U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

PRESENTATION TO
THE NUCLEAR WASTE TECHNICAL REVIEW BOARD

SUBJECT: WASTE FORM ALTERATION/DISSOLUTION FOR RELEASE RATES

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PRESENTER'S TITLE AND ORGANIZATION: TECHNICAL AREA LEADER
WASTE FORM CHARACTERIZATION
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Waste Form Characteristics—Release Rate Design/PA

Why? Requirement Statements NRC part 60

- Substantially complete containment of waste package
- Release rate limit (1000 yr inventory) engineered barrier system

What Characteristics? Initial state and rate response

- Radionuclide inventory evolution
- Alteration rate response
- Dissolution rate response

Focus of Presentation

- Spent Fuel Alteration and Dissolution Testing/Modeling for Release Rate Response

Waste Form Characteristic – Use of Rate Responses

Release Rate Expression (Rapid Release neglected) from Waste Form

$\dot{R}_{aqueous}$ ~ {Containers Failed} ⊛ {Waste Area Exposed} ⊛ {Waste Area Wetted} ⊛ {Water Volume} ⊛ {Inventory Dissolution Rate}

where $\dot{R}_{aqueous}$ is subject to solubility limit constraints if applicable (non-colloidal solutions).

Waste Area Exposed	——>	Alteration Rate Response
Inventory Dissolution Rate	——>	Dissolution Rate Response and Inventory Evolution

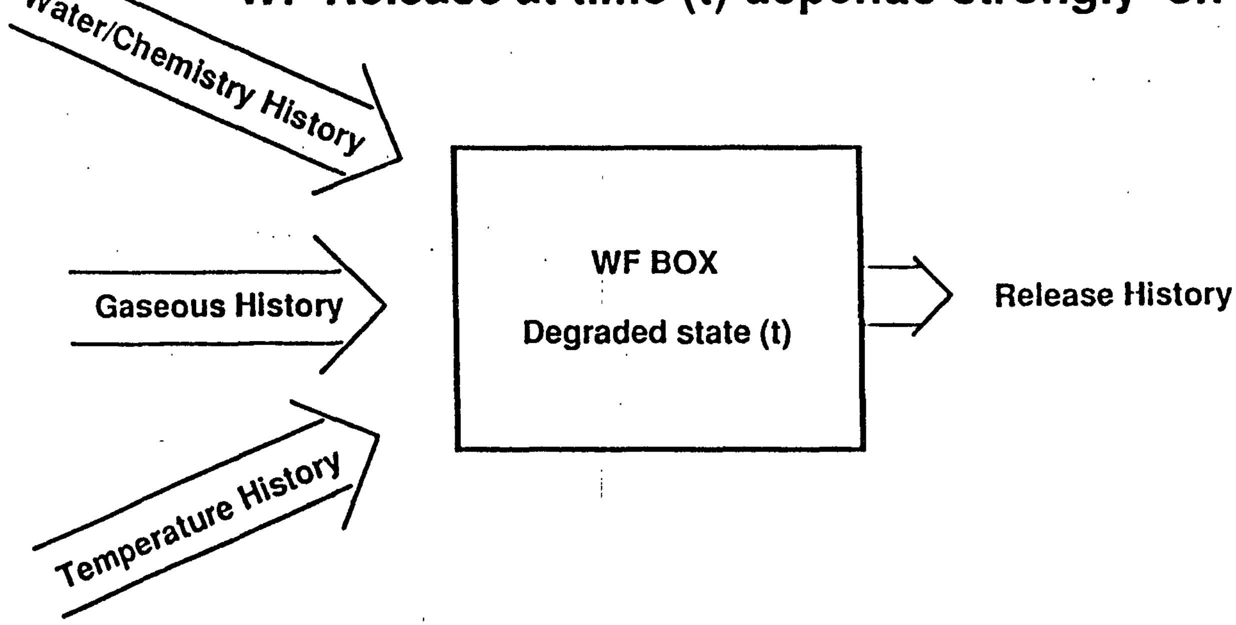
Basis of WF Testing and Modeling Activities

Waste Form (WF)
- Spent fuel + DHLW (glass) + ?
- Characterized by a set of "state variables"

Waste Form Responses
- Time history of "state variables"

WF Initial State (t = 0) ⟹ evolves/degrades in time as a function of temperature environment, gaseous environment and water/ chemistry environment to a ⟹ WF State (t)

WF Release at time (t) depends strongly on WF State (t)



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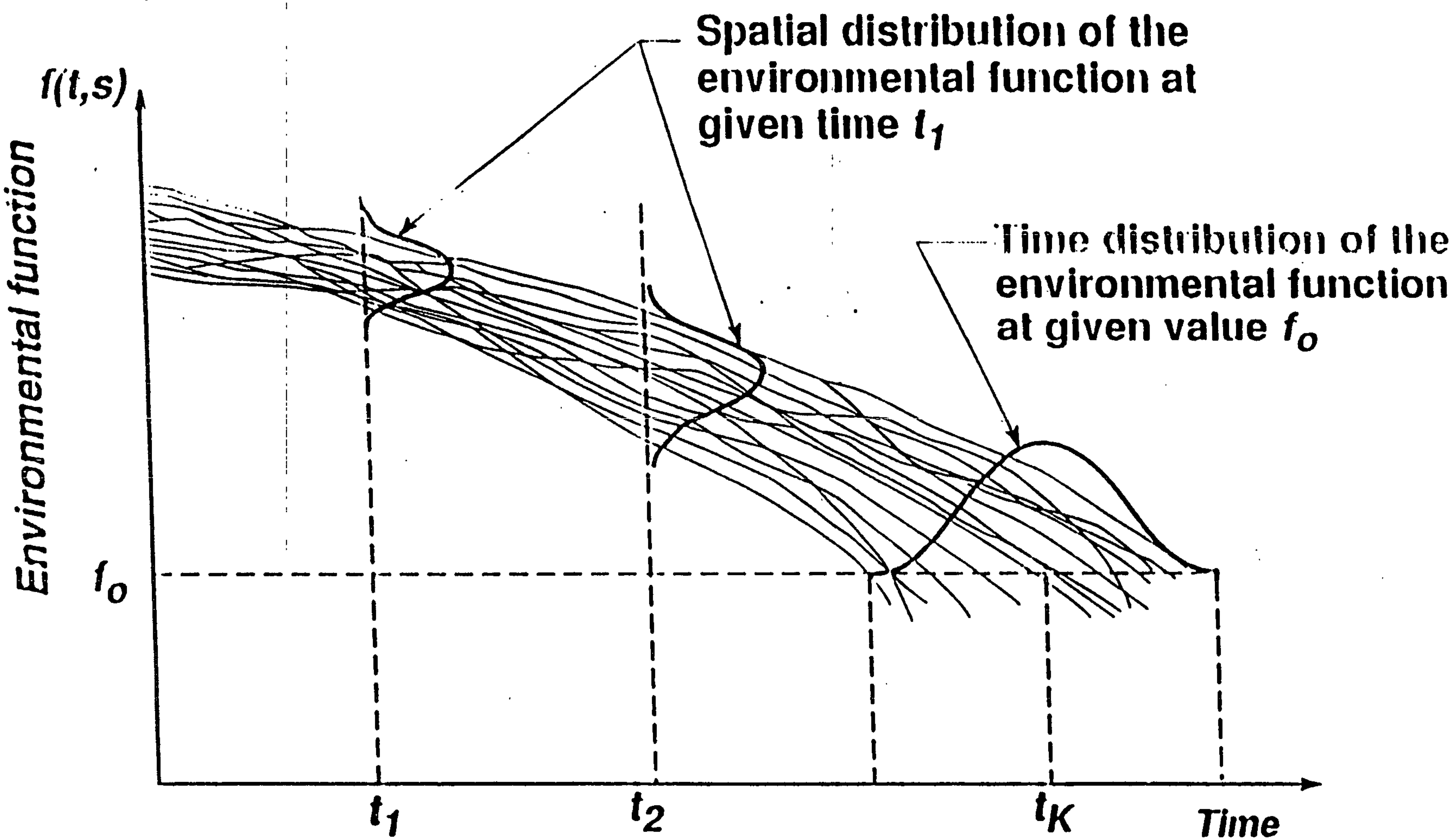
Waste Package Environmental Boundary Conditions



Stochastic illustration in the spatial values of the environmental functions over time.

ORNL DWG 86-332

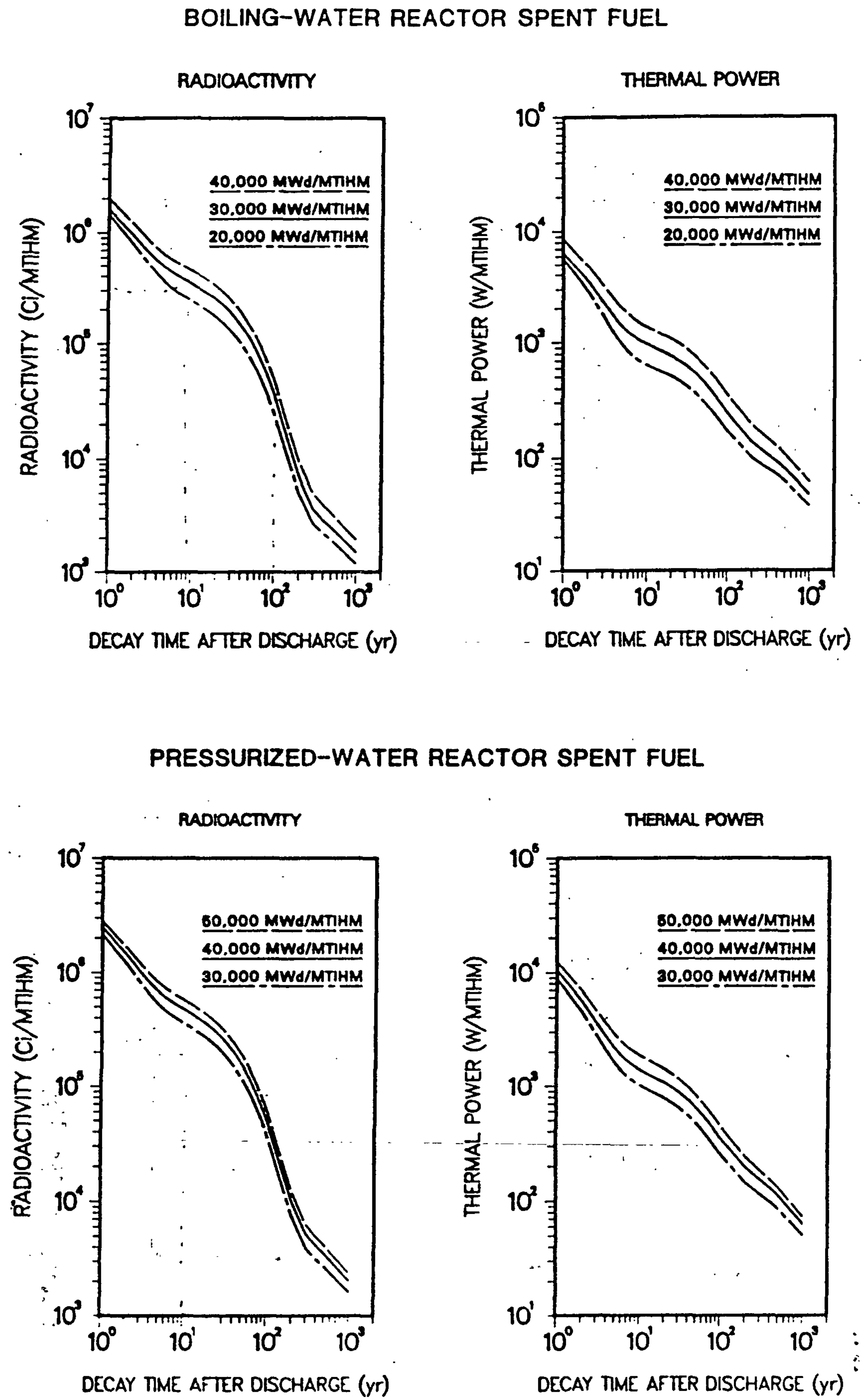
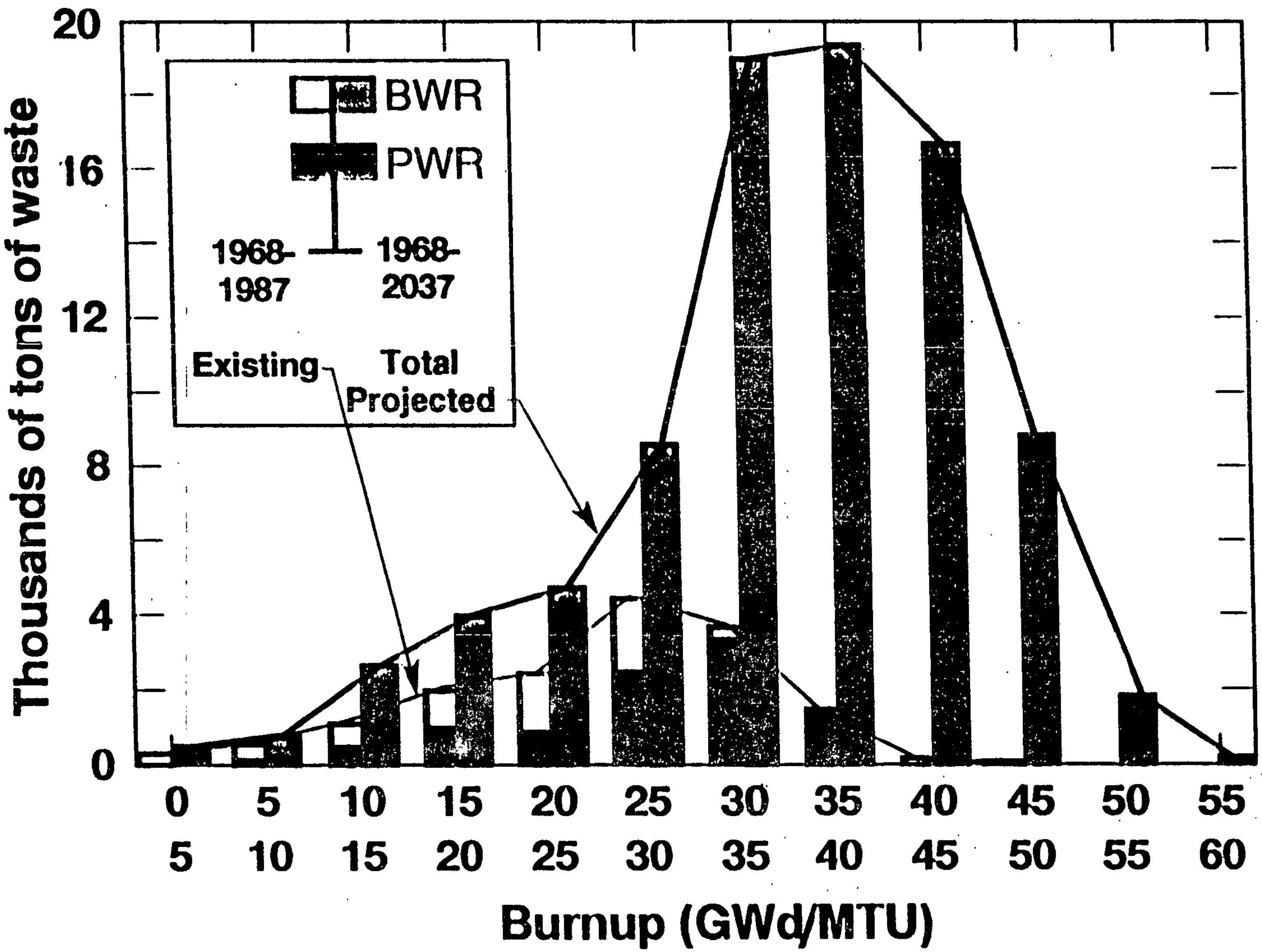


Fig. 1.5. Radioactivity and thermal power of 1 metric ton of heavy metal of BWR and PWR spent fuel as a function of burnup and time from reactor discharge.

WASTE INVENTORY-HISTORY AND PROJECTION



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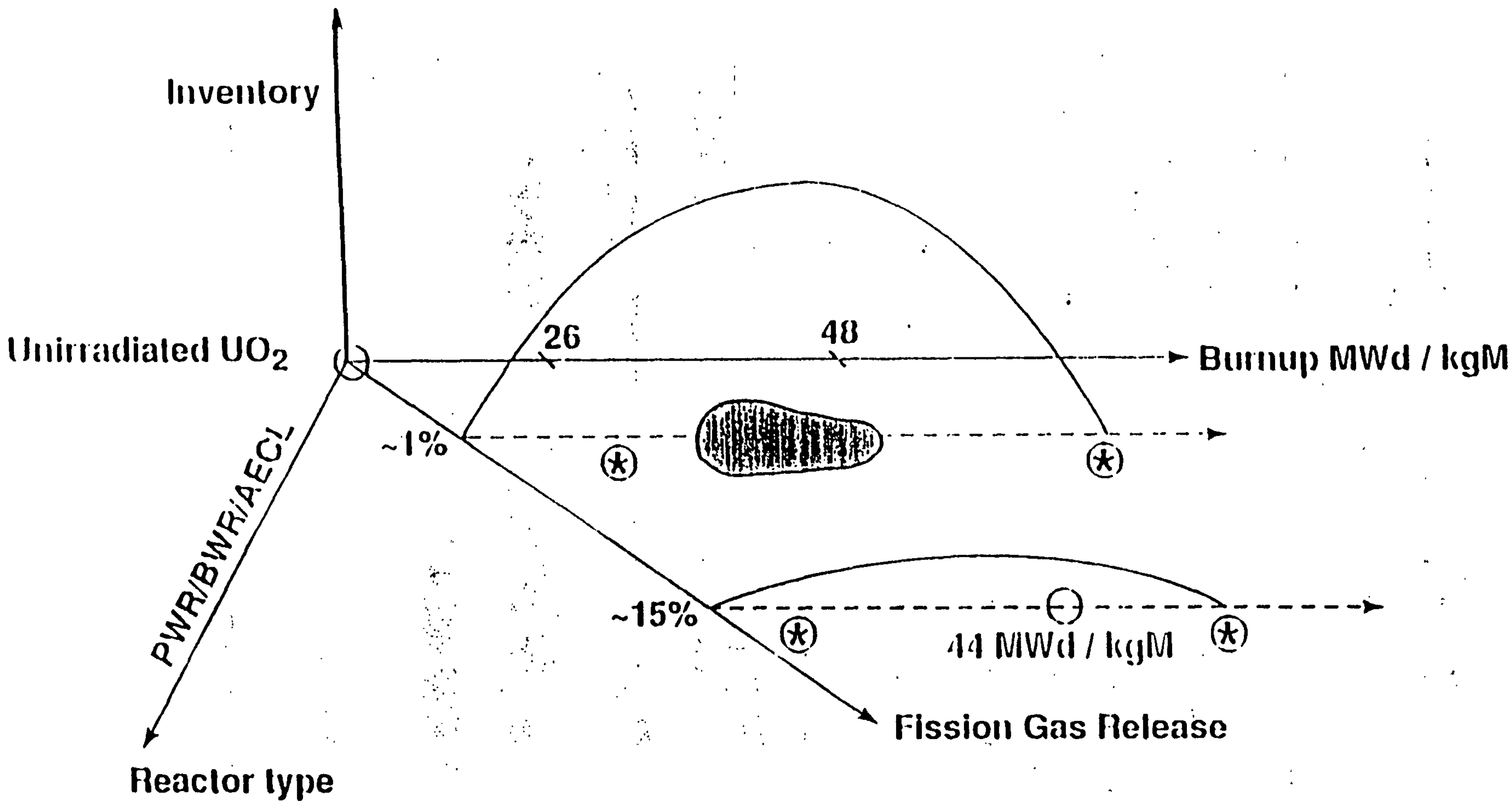
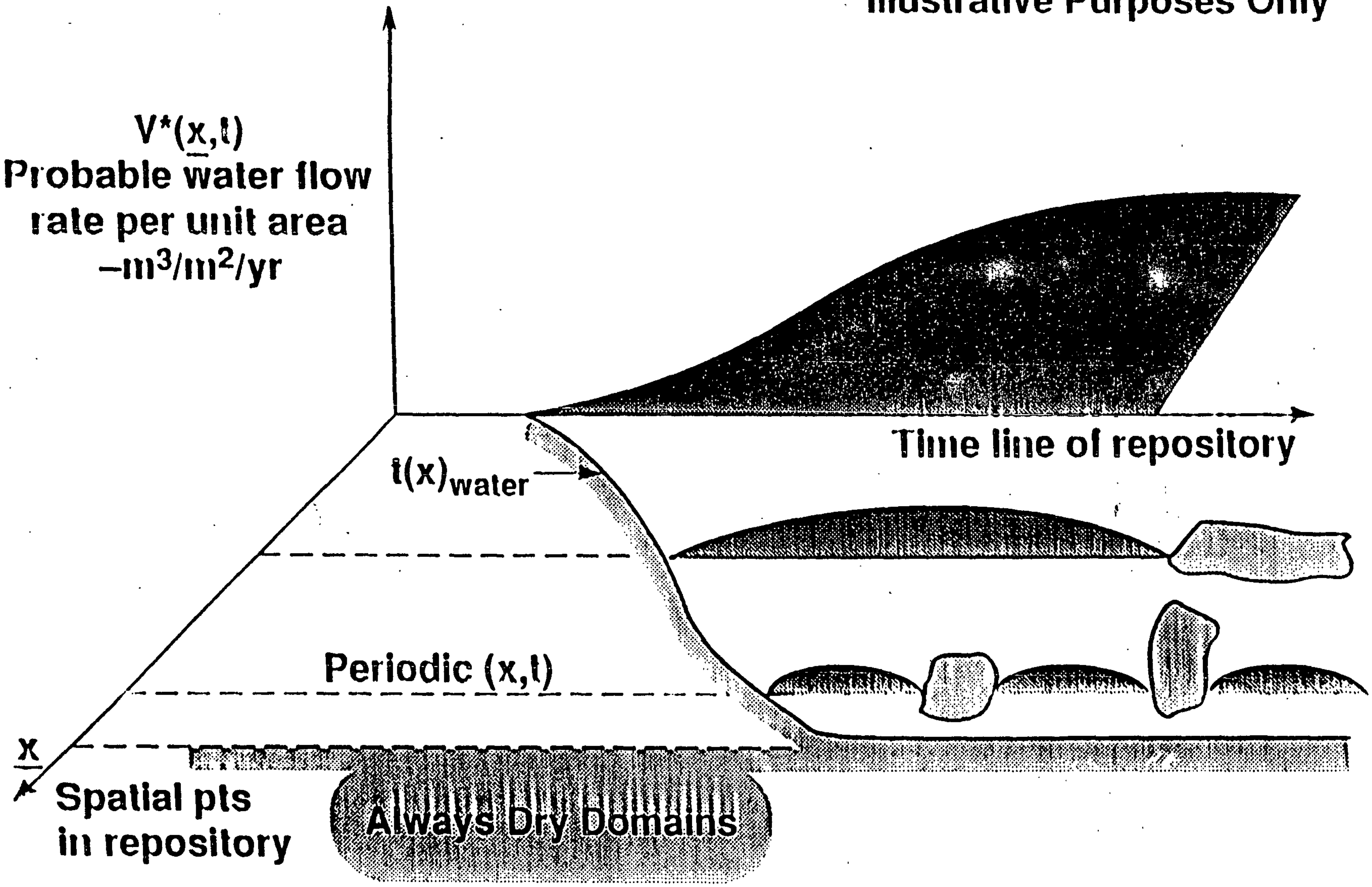
Spent fuel inventory attributes for test matrix (Illustrative)

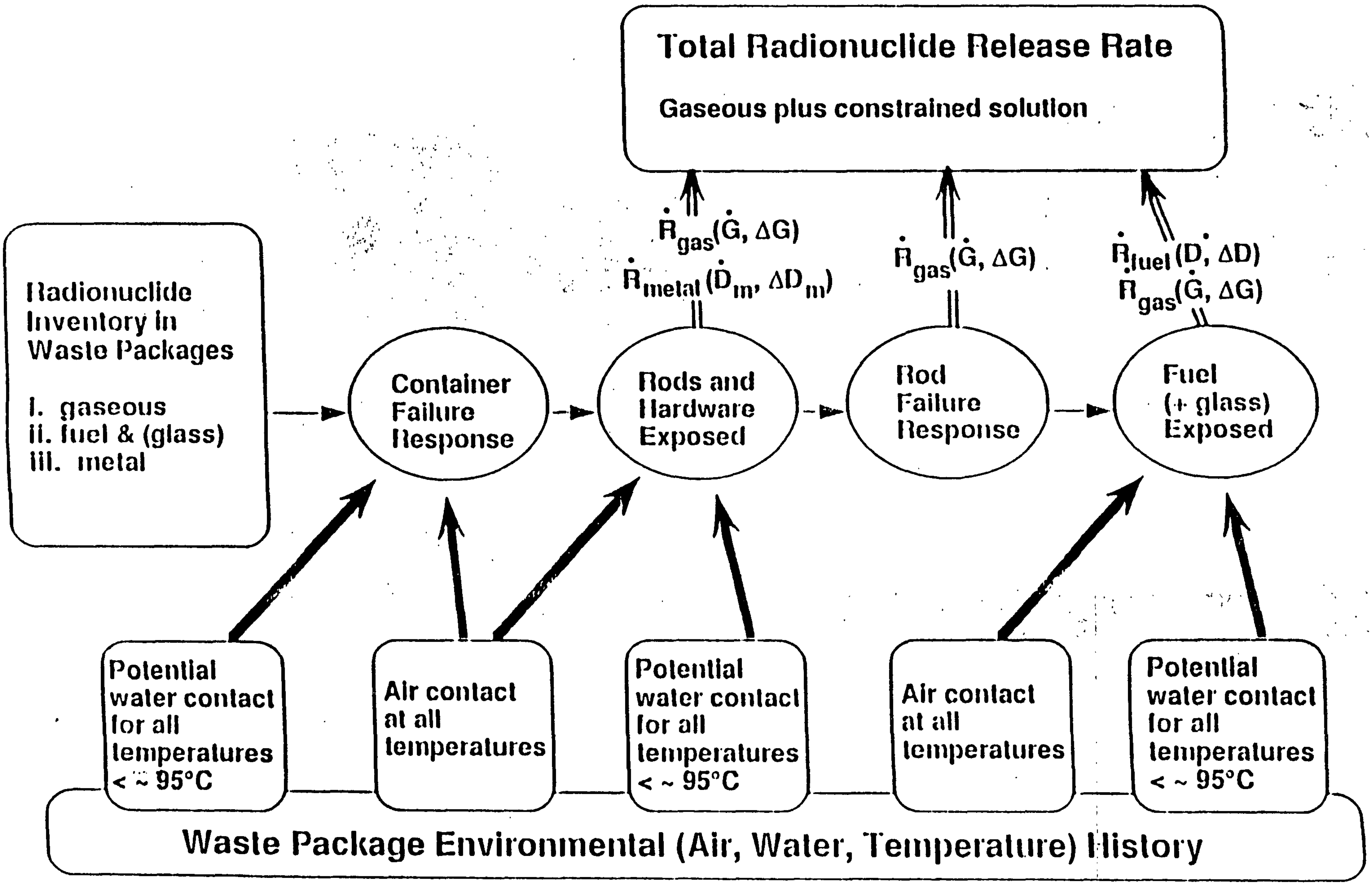


⊛ Future SF testing inventory:
low and high burnup with low and high FGR.

Illustrative Purposes Only



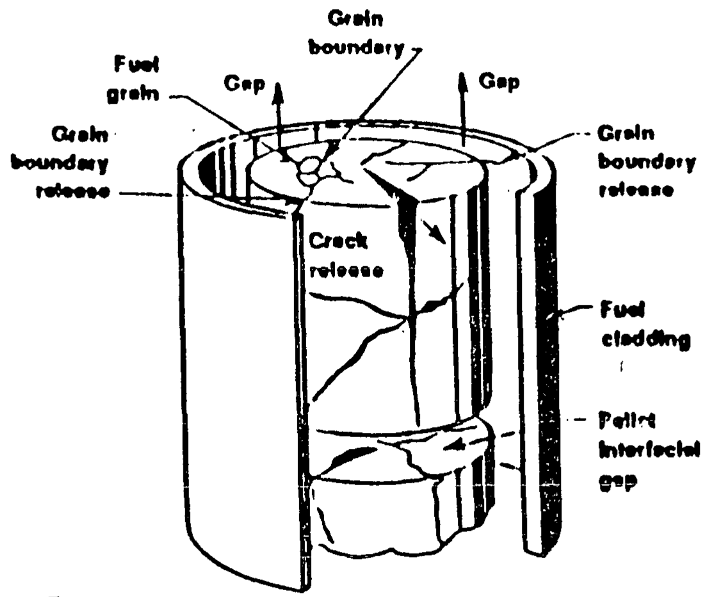
Source Term Release Rate Diagram

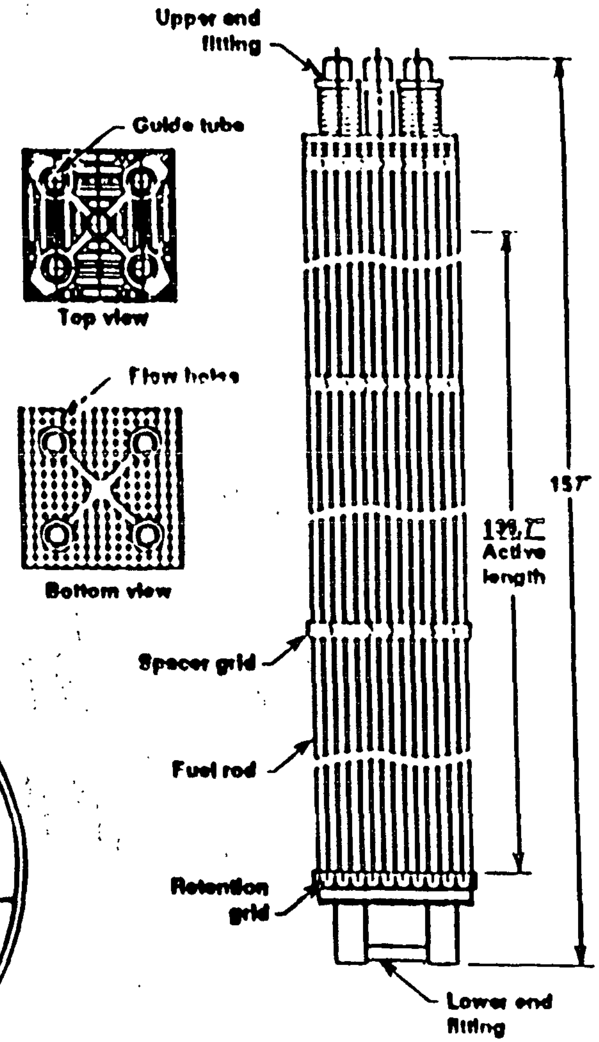


Spent Fuel Development — Length and Time Scale Problems

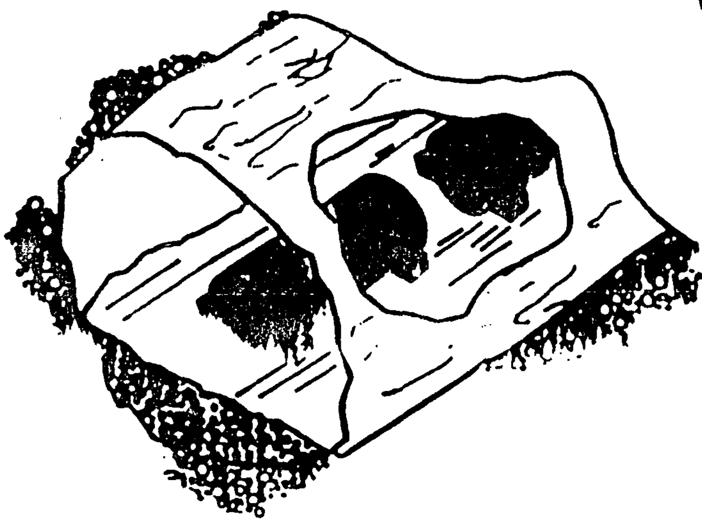
Spent Fuel Details

pellet fragments
and cladding

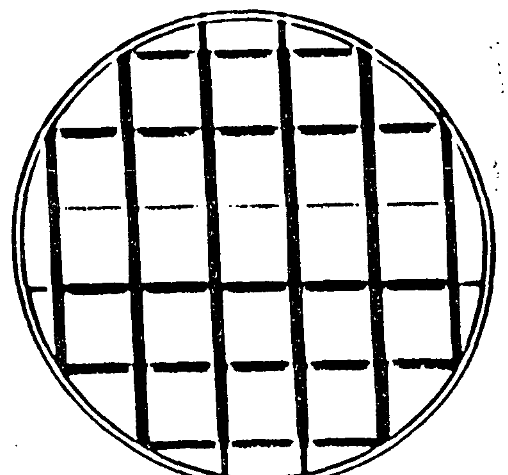




Spent Fuel Assembly

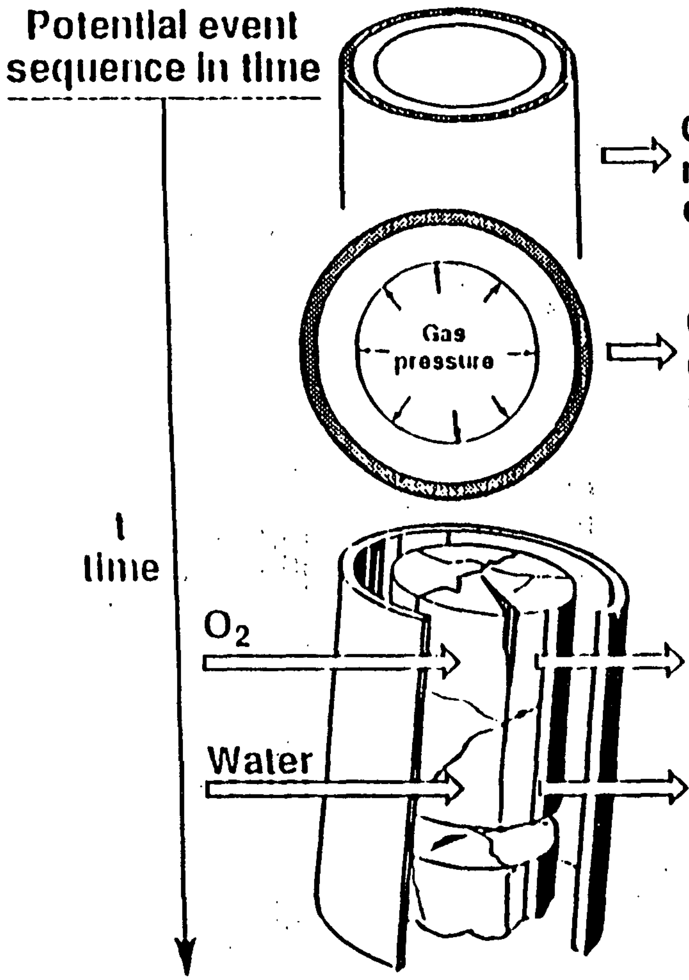


Waste Package Drift
Emplacement



21 PWR Assembly MPC

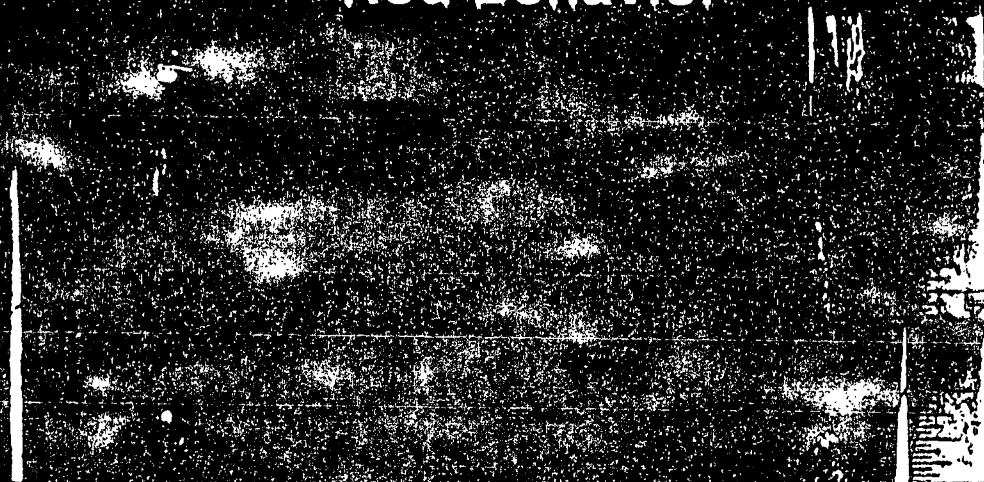
Spent Fuel Responses



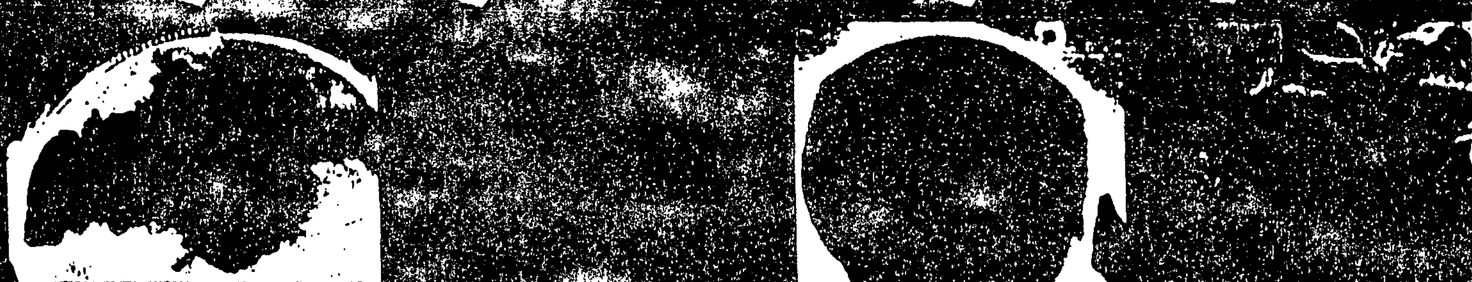
Gaseous release response from cladding	— Carbon ^{14} release	— $\dot{G}$ and ΔG	
Cladding degradation response	— Rod failure time response	— $\dot{R}_f$	
UO_2 oxidation response	— Phase change kinetics	— P_{NM}, eg	$P_{12} \sim UO_2$ $P_{49} \sim U_4O_9$ $P_{38} \sim U_3O_8$
	— Oxidation response	— $\dot{O}$	
UO_2 dissolution response	— Dissolution response	— $\dot{D}$ (gm/m^2/day) and ΔD	
⇩			
Geochemistry solution response	— Solubility limits and Colloidal response	— S_L and C_R	

Oxidation Progression

Rod Behavior



$$UO_2 \rightarrow U_4O_9 \rightarrow U_3O_7 \rightarrow U_3O_8 \rightarrow UO_3 \rightarrow UO_3 \cdot 2H_2O$$



Fragment Behavior

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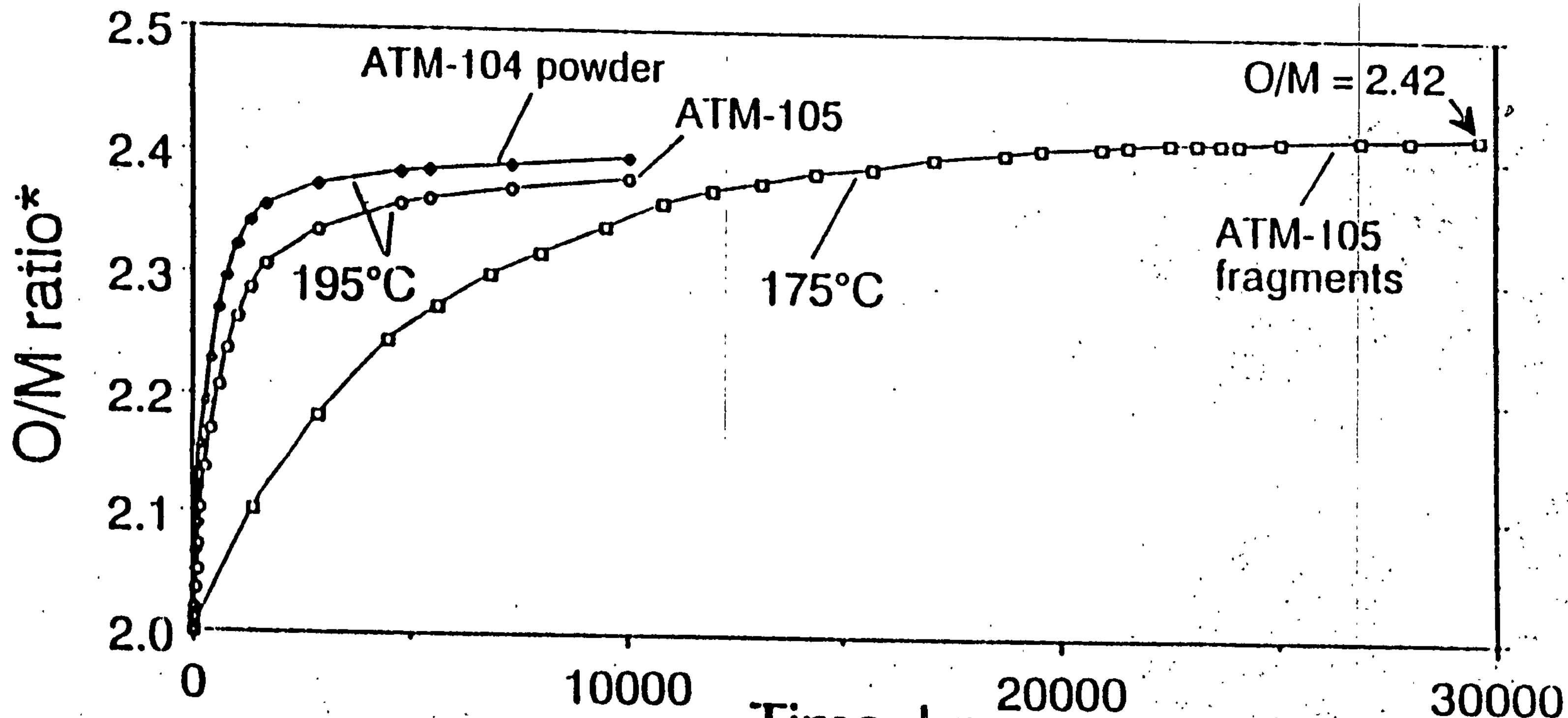
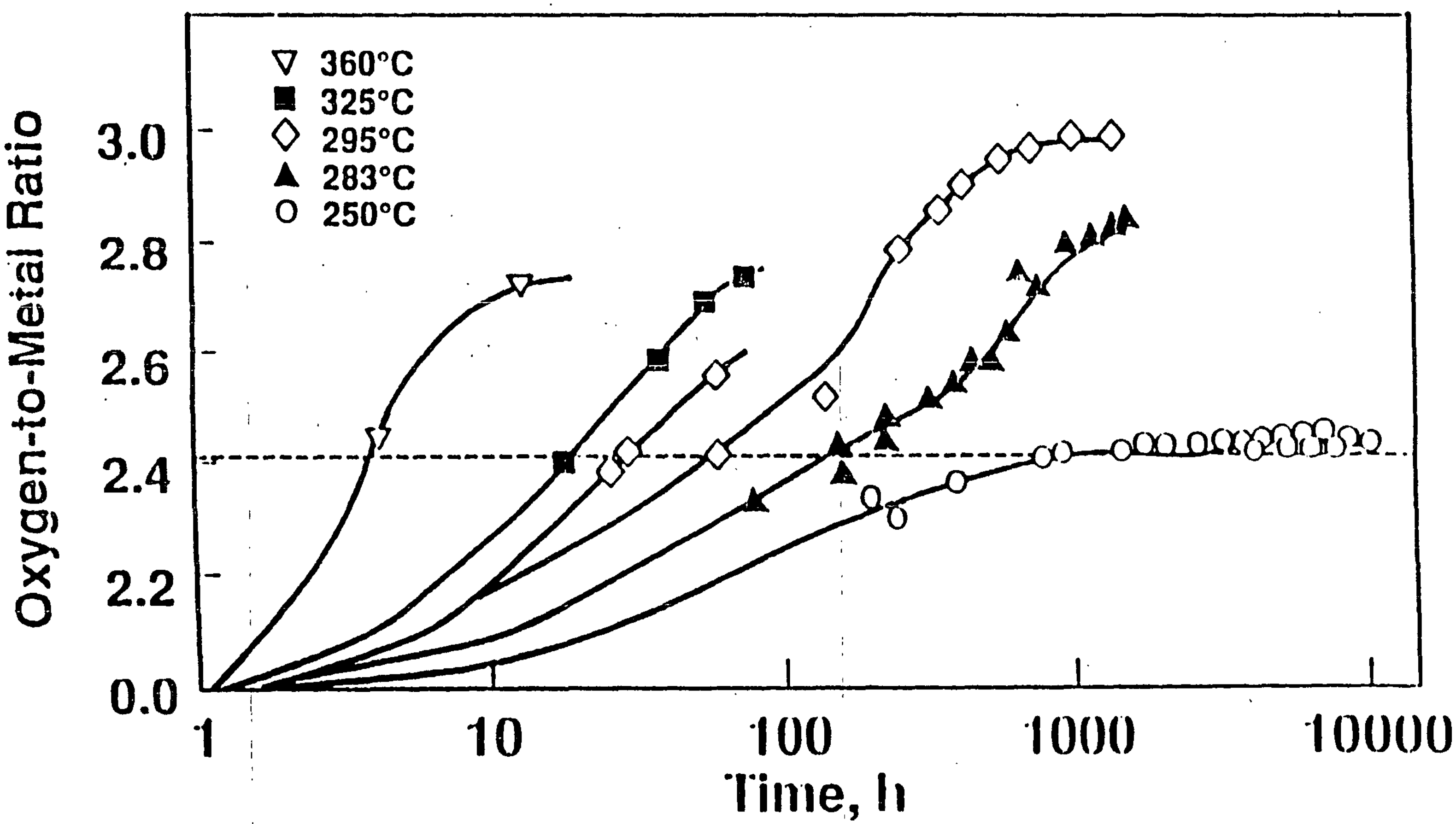
Oxidation of LWR Spent Fuel

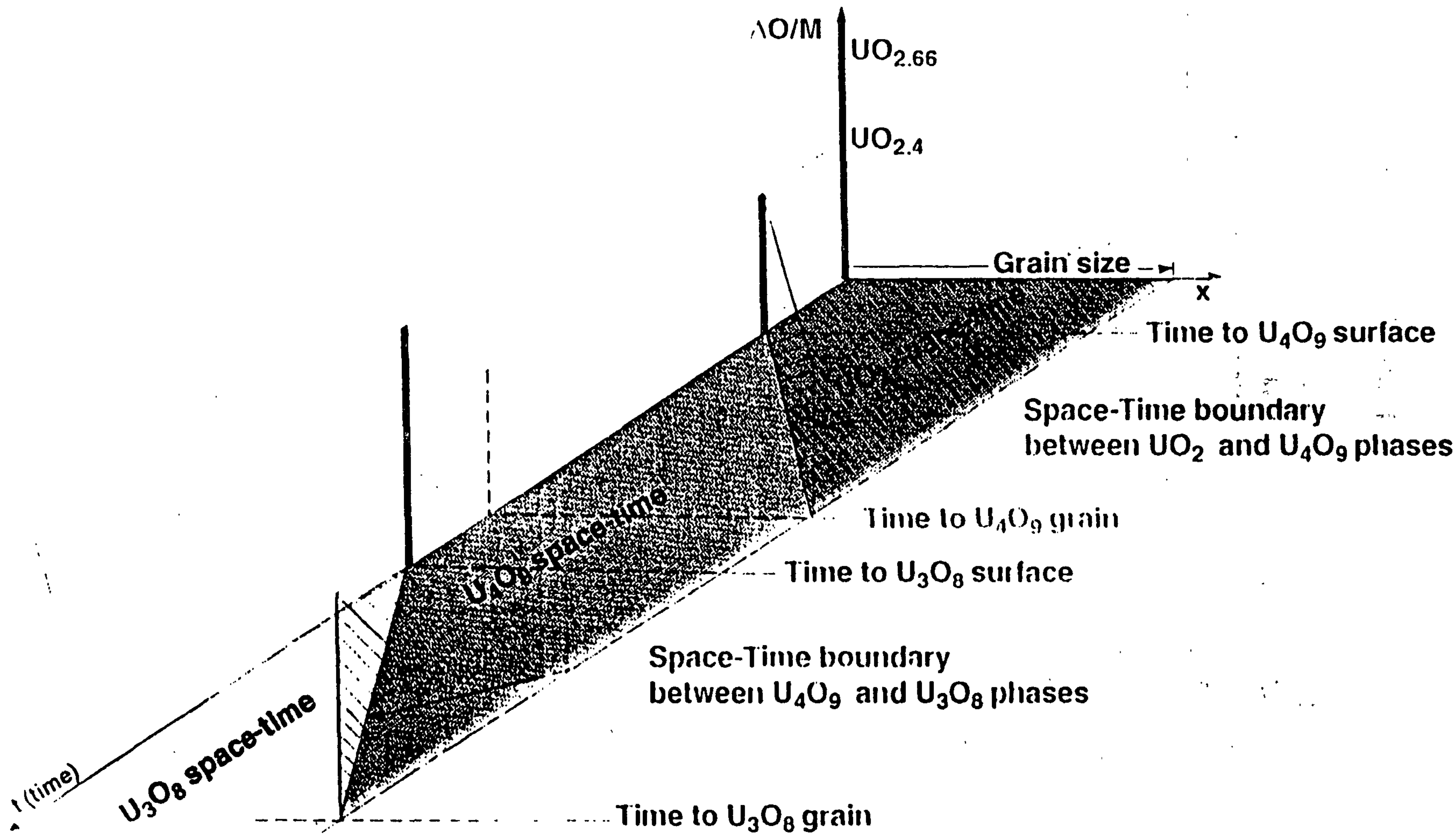


*from weight gains

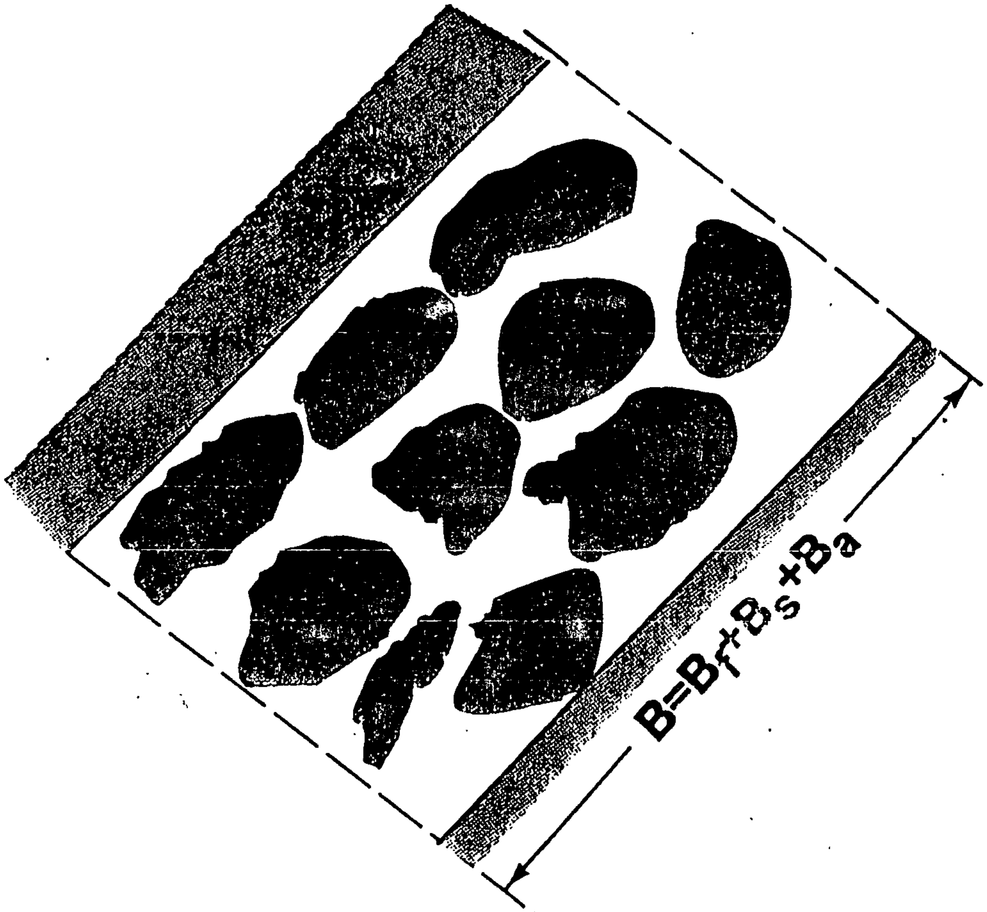
Oxidation of Fragments of Turkey Point Fuel



Spent Fuel Oxidation Response—Conceptualization for Model



Dissolution/Release Rate Testing



Types of Testing:

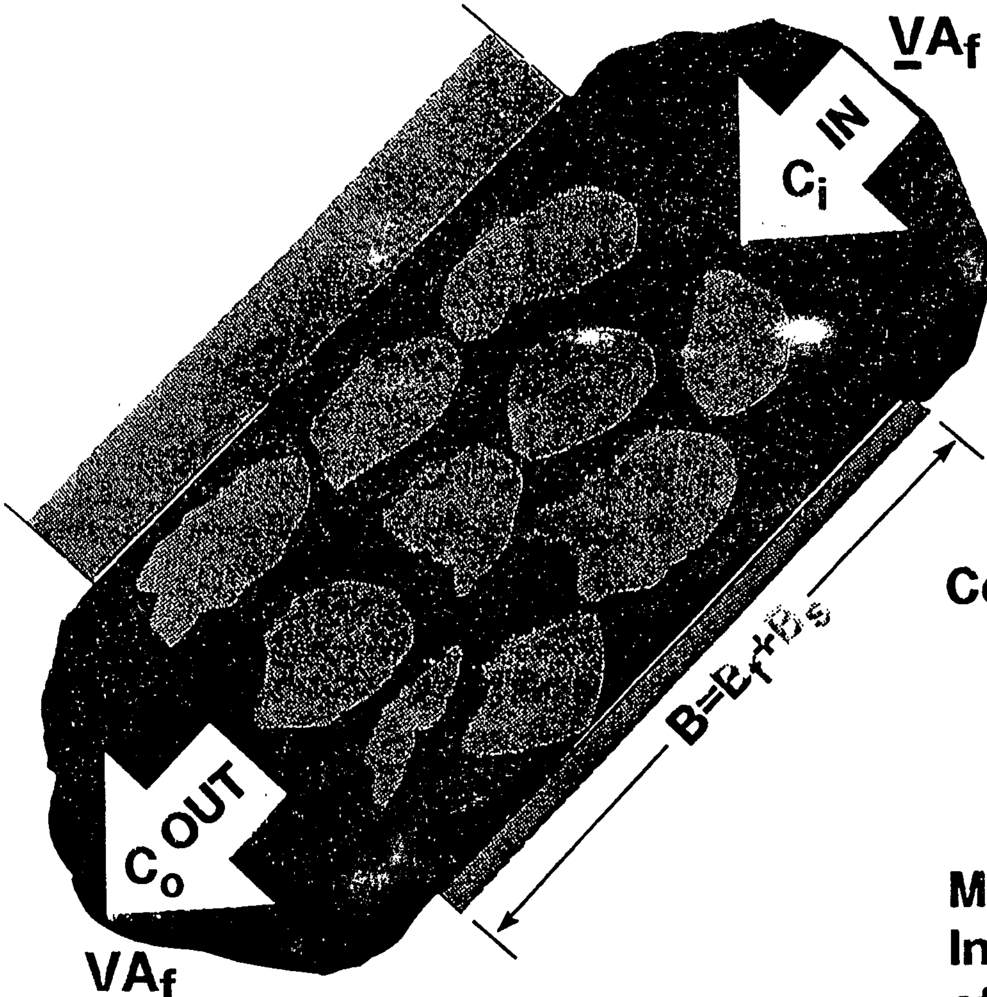
1. Flow thru dissolution
2. Saturated dissolution
3. Unsaturated dissolution

B... Volume that can contain subvolumes of Water - B_f, Spent Fuel (SF) - B_s, and Moist air - B_a

All three tests have same mass balance equation:

"Rate of concentration change in water" equals "the spent fuel rate of dissolution from spent fuel surface" minus "rate of precipitate formation" minus "rate of colloid formation "

Dissolution Testing— Flow Through Test

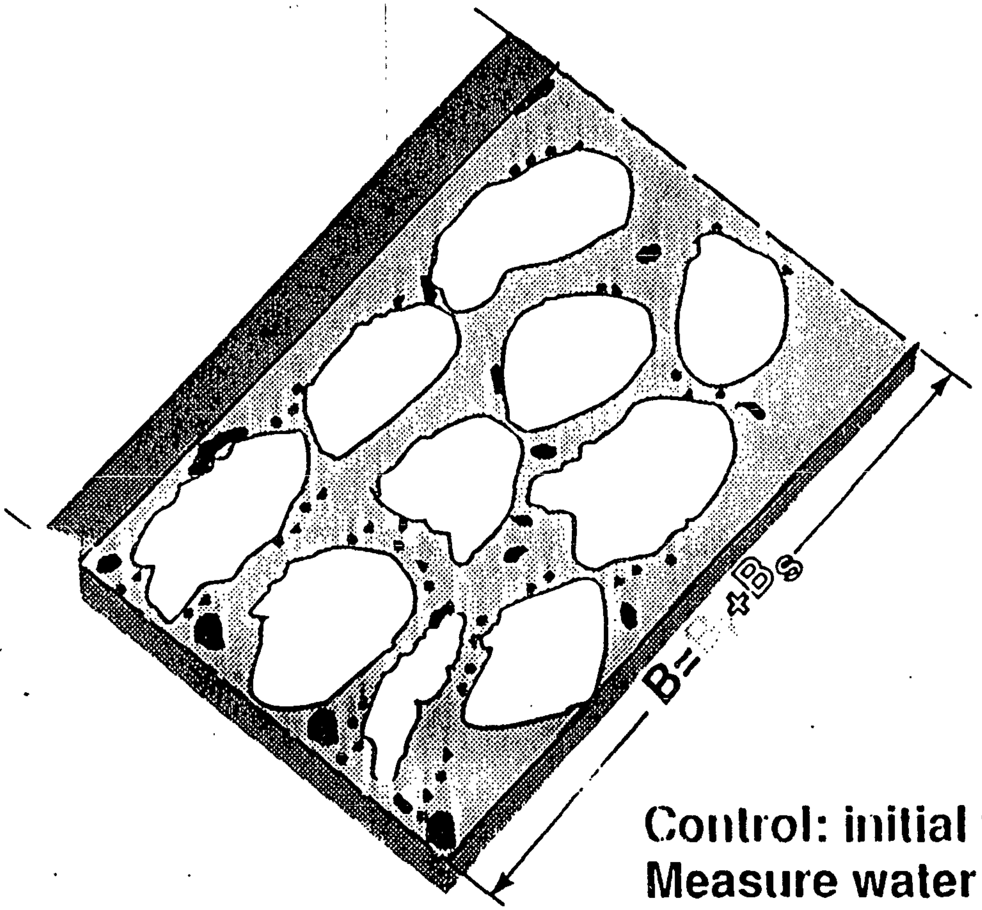


Control: inlet water chemistry-C_i
rate of flow-$\underline{V}A_f$
temperature - T
solid surface (SF) - A_s
spent fuel phase U_NO_M

Measure outlet water chemistry- C_o
Infer "dissolution rate" as function of temperature and water chemistry

ES6/24/94RS#5-03

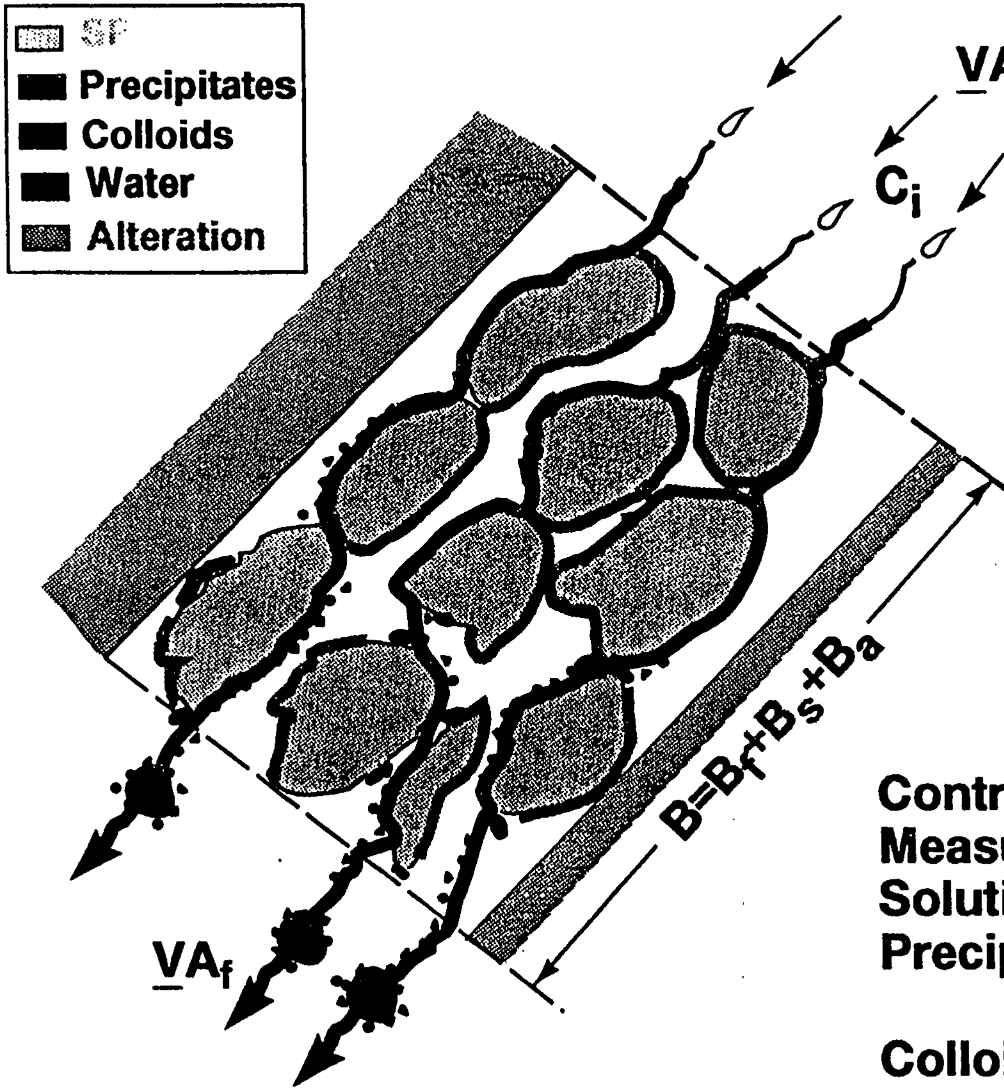
Dissolution Testing—
Saturated Test (lots of water) - not moving-



- SF
- Precipitates
- Colloids

Control: initial water chemistry(WC) temperature (T)
Measure water chemistry (discrete times)
Infer (soluble)"dissolution rate"
Infer (precipitates)"solubility limits"C_p
See Colloidal particles -filtration-

Dissolution/Release Rate Testing— Unsaturated Tests (with water moving)



Control: inlet WC; C_i, T, $\underline{V}A_f$
Measure: outlet WC; C~C_o+C_c+C_p
Solution concentration C_o
Precipitates~C_p- Speciation
- Solubility Limits
Colloids~C_o
Surface Area~A_s
Infer-Release Rate~(C_o+C_c+C_p)/$A_s\Delta t$

EB4/24/04RS#6-02

Model Development Testing

Type of Testing	Time	Precipitation/ Solubility limited	Colloids	Test Control	Data Obtained
Flow Thru (fully wetted flow)	Short (weeks)	No	No	Excellent	Dissolution Rate
Saturated (fully wetted, no flow)	Long (years)	Yes	Yes (some)	Good	Dissolution/ Release Rate, Speciation/ Solubility, and colloids (some)
Unsaturated (film wetted, flow)	Long (years)	Yes	Yes (lots)	Difficult	Dissolution/ Release Rate, Speciation/ Solubility and Colloids (lots)
SF Wetted in defected cladding	Short & Long	Yes	Yes	Difficult	Dissolution/ Release Rate Defect Effect

Spent Fuel Data Show Temperature and Oxygen Interaction

- Classical Chemical Kinetic Rate Law:

  → Rate = $k[A]^a[B]^b[C]^c[D]^d \ldots \exp(E_a/RT)$

- UO_2: $\log(D)\{mg/(m^2/day)\} = 4.824+0.275\log_{10}[CO_3]+0.448\log_{10}[O_2]-0.27\log_{10}[H]-1685/T$ $r^2=0.79$

- SF: $\log(D)\{mg/(m^2/day)\} = 9.234+0.142\log_{10}[CO_3]-16.73\log_{10}[O_2]-0.140\log_{10}[H]-2133/T+\boxed{6.81\log_{10}(T)\log_{10}[O_2]}$ $r^2=0.85$

  → ATM-103 [PWR, 33MWd/kgM, 0.25% FGR]

Regression Fits of 20% Oxygen Results Similar

- UO_2: $\log(D)\{mg/(m^2/day)\} = 4.650+0.274\log_{10}[CO_3] - 0.187\log_{10}[H]-1500/T$

  $r^2=0.79$

- SF: $\log(D)\{mg/(m^2/day)\} = 7.202+0.226\log_{10}[CO_3] - 0.091\log_{10}[H]-1628/T$

  $r^2=0.95$

SPENT FUEL RADIONUCLIDE RELEASE
- Depends on fuel type and test conditions

- Release under Unsaturated Conditions
  - Colloids identified as clays containing soddyite and schoepite

Fifth Leach period, High-Drip Rate, ATM-103 Fuel

Species	Unprecip. (μCi/mL)	3-nm Filter (μCi/mL)	Colloidal (μCi/mL)
Cs-137	4	N.A.	N.A.
Pu-239	5×10^{-5}	4×10^{-7}	5×10^{-5}
Am-241	2×10^{-4}	3×10^{-6}	2×10^{-4}
Cm-244	4×10^{-4}	3×10^{-6}	4×10^{-4}

- Release under Saturated Conditions

Third Cycle, Final Solution, Turkey Point Fuel

Species	400-nm Filter (μCi/mL)
Cs-137	4
Pu-239	2×10^{-7}
Am-241	2×10^{-7}
Cm-244	8×10^{-8}

The release of radionuclides from glass depends on the reaction conditions, the glass reaction rate, and the reaction progress.

Example 1: Glass aged by contact with vapor, water contact in bathtub mode

		Soluble	Particulate
Radionuclide	Am	4×10^{-6}	7×10^{-3}
Released to	Pu	8×10^{-6}	6×10^{-3}
Solution (μCi/mL)	Np	1×10^{-5}	1×10^{-5}

Colloids observed: iron-rich clays, iron silicates, calcium actinide phosphate, uranium silicates

Example 2: Glass aged by contact with vapor, water contact in dripping mode

- Initially all of the radionuclides are released as a soluble fraction with the solubilities ranging from 7×10^{-3} to 1×10^{-5} μCi/mL
- After several years, the release values revert to distributions shown in Example 1

Example 3: Fresh glass, high surface area (glass), bathtub mode

- Tc and Np are released as soluble fractions at a long-term rate of up to 0.2 and 8 μCi/m^2/day

Performance Assessment – Basis of Design

PA Radionuclide Release Response Analysis (Aqueous)

[Release Response (t) Stochastic/Probabilistic] ≃ [Container Failure] ⊗ [Amount WF Area Inventory Exposed] ⊗ [Water Wetted Area] ⊗ [Dissolution Rate $gm/m^2/yr$]

Release Response (t) Stochastic/Probabilistic	Container Failure	Amount WF Area Inventory Exposed	Water Wetted Area	Dissolution Rate $gm/m^2/yr$
↑	↑	↑	↑	↑
Subject to solubility limit/colloidal constraints	Container + material response	WF state response (cladding/ oxidation/ alteration) Area increases	Hydrology/ water chemistry responses	WF dissolution (degraded state) response

"Design" – do things to minimize release response "history" to meet repository requirements specifications

Design – parameter/controls (interdependent)

1. container/material response
2. temperature history
3. hydrology (thermal) history
4. water chemistry history

} coupled with fact that waste form response is waste form response

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Summary — Waste Form Alteration/Dissolution

- Provided preliminary WF response models for TSPA93

- Focused spent fuel testing:

  — alteration response of spent fuel by oxidation to U_4O_9 and U_3O_8

  — dissolution testing of spent fuel over inventory, oxidation phase, and water contact modes

- Colloidal characterization activities planned for both spent fuel and glass waste forms