCES AND ENGINEERING DIVISION
SCIENTIFIC NOTEBOOK REVIEW CHECKLIST RECORD

Scientific Notebook No. 1093E Project Numbers: 14010.01.002 Title: Evaluation of Drying Adequacy for Extended Spent Fuel Dry Storage

Accomplished

☒ 1. Initial entries per QAP–001

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