NRC OVERVIEW OF THE PERFORMANCE OF HIGH-LEVEL WASTE FORMS IN A REPOSITORY ENVIRONMENT

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PRIMARY NRC POST FOR WASTE FORM

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	OUTLINE
(1)	Purpose
(2)	Background
(3)	REGULATORY REQUIREMENTS
(4)	Source Term: Glass and Spent Fuel
(5)	PROCESS VARIABLES IN VITRIFICATION
(6)	GLASS PERFORMANCE IN AQUEOUS ENVIRONMENTS Leaching and Colloid Formation
(7)	Spent Fuel Performance in Aqueous Environments:
	(A) DISSOLUTION (B) Colloid Formation
(8)	SPENT FUEL PERFORMANCE IN DRY ENVIRONMENTS:
	(A) Oxidation(B) Fracture(C) Radionuclide Release
(9)	CONCLUSION

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PURPOSE

IN THE ASSESSMENT OF WASTE FORM PERFORMANCE,

- PRESENT NRC REGULATORY REQUIREMENTS.
- PRESENT NRC UNDERSTANDINGS.

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- FAMILIARIZE WITH DOE TESTINGS AND RESULTS.
- Exchange NRC Views with DOE.

BACKGROUND

- NEED TO ASSESS CONSEQUENCE OF PERFORMANCE ALLOCATION ON GLASS AND SPENT FUEL.
- NEED REPOSITORY (YUCCA MOUNTAIN) RELEVANT Information such as that from Drip Drop or Dry Condition.
- NEED TO ASSESS EFFECTS OF PROCESS VARIABLES OF VITRIFICATION ON GLASS PERFORMANCE.
- NEED INFORMATION FROM OTHER ADVERSE CONDITIONS -such as Immersion or High Flow.
- NEED RELATED INFORMATION SUCH AS IN ANALOGUES, AND REACTOR PERFORMANCE OF FUEL.

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10 CFR PART 60 REQUIREMENTS RELATED TO DESIGN AND PERFORMANCE OF HIGH-LEVEL WASTE FORM

(A) 10 CFR 60.113:

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The release Rate of Any Radionuclide from the Engineered Barrier System (Waste Packages and Underground Facility) Following the Containment Period (300 to 1,000 Years) shall not Exceed One Part in 100,000 per Year of the Inventory of that Radionuclide Calculated to be Present at 1,000 Years Following Permanent Closure --Provided that this Requirement does not Apply to any Radionuclide which is Released at a rate Less than 0.1 % of the Calculated Total Release Rate Limit.

(B) 10 CFR 60.135:

No Adverse Effects on Waste Package Performance by Explosive, Pyrophoric and Chemically Reactive Materials, and Free Liquid.

WASTE FORM CRITERIA: Solidification, Particulate Consolidation, and No Adverse Effects of Combustibles.

10 CFR 60.112: PERFORMANCE REQUIREMENTS FOR THE OVERALL REPOSITORY SYSTEM OF ENGINEERED AND NATURAL BARRIERS - 40 CFR 191 (EPA): HAVE A LIKELIHOOD OF LESS THAN ONE CHANCE IN 10 OF EXCEEDING THE QUANTITIES, THE CUMULATIVE RADIONUCLIDES IN THE ACCESSIBLE ENVIRONMENT FOR 10,000 YEARS AFTER DISPOSAL FROM ALL SIGNIFICANT PROCESSES AND EVENTS THAT MAY AFFECT THE DISPOSAL SYSTEM --. 10 CFR 60.21 (c)(1)(II)(D): ALTERNATIVE DESIGN. 10 CFR 60.131 (B) (7): CRITICALITY CONTROL. Rules FOR RADIONUCLIDE RELEASE CURRENT ARE ADDRESSED INTERMITTENTLY THROUGHOUT THIS TALK. WE DISCUSSION TO FULL PERFORMANCE RESTRICT OUR ALLOCATION ON WASTE FORM IN A DETERMINISTIC Тне Release RATE OF A KIND MANNER. **OF** NRC RADIONUCLIDE WILL EXCEED CRITERIA 0F CONTROLLED RELEASE RATE IF THE TOTAL INVENTORY OF THE RADIONUCLIDE IS MORE THAN THE EPA LIMIT AND Released within 10⁴ Years, in General. NRC/TMA/10.15.93/ANL/PAGE 7

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RADIOACTIVITY SOURCE TERM

Radionuclide (Half Life: Years)	SF	glass	EPA limit	Daughter Product (Half Life: Years)
C-14 (*)	1.54	0.0	0.1	
Pu-(239+240)	744, 704	1.2 - 6.4	0.1 + 0.1	
Am-241 (433)	1,770, 1,510	2 ~ 7 (21, 100)	0.1	
Cm-244 (18)	1,280, 990	0.1 ~ 64	0.1	Pu-240 (6,563)
Np-237	0.24, 0.22	0.002 ~ 0.02	0.1	
Tc-99 (**)	10	1.8	10.0	
Ρυ-238 (88)	2,330	882	0.1	U-234 (2.5x10 ⁵)

INVENTORY (CI/MTHM)

* Release from Dissolution and Dry Release. ** Release from Dissolution. The Rest for Solubility-limited Release.

SPECIFIC ACTIVITY OF RADIONUCLIDE (CI/G)

Pu-239	Pu-240	Am-241	Pu-238	U-234	Np-237
6.2 x 10 ⁻²	2.3 x 10 ⁻¹	3.4	17	6.2 x 10 ³	7.1 x 10⁴

NUMBER OF CONTAINERS (YEAR 2,020): 38,000 (SF) AND 15,000 (GLASS).
 MTHM (YEAR 2,020): 86,000 (SF) AND 27,000 (GLASS).

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[Constant Activity in Leachates]						
 Cumulative Release for 10,000 Years (CUMREL) = [Activity per Unit Leachate Volume] x [Flow Rate] x [Number of Containers] x [10,000 Years] 						
EPA LIMIT FOR TOTAL [EPA LIMIT PER]	. INVENT 1,000 MT	ORY (EPAL) HM] x [MTHM	= 1] x [0.001]			
• Example for constan L per container and	F ACTIVI Per yea	TY AND FLOR:	W RATE OF 1			
CUMREL = 10^4 PCI/ML x 1,000 ML/(YEAR X CONTAINER) X 53,000 CONTAINERS X 10,000 YEARS = 5.3 X 10^3 CI EPAL = 0.1 X [27,000 + 86,000] = 1.1 X 10^4 CI						
pCi/mL from Glass c	<u>ULASS 1</u> 5xc	10 x c	100 x c			
[(pCi/mL) from SF] Percentage of Glass 28 Contribution	66	80	98			
 [DISSOLUTION CONTROL] : RELATIVE MAGNITUDE OF DISSOLUTION RATES EXAMPLE: GROWTH RATES OF REPRECIPITATES (85~90)° C SF ~ 3x10⁻⁹ cm/day. GLASS > 10⁻⁶ ~ 10⁻⁷ cm/day. 						
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•	MEASURED	(PUI/ML) IN LEACHATES
	- GLASS:	DRIPPING GROUNDWATER TEST: (1.6 ~ 9.7) $\times 10^4$ of Am-241. (9~ 50) of Np-237. Error ~ 100. New Confirmation ~ 1/10. Half Life Factor ~ 1/10. (6.2 ~ 12.4) $\times 10^{-3}$ for Pu-239.
		IMMERSION TEST: ~ 640 OF AM-241 AND ~ 910 of Pu-(239+240).
	- SF:	
		DRIPPING GROUNDWATER TEST:
		6x10 ³ of Am-241 colloid. 6x10 ⁵ of Am-241 dissolved ion.
		U0 ₂ test conversion: $(2 \sim 4) \times 10^4$ of Pu- (239+240). $(4 \sim 9) \times 10^4$ of Am-241.
		IMMERSION TEST: ~ 300 OF PU-(239+240) AND AM-241.
•	FLOW RATE	E SPANS FROM 0.1 L/YEAR TO 20 L/YEAR.
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VITRIFICATION OF LHLW IN WASTE ACCEPTANCE PROCESS EFFECTS OF PRETREATMENT ON COMPLIANCE
 METHOD OF RADIONUCLIDE CONCENTRATION. Special Additives such as Corrosion Prevention Chemicals. Sludge and Precipitates Treatment. Toxic Chemical Recovery. Organic Removal. Blending and Mix Concentration.
 EFFECTS OF VITRIFICATION PROCESS ON COMPLIANCE GLASS MAKING ADDITIVES. WASTE LOADING. Melting : Heating, Conductivity, Redox, Residence Time, Cooling Rate, Foaming or Volatilization.

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EFFECTS OF ERROR ON COMPLIANCE

- COMPOSITION.
- PROCESS TROUBLE.
- BATCHING.

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- OVERALL OPERATIONAL VARIATION.
- DETERMINATION OF ACCEPTABILITY.

EFFECTS OF OVERALL PROCESS ON COMPLIANCE:

SIMPLICITY, FLEXIBILITY, AND PRODUCTIVITY.

WASTE ACCEPTANCE PRELIMINARY SPECIFICATIONS:

(A) COMPLIANCE WITH 10 CFR 60.135.

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(B) COMPLIANCE WITH 10 CFR 60.113 AND 40 CFR 191.

UNCERTAIN AREAS:

- (A) PROPER LOADING AND ANALYSIS OF RADIONUCLIDE.
- (B) HANFORD REMEDIATION PLAN.
- (C) IDAHO CERAMICS: LACK OF DATA BASE.
- (D) PRODUCT CONSISTENCY.



HLW GLASS LEACHING AND COLLOID FORMATION

- RADIONUCLIDES: PU-(239+240), AM-241 AND TC-99
- SOURCE: COLLOIDS FROM DRIPPING-GROUNDWATER TESTS.
 - Colloids from Immersion Tests if Cumulative.
 - CONTINUOUS DISSOLUTION.
- IT IS NOT CERTAIN THAT THE EXTENT OF MATRIX Dissolution and Colloid Formation will lead to Compliance. Following Observations Provide further Conditions for these Adverse Effects:
 - (A) LEACH EXCURSION.
 - (B) OFFSET OF REPRECIPITATED LAYERS.
 - (c) B Release ?
 - (D) PALAGONITE ALTERATION OF ANALOGUE GLASS AND MIIT RESULTS.
 - (E) THERMAL- OR RADIATION-INDUCED GLASS CRACKINGS.
- NEED

CLARIFICATION OF UNCERTAIN AREAS.

GEOCHEMICAL ANALYSES OF COLLOIDS IN THE CASE OF NON-COMPLIANCE.

• Uncertain Areas

- EFFECTS OF HYDRATION, DEVITRIFICATION, ALTERATION OF GROUNDWATER CHEMISTRY, AGITATION, IRON AND CRACKINGS.
- CUMULATIVE EFFECTS.
- DYNAMIC BALANCE:
 - (A) FLOCCULATION, GROWTH, DIS-INTEGRATION OR SEDIMENTATION.
 - (B) ESCAPE BY GROUNDWATER FLOW.
- [FLOW-RATE/SURFACE-AREA] EFFECTS IN COLLOID FORMATION.
- CONTINUOUS DISSOLUTION.
- ROLE OF BACKFILL.
- OPEN SYSTEM VERSUS CLOSED SYSTEM.
- GAMMA-RAY EFFECTS.
- ROLE OF REPRECIPITATES DISSOLUTION.

[DETAILS IN THE SF SECTION]



SPENT-FUEL DISSOLUTION

• HIGH SOLUBILITY RADIONUCLIDES:

TC-99 AND C-14.

• KEY QUESTIONS:

(A) CONTINUOUSLY DISSOLVE ?

(B) RAPID INTER-GRANULAR ATTACK ?

- METHODS OF DETERMINING DISSOLUTION RATES:
 - (A) IMMERSION TESTS: SR-90 SATURATION AND FUEL PARTICLES IN REPRECIPITATES ? GAMMA-RAY EFFECTS ?
 - (B) FLOW-THROUGH TESTS AND ELECTROCHEMISTRY: RADIOLYSIS EFFECTS ? GEOCHEMISTRY ? (SUPER)SATURATION EFFECTS?

OBSERVATIONS OF REGULATORY CONCERN

- (A) UNPROTECTIVE NATURE OF SF: RADIATION, MICROBE, STRESS, AND INHERENT NATURE.
- (B) FLOW-THROUGH TESTS ~ IMMERSION TESTS (TABLE).
- (c) Absence or Offset of Reprecipitates.
- (D) MASSIVE TRANSFORMATION OF URANINITES TO URANOSILICATES IN THE PENA BLANCA URANIUM DEPOSITS.
- (e) POTENTIAL VIOLATION OF PHASE RULE AND UNRELIABLE SOLUBILITY LIMITS.
- (F) KINETICS OF PARAGENESIS.
- (G) CYCLIC BEHAVIOR OF LEACHATES.
- (H) ENVIRONMENTAL VARIATIONS: TEMPERATURE GRADIENT, Wet-dry Cycle, Seismic Events and Occluded Area.

ERRATIC BEHAVIOR IN THE RELEASE OF FISSION PRODUCTS

- (A) LINEAR WITH TIME.
- (B) SATURATION EFFECTS.
- (c) Effects of Grain Boundaries and Rims.
- (D) TRANSIENT EFFECTS OR SOLID-STATE DIFFUSION CONTROL.

OVERALL CURRENT UNDERSTANDINGS

- (A) INTERFACE-REACTION CONTROL:
 - OVER-POTENTIAL OR SOLUBILITY LIMITS.
 - LINEAR DISSOLUTION WITH TIME.
- (B) SOLID-STATE DIFFUSION CONTROL:
 - NON-LINEAR DISSOLUTION WITH TIME.

INTERFACE-REACTION CONTROL

[EQUATIONS] [TABLE]

- NOT CERTAIN TO COMPLY WITH RULES.
- LEACHATES: (A) SUPER-SATURATED WITH COLLOIDS; (B) SUPER-SATURATED WITHOUT COLLOIDS; (C) LEACHATE OF SOLUBILITY LIMIT WITH COLLOIDS; AND (D) LEACHATE OF SOLUBILITY LIMIT WITHOUT COLLOIDS.
- UNCERTAIN AREAS:
 - ROLE OF CLADDINGS, RIMS AND GRAIN BOUNDARIES.
 - EFFECTS OF ALTERATION OF GROUNDWATER, AGITATION AND IRON.
 - EFFECTS OF OXIDATION.
 - GAMMA-RAY EFFECTS.
 - ROLE OF REPRECIPITATES DISSOLUTION.

NON-DIFFUSIONAL DISSOLUTION KINETICS OF SF FOR A SPECIES

$$R_{dis} = \frac{S}{V} K_{-} (C_{s} - C_{t})$$

OR

$$= \frac{S}{V} K_e f(E)$$

AND BALANCED BY

 $= \frac{A}{V} K_{\star} (C_t - C_o) + \frac{F}{V} C_t + N_{par} C_t$

C, IS THE CONCENTRATION OF THE ELEMENT UNDER CONSIDERATION AT TIME T: S IS THE SURFACE AREA OF THE DISSOLVING PHASE; A IS THE SURFACE AREA OF THE ALTERED PHASE; V IS THE LEACHATE VOLUME; F IS THE FLOW RATE OF GROUNDWATER; K IS THE RATE CONSTANT FOR DISSOLUTION; K_{+} is the rate constant FOR GROWTH OF THE ALTERED PHASE; K. IS THE RATE CONSTANT FOR THE ELECTROCHEMICAL DISSOLUTION; F(E) IS THE DEPENDENCE OF THE DISSOLUTION RATES ON THE ELECTROCHEMICAL POTENTIAL E AND IS ASSUMED TO BE CONSTANT OVER TIME FOR ILLUSTRATION PURPOSE; C. IS THE EFFECTIVE SOLUBILITY LIMIT OF THE DISSOLVING PHASE INCLUDING ACTIVATED COMPLEXES; C_o is the SOLUBILITY LIMIT OF THE ALTERED PHASE; AND N_{dar} is THE FORMATION OR GROWTH RATE OF COLLOIDS PER UNIT LEACHATE CONCENTRATION IF ANY.

• LINEAR DISSOLUTION WITH TIME AND COMPLIANCE IS NOT CERTAIN, ESPECIALLY WITH GRAIN-BOUNDARY AND RIM EFFECTS.

The First Two Equations are set to be equal to the Third Equation and a few algebraic arrangements give \boldsymbol{C}_t as

$$C_{t} = C_{o} \left[1 + \frac{K_{-} \frac{S}{V} \left(\frac{C_{s} - C_{o}}{C_{o}}\right) - \left(\frac{F}{V} + N_{par}\right)}{\frac{A}{V} K_{+} + \frac{S}{V} K_{-} + \frac{F}{V} + N_{par}}\right]$$

OR

$$C_{t} = C_{0} \left[1 + \frac{\frac{S}{V} K_{e} f(E) \frac{1}{C_{0}} - (\frac{F}{V} + N_{par})}{\frac{A}{V} K_{+} + \frac{F}{V} + N_{par}}\right]$$

- SUPERSATURATION.
- EXISTING MODELS VALID ?

TABLE.	Mass	TRANSFER	CALCULATIONS	0F	ABOVE			
EQUATIONS [Ahn, 1993]								

	(S/V)	қ с,	(S/V) K, f(E)	(٨/٧)	К₊Ҁ	(FA	ስፍ	N _{ja} , C,
	25° C	85° C	25° C	25° C	85° C	25° C	85° C	25° C
U	(0.3 -1.2) x10 ⁴ g/day, or (1.7-6.0) x10 ⁴ fraction (f) /day		(4x10 ⁻⁴ 2x10 ⁻³) g/day	(10 ⁴ ~ 10 ³) g/day	8x10 ⁻⁴ g/day	(2 ~ 4) x10 ⁴ g/day	(1 - 2) x10 ⁴ g/day	< (0.4-4) x10 ⁵ g/day
Рь- (239+ 240)	(0.3 - 1.2) x10 ⁴ g/day			5x10 ⁴ g/day	7x10* g/day	(1-3) x10 ¹¹ g/day	(1-3) x10 ¹³ g/day	< 10 ⁻⁷ ~10 ⁻⁴ g/day
Sr-90	(2~4)x10 ⁴ f/day for 20~120 days			4x10 ⁷ f/day, 7x10 ⁷ f/day, 1x10 ⁴ f/day	2x10* g/day			
Based on PNL and AECL Data. Normalized Over 205 cm ² . Maximum Values for Colloid Contribution.								
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SOLID-STATE DIFFUSION CONTROL

THE DISSOLUTION RATE

 $R_{dis,d} = k S (t+a)^{-\frac{1}{n}} (n \ge 2)$

$$d_a = 2 k A (t + a)^{\frac{1}{2}}$$
 (n = 2)

WHERE K, A AND N ARE CONSTANTS AND N IS AN INTEGER, AND D_a is the total amount of materials from the matrix dissolution.

• Non-linear Dissolution with Time and Likely to Comply with Rules unless Grain-Boundary and Rim Effects are Significant.

COLLOID FORMATION: PU-(239+240) AND AM-241

CONDENSATION PROCESS FOR COLLOID FORMATION AND UNCERTAINTIES ABOUT SOLUBILITY LIMITS

• SOURCES:

- (A) HYDROLYSIS, AND SUBSEQUENT MOLECULAR CONDENSATION THROUGH DEHYDRATION.
- (B) AGGLOMERATION OF HYDROLYZED AND SUBSEQUENTLY Oxidized Molecules.

• Approach:

- (A) STABILITY CONSTANTS.
- (B) REACTION KINETICS OF REACTIVITY: REACTION ORDER.
- (c) Overall Energetics: Thermodynamic Treatment.

• NUCLEATION RATES:

$$R_{nuc} = n k \frac{T}{h} e^{-\Delta G_o/RT} e^{-\Delta G_c/kT}$$

THE NUMBER OF PRECIPITATING MOLECULES IS IN N LEACHATES, K IS THE BOLTZMAN CONSTANT, T IS THE TEMPERATURE, H IS THE PLANCK CONSTANT, ΔG_d is the ACTIVATION ENERGY OF MOLECULAR DIFFUSION IN LEACHATES, R is the gas constant, and ΔG_c is the activation energy FOR THE FORMATION OF THE CRITICAL SIZE OF A NUCLEUS. ΔG_c is given as [16 $\pi \gamma^3 M^2$]/[3 $\rho^2 \Delta G_v^2$] where γ is the SURFACE ENERGY PER UNIT AREA OF COLLOIDS, M IS THE MOLECULAR WEIGHT OF THE CHOSEN SECOND PHASE, p IS THE DENSITY OF THE SECOND PHASE, AND ΔG_{ν} is the driving FORCE FOR THE NUCLEATION APPROXIMATED BY {- R T $LN[C_s/C_3]$.

- THERMODYNAMIC TREATMENT PROVIDE INFORMATION ON CUMULATIVE EFFECTS.
- ENERGY BARRIER ASSOCIATED WITH NUCLEATION MAY NOT EXIST.

• UNCERTAINTIES:

- (A) TRANSITORY PHENOMENA: U AND PU AT NEAR BOILING POINTS.
- (B) CUMULATIVE EFFECTS.
- (C) DYNAMIC BALANCE:
 - FLOCCULATION, GROWTH, DIS-INTEGRATION OR SEDIMENTATION.
 - ESCAPE BY GROUNDWATER FLOW.
 - ENERGETICS ASSOCIATED WITH COLLOID FORMATION.
- (d) Role of Cladding, Iron, and Alteration of Groundwater Chemistry.
- (E) SUPER-SATURATION.
- (F) MORPHOLOGICAL CONFIRMATION.

DISPERSION PROCESS FOR COLLOID FORMATION

• SOURCES

- SPALLATION OR EROSION OF REPRECIPITATES.

- INTER-GRANULAR DISSOLUTION.
- HIGH-VALENCE OXIDES.

Approach

- INSUFFICIENT INFORMATION FOR MECHANISTIC MODELING.

- PHENOMENOLOGICAL WEAR:

IN GENERAL W = F[A, F, L, 1/K_{ic}, 1/H] SUCH AS $w \approx \frac{A F^{k} L^{1}}{K_{ic}^{m} H^{n}}$

F IS AN APPROPRIATE FUNCTION, A IS THE SURFACE area of SF particles, F is the flow rate, L is load applied and can be replaced by the liquid impact pressure, K_{ic} is the fracture toughness of the secondary phase, and H is the hardness of the reprecipitated phase. The latter two values might be dependent on temperature or fuel types, and (K, L, M, N) are appropriate constants.

THE ELASTIC STRAIN ENERGY STORED <u>PER UNIT VOLUME</u> ASSOCIATED WITH OXIDATION:

$$\epsilon = \frac{E}{2(1-2\nu)} \left(\frac{\Delta V}{3V}\right)^2$$

 $(\Delta V/V)$ represents the volume expansion (or contraction), E is the Young's modulus, and v is Poisson's ratio.

- UNCERTAINTIES
 - SOLUBILITY LIMITS DUE TO ACIDIFICATION BY RADIOLYSIS.
 - SPALLATION MECHANISM.
 - CUMULATIVE EFFECTS.
 - DYNAMIC BALANCE: FLOCCULATION, GROWTH, DIS-INTEGRATION OR SEDIMENTATION, ESCAPE BY GROUNDWATER FLOW.
 - [Flow-Rate/Surface-Area] Effects and Role of Backfill Materials.
 - OPEN SYSTEM VERSUS CLOSED SYSTEM.
 - EFFECTS OF ALTERATION OF GROUNDWATER CHEMISTRY, AGITATION, IRON AND OXIDATION.
 - MORPHOLOGICAL CONFIRMATION OF COLLOID SOURCE.
 - TC-99 AND C-14.

PSEUDO-COLLOID FORMATION

THE AMOUNT OF SORBED RADIONUCLIDES IS APPROXIMATED BY

 $W_a = M_g K_d C_a$

 M_g is the mass of groundwater colloids, $C_{_{\!B}}$ is the activity level of radionucildes in leachates, and K_d is sorption coefficient.

• UNLIKELY TO YIELD OBSERVED ACTIVITIES UNLESS HETEROGENEOUS CONDENSATION TAKES PLACE.

SPENT FUEL PERFORMANCE IN DRY ENVIRONMENTS:

- (A) OXIDATION(B) FRACTURE(c) RADIONUCLIDE RELEASE

OXIDATION AND FRACTURE OF SPENT FUELS

- RADIONUCLIDES : C-14
- LOWER-VALENCE OXIDATION :
 - Not Certain to have 100 % Oxidation for 10,000 Years at near Boiling Point of Groundwater.
 - THE SPHERE MODEL IS THE BEST CHOICE BOTH FOR Matrices and for Grain-Boundaries in the Diffusion Limit. Deviation from Parabolic Laws Appears to be Significant.
 - NEED CONFIRMATION OF NO MOISTURE EFFECTS UNDER Pressurized Conditions if Exist.
 - NEED THE ASSESSMENT OF (A) REACTION CONTROL AND (B) DIFFUSION CONTROL IN OXIDE MIXTURE.



• UNCERTAINTIES:

- $U_3 O_8$ formation especially at grain boundaries in either crystalline or amorphous phases.

- Amorphization of U_3O_8 and U_4O_9 .

- Low Temperature Kinetics of U_3O_8 .

- ALPHA-DECAY EFFECTS.

[TABLE]

KINETIC APPROACH FOR THE ASSESSMENT OF UO_{2.4} Transient

THE TIME DELAY, δ , FOR THE NUCLEATION IS NORMALLY DESCRIBED TO BE PROPORTIONAL ~ ΔG_v^{-6} OR ~ (T ΔG_v^{-3}) FOR THE DILUTE SUPERSATURATION, RESULTING IN [Ahm, 1992 and 1993]

$$\delta \propto \frac{1}{\left[-\Delta H_f \left(T_E - T\right)/T_E + \epsilon\right]^6}$$

OR

$$\frac{T}{\left[-\Delta H_{f}\left(T_{E}-T\right)/T_{E}+\epsilon\right]^{3}}$$

The driving force for the nucleation, ΔG , has been generally approximated to be $\{-\Delta H_f (T - T_e)/T_e + \epsilon\}$ where ΔH_f is the transformation enthalphy, T_e is the temperature of the boundary between equilibrium phases which can be approximated based on the thermodynamic data base, and ϵ is the strain energy associated with the transformation. Additional energy input such as radiation can be added too if necessary.

EQUILIBRIUM APPROACH FOR THE ASSESSMENT OF UO_{2.4} Transient

Hypothetical activities of higher oxides in equilibrium: $exp(-\Delta G_f/RT)$ where ΔG_f is the free energy of formation of the higher oxides.

CALCULATED RELATIVE VALUES OF THE TIME DELAY AND OF THE EQUILIBRIUM CONCENTRATION.

	time delay			ilibrium entration
T - T _E (* C)	δ for the First Equation	δ for the Second Equation	T (* C)	C _B at 360° C (*1)
1	TA	τ _B	280	$\sim 10^{-12} C_{\rm B}$
10	$-10^{-3} \tau_{\rm A}$	$\sim 10^{-6} \tau_{\rm B}$	250	- 10 ⁻¹⁷ C ₃
100	$-10^{-4} \tau_{\rm A}$	$\sim 10^{-12} \tau_{\rm B}$	150	~ 10 ⁻⁴¹ C _B

*1 : For a chosen value of $\Delta G_f = 242$ kcal (1,000 kJ)/mol.

MAJOR ALPHA-EMITTING RADIONUCLIDES IN LWR SF

Radionuclides	Half Life (Years)	Activity (Ci/MTIHM): 10 Years after Discharge	Activity (Ci/MTIHM): 100 (300) Years after Discharge	Daughter Product (Half Life in Years)
Pu-238	87.7	2,330	1,150 (237)	U-234 (2.45x10 ⁵)
Pu-239	2.41x10 ⁴	313	312	U-235 (7.04x10 ⁸)
Pu-240	6.56x10 ³	527	526	U-236 (2.34x10 ⁷)
Am-241	433	1,690	3,750 (2,750)	Np-237 (2.14x10 ⁶)
Cm-244	18.1	1,320	42 (0.02)	Pu-240 (6.56x10 ³)

• Both SF and Unirradiated UO_2 may Need to be Tested if Alpha Damage is Responsible for the $UO_{2.4}$ Transient.

FRACTURE

THE STRESS (OR PRESSURE) DEVELOPED ASSOCIATED WITH THE VOLUME CHANGE IS GIVEN BY

 $\sigma = \frac{E}{(1-2v)} \frac{\Delta V}{3V}$

The Determination of Differential Stress Caused by the UO_2 Oxidation

	E (MPa)	٧	Fracture Strength (MPa)	Calcu Equatio Values	lated σ (MPa, on 4) for Three of $\Delta V/V$ (%)
Properties	145,000	0.302	16 ~ 42 (*1)	$\Delta V/V = 1$	σ = 1,219
				3	3,656
T (° C)	0 - 1,000	-	-	35.8	43,630

The manufacturing process of UO_2 was not specified for E and ν , whereas fracture strengths are for various manufacturing processes of UO_2 .

*1 : Modulus of rupture.

CALCULATED VALUES OF THE INCREASE OF THE SURFACE Area Associated with Fractures in 100 % Oxidized SF

ΔV/V (%)	€ (erg/cm ⁵)	Surface Increase (factor)	Fracture Path
1	2.03 x 10 ⁷	2.2 x 10 (0.71)	grain boundary
3	1.83 x 10 ²	2.0 x 10 ² (6.40 : all)	grain boundary
35.8	2.60 x 10 ¹⁰	1.9 x 10 ⁴ (620 :all)	matrix

[Parameters Used in the Calculations] :

(a). A spherical particle with a radius of 0.055 cm (an arbitrary value between 0.025 and 0.07 cm).

(b). A spherical grain of a radius of 1.75×10^{-3} cm.

(c). A factor 4 % was used in the conversion of the strain energy to the surface energy.

(d). The surface energy, 1,000 erg/cm², was used and 1/3 of the surface energy was assumed to be the high-angle grainboundary energy.

(c). The parentheses of surface increase are ratios to total grain-boundary areas.

(f). Other parameters were from the Table of stress calculation.

(g). Because many steps are involved in the oxidation as shown previously, the percentages of volume changes are with respect to UO₂. Minor corrections can be made for various precursory oxides.





EFFECTS ON THE BEHAVIOR OF C-14

- CHEMICAL AND PHYSICAL FORMS IN THE AS-RECEIVED SF:
 - BOUND C-14.
 - CARBIDES (OR OXICARBIDES): NEED CONFIRMATION.
- EFFECTS OF OXIDATION:
 - CARBIDES OR OXICARBIDES: OXIDATION MAY BE SIGNIFICANT UNDER CONDITIONS OF RADIATION OR HIGHER-OXIDE FORMATION.
 - C-14 Release from Surface Reaction through Matrix Powdering by Higher Oxide Formation.





CLADDING FAILURE

- RADIONUCLIDES: C-14.
- OXIDATION: SIMILAR TO THE CASE OF MATRIX OXIDATION. INVOLVES (A) PRE-TRANSITION AND POST-TRANSITION OXIDATION; (B) GRAIN-BOUNDARY OXIDATION AT A FINITE THICKNESS; AND (C) PLASTIC DEFORMATION.
- C-14 RELEASE:
 - CHEMICAL AND PHYSICAL FORMS IN THE AS-RECEIVED CLADDING: BOUND C-14 OR CARBIDES (NEED CONFIRMATION).
 - C-14 MOBILITY IN UNOXIDIZED CLADDINGS: RELEASE IS UNLIKELY TO BE SIGNIFICANT BUT A POTENTIAL PROBLEM.
 - EFFECTS OF OXIDATION: MOBILITY OF C-14 ATOMS MAY BE INCREASED. BOUND C-14 TO OXYGEN MAY BE MOBILE ONLY WITH (A) CONTINUOUS NETWORK OF DISLOCATIONS AND GRAIN BOUNDARIES AND (B) FORMATION OF POST- TRANSITION OXIDES. CARBIDES MAY DECOMPOSE WITH RADIATION.
- UNCERTAINTIES: (A) C-14 GRAIN-BOUNDARY SEGREGATION, (B) OXIDE TRANSITION, AND (C) RATE-LIMITING PROCESS OF DETRAPPING OR TRANSPORT.

• EXISTING DATA:

DIFFUSION (AND DETRAPPING) OF ATOMIC C-14 MAY BE SIGNIFICANT IN BOTH THE UNOXIDIZED AND THE OXIDIZED SF MATRIX. ROLE OF POST-TRANSITION OXIDE AND OTHER RATE-LIMITING STEPS MAY LEAD TO DIFFERENT CONCLUSIONS.

THE CALCULATED OXIDE-VOLUME AND THE TRANSITION TIME FROM THE PROTECTIVE PRE-TRANSITION OXIDE TO THE NON--PROTECTIVE POST-TRANSITION OXIDE.

Temperature (* C)	Transition Time (Years)	Oxide Thickness (cm for 10,000 Years)
100	1.62x10 ^s	1.15x10 ⁻⁵
150	3,636	9.48x10 ⁻⁵
200	182	2.18x10 ⁻³

* From the Hillner equations used by Rothman and the density of -5.89 of $2rO_2$.

* Although it is known that the post-transition oxide forms in air at temperatures above 350° C, following Van der Linde equation, the pre-transition oxidation kinetics are considered to be essentially the same in water or steam, fused salt or air at 350° C. However, the equation of Van der Linde gives less oxides than Hillner equation.

C-14 RELEASE FROM POST-TRANSITION OXIDE OF THE CLADDING [Ahn, 1993]

Temperature (* C) Time to Total Release (Years)		lelease (Years)
	parabolic	46
200	cubic	2.94x10 ⁴
	parabolic	1.50x10 ³
100	cubic	5.46x10 ⁶

CARBON	- OR SELF-D AND	THEIR OXIDES [Ahn, 1993]	, ZIRCALOY
Diffusion Species	Matrix	Diffusivity (cm ² /sec) {D Values at 100° C} <d 200°="" at="" c="" values=""></d>	Temp.(*C)
C-14	α-Zs	3.51x10 ⁻⁵ x exp(-30,700 cal/RT) {4.7x10 ⁻²² } <2.8x10 ⁻¹⁹ >	600-800
С	a-Zircaloy -2	1.41x10 ⁻³ x exp(-38,000/RT) {1.1x10 ⁻²³ }<5.1x10 ⁻²¹ >	600-770
С	β-Z. 1	8.90x10 ⁻² x exp(-32,060/RT) {1.9x10 ⁻²⁵ } <1.7x10 ⁻¹⁶ >	870-1,250
С	β-Zircaloy -2	$2.45 \times 10^{-1} \text{ x}$ exp(-35,920/RT) $\{3.0 \times 10^{-22}\} < 7.9 \times 10^{-18} >$	990-1,250
0	ZrO ₂	0.9x10 ⁻³ x exp(-28,700/RT) {1.8x10 ⁻²² } < 6.0x10 ⁻¹⁷ >	334-470
		$\begin{array}{c} 1.36 \times 10^{-4} \text{ x} \\ \exp(-28,400/\text{RT}) \\ \{4.0 \times 10^{-21}\} < 1.2 \times 10^{-17} > \end{array}$	875- 1,050
•		9.7x10 ⁻³ x exp(-56,000/RT) {2.4x10 ⁻³³ } <1.9x10 ⁻²³ >	800- 1,000
0	UO _{2.002}	1.2x10 ³ x exp(-65,300/RT)	400-800
·	UO _{2.004}	$\{1.2 \times 10^{-7}\} < 1.3 \times 10^{-7} >$ $7 \times 10^{4} x$ $\exp(-29,700/RT)$	400-800
	UO _{2.00} 3	$\{3.6x10^{-23}\} < 1.6x10^{-19} > 2.06x10^{-3} x$ exp(-29,700/RT) $\{1.1x10^{-20}\} < 4.8x10^{-17} >$	400-800
_		7.5x10* 2.2x10* 2.0x15*	800 800 800
Self	β-Zr	0.0024 x exp(-38,000/RT) {1.8x10 ⁻²³ }	
Self	γ- U	0.0018 x exp(-27,500/RT) {1.8x10 ⁻¹⁹ }	



CONCLUSION NEED FURTHER STUDIES OF - HIGHER OXIDE FORMATION AND C-14 RELEASE IN DRY ENVIRONMENTS, - (A) VITRIFICATION PROCESS VARIABLES, (B) VITRIFICATION PRODUCT CONSISTENCY, - (A) SF AND GLASS MATRIX DISSOLUTION, (B) COLLOID FORMATION IN SF AND GLASS,(C) CRITICALITY RELATED TO ALTERATION, • REFOCUS CURRENT TECHNICAL ASSESSMENTS FOR FUTURE NAS AMENDED RULES.

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