OXIDATIVE RELEASE MODELS

PRESENTATION IN
DOE/NRC TECHNICAL EXCHANGE ON
TOTAL SYSTEM PERFORMANCE ASSESSMENT (TSPA)
FOR YUCCA MOUNTAIN REPOSITORY
MAY 25-27, 1999, SAN ANTONIO, TX

Tae M. Ahn
Projects and Engineering Section/High-Level Waste Branch
Division of Waste Management
Office of Nuclear Material Safety and Safeguards
(301)415-5812/TMA@NRC.GOV

OUTLINE OF PRESENTATION

- Model Assumptions
- Models for Oxidative Dissolution of Spent Fuel
- Comparison with Other Models
- Supporting Data Base
- Summary and Future Work

MODEL ASSUMPTIONS

- Bathtub (Immersion)
- Oxidative Reaction
- Groundwater: J-13 Well Water with Ca and Si Ions
- The release rate of highly soluble radionuclides such as ^{99}Tc and ^{129}I is proportional to the dissolution rate of uranium in the primary phase.

MODELS FOR OXIDATIVE DISSOLUTION OF SPENT FUEL
(Model 2, Nominal Case)

- Data:
  (1) Immersion Test of Spent-Fuel Particles (~ 1 mm) J-13 Well Water at 25° and 90° C (Wilson, 1990)
  (2) Flow-through in J-13 Well Water at 25 ° C
  (Gray and Wilson, 1995; Gray, 1992) - Figures

- Dissolution Rate, r (mg m^{-2} d^{-1}) =
  $r_o \exp[-34.3/(R\,T)]$

  - r_o (mg m^{-2} d^{-1}) from 1.4×10^4 to 5.5×10^4, and R (kJ mol^{-1} K^{-1})
  - The release rate is with respect to the real surface area, including grain (~ 10 μm) boundary penetration. The activation energy is from the dissolution rate obtained in pure carbonate solution (modifications in later pages).

- Alternative Models:
  (1) pure carbonate solution (Model 1, user supplied)
  (2) J-13 well water drip (Model 3, user supplied)
  (3) others: W. Murphy

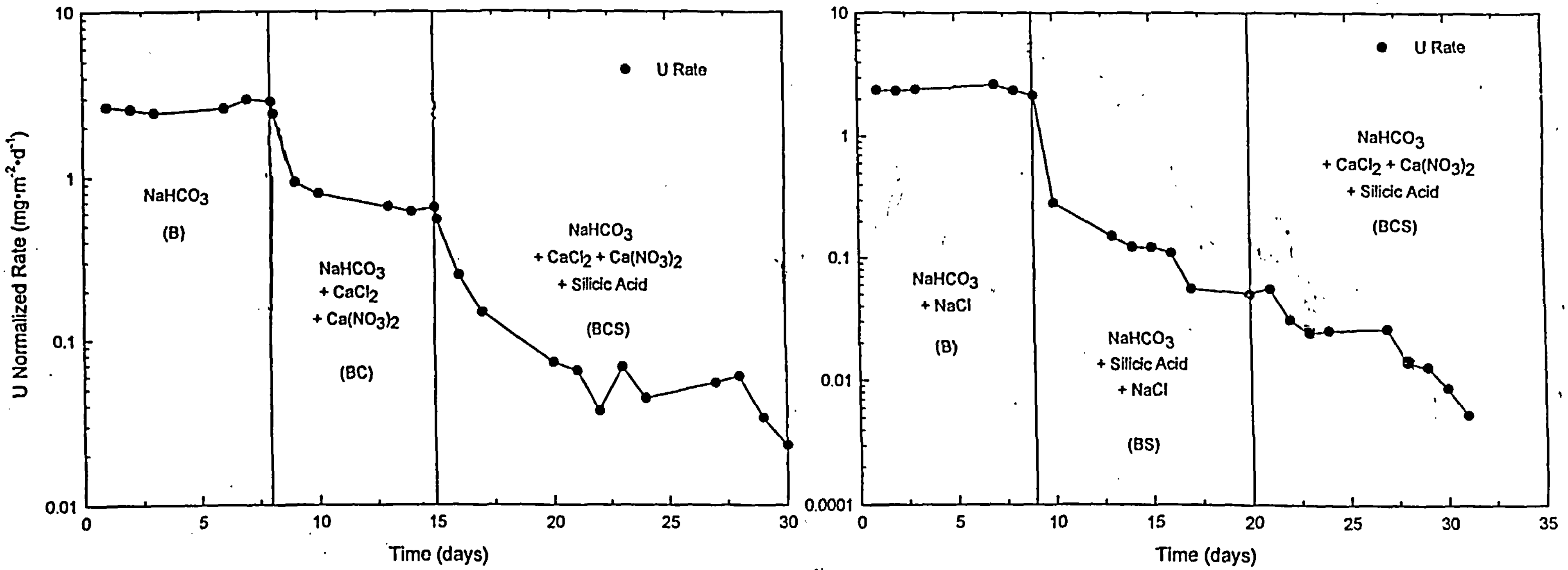


Figure. Effects of Solution Composition on Dissolution Rate, Flow-through Tests of 44 ~ 105 µm UO_2 at 25 °C (Gray and Wilson, 1995)

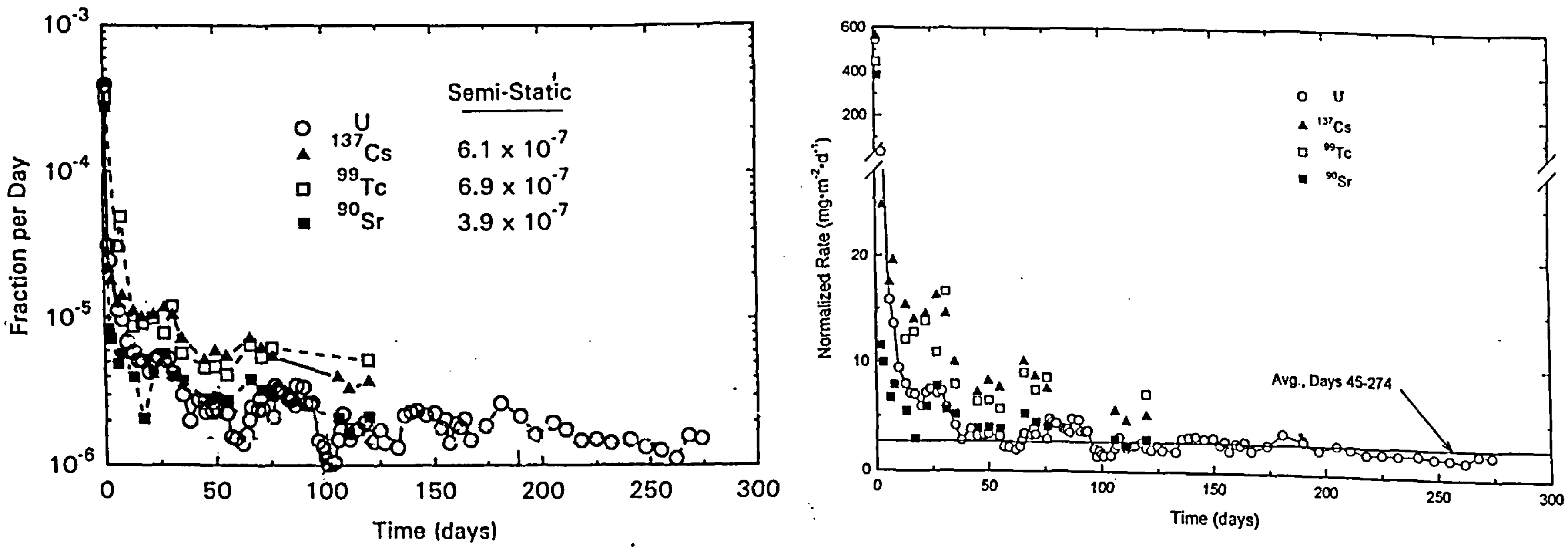


Figure. Spent-Fuel Dissolution Rates of Archived Particles, Flow-through Tests at 25 °C (Gray and Wilson, 1995; Gray, 1992; Wilson, 1990)

COMPARISON WITH OTHER MODELS

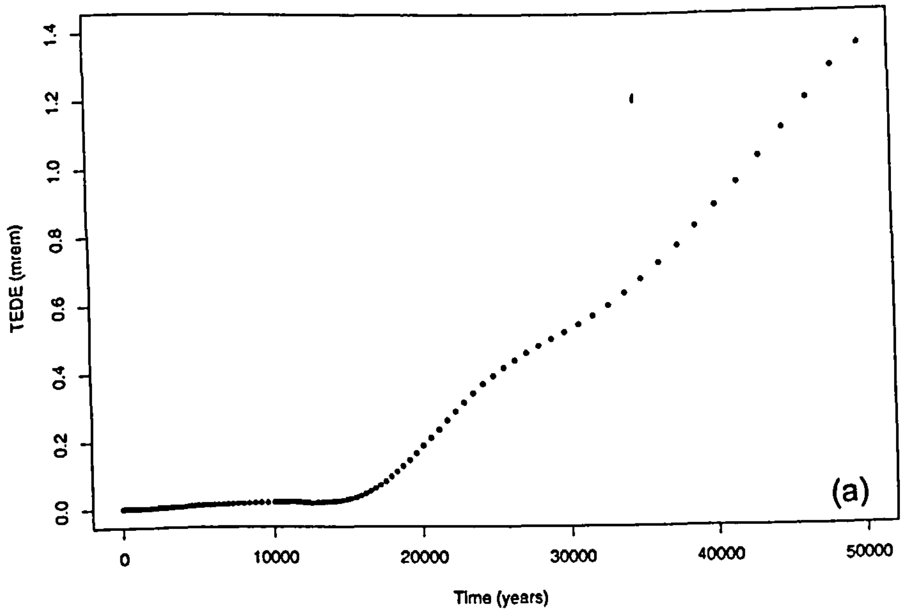
- Dissolution Rate ($mg\ m^{-2}\ d^{-1}$) at 25° C

This Base Model (NRC Model 2, Grain)	$(1 \sim 5)x10^{-2}$
DOE Model (NRC Model 1, Pure Carbonate Solution, Grain, User Supplied)	~ 3 ($[CO_3]=2x10^{-3}M$, $P_{O_2}=0.2$ atm, pH=8.4)
ANL Drip Test Model (NRC Model 3, Particle, User Supplied)	$7 \sim 110$

- Uncertainties

  - Grain boundary openings increase the surface area, resulting in the increased dissolution rate.
  - Grain boundary inventory could have contributed to the apparent dissolution rate. Because the PA Codes have separate inputs of the grain boundary inventory, the real dissolution rate of the matrix may be lower.

- - TPA Code has an option of particle and grain models (Figures)



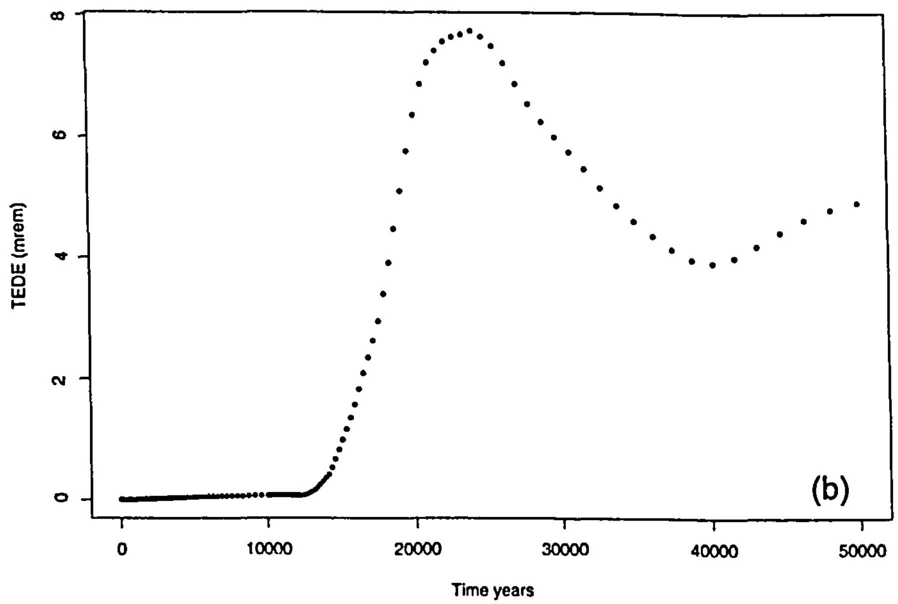


Figure. TPA3.2 Outputs (a) Nominal Case of particle model (McCartin, 1999) (b) Grain Model (Contardi, 1999)

SUPPORTING DATA

(1) Activation Energies are from immersion tests (Wilson, 1990)

(2) Three groups of dissolution rate

- J-13 well water, synthetic groundwater, granitic groundwater, tap water, and distilled water: ($2.4x10^{-4}$ ~5.4) mg m^{-2} d^{-1} at room temperature (RT)
- chloride solution: ($5x10^{-3}$ ~5.7) mg m^{-2} d^{-1} at RT
- carbonate solution: (0.23 ~ 3.3) at RT

(3) Tests of particles may increase the dissolution rate by as high as a factor 10 compared with grain tests, but the difference depends on (1) details of sample types such as size or oxidation state, (2) spent-fuel types such as fresh, archived, or different burnup, and (3) contribution of grain boundary inventory.

SUMMARY

(1) The dissolution rate of spent fuel in oxidative J-13 well water containing Ca and Si ions is approximately 10 ~ 100 times lower than that in pure carbonate solution. A representative kinetics of this lowered dissolution was presented.

(2) Dissolution rates from various models were compared. Uncertainties associated with grain boundary opening and the release of grain boundary dissolution were discussed.

(3) To refine the present model, literature data obtained in mineral waters were tabulated.

FUTURE WORK

(1) Sample the activation energy and the rate constant in the PA exercise

(2) Use DOE's new data obtained in J-13 well water

SUPPORTING DATA

Calculated Values of Activation Energy, Q (kJ mol^{-1} K^{-1}), from Immersion Tests Based on Soluble Radionuclides

^{137}Cs	^{90}Sr	^{99}Tc	^{129}I
18(10),16	-37 (-32), -14	33(28),26	29(33), 24

- The first for HBR fuels and the second for TP fuels
- All from PNL-7169 except the parentheses from PNL-7170 RT data

Dissolution Rate (mg/[m^2-day]) (U, otherwise specified)	Temperature (°C)	Sample Type	Test Method Solution	References
3	22	PWR: archived SF particles	flow-through J-13	Gray and Wilson, PNL-10540, 1995
0.85 (^{137}Cs) 0.96 (^{99}Tc) 0.54 (down to 0.19) (^{90}Sr)	25	SF particles	immersion J-13	derived from Gray and Wilson, PNL-10540, 1995, analysis of Wilson, 1990 ($3.9x10^{-7}$/d → 0.54 mg/[m^2-d] from SF particle tests
$3x10^{-2}$	25	powder particles UO_2 44 ~ 105 μm (Grains decrease diss. rate by a factor of an approx. max. 10, but these are bigger particles than grains)	flow-through $NaHCO_3$ + $CaCl_2$ Ca $(NO_3)_2$ + silicic acid	Gray and Wilson, 1995
$5x10^{-3}$	25	powder particles UO_2 44 ~ 105 μm (The same as particles)	flow-through $NaHCO_3$ + $CaCl_2$ + Ca $(NO_3)_2$ + silicic acid	Gray and Wilson, 1995
4.5	25	UO_2	DIW + Ca + Si	UCRL-ID-108314, 1998
$8x10^{-3}$	25	grains,UO_2	flow-through U3SW $NaSiO_3$	Tait, 1997
$2.5x10^{-2}$	25	grains,UO_2	flow-through U3SW $CaCl_2$	Tait, 1997

Dissolution Rate (mg/[m^2-day]) (U, otherwise specified)	Temperature (°C)	Sample Type	Test Method Solution	References
2×10^{-1} (^{137}Cs, ^{90}Sr) 1×10^{-1}	25	CANDU SF particles	flow-through SCSSS + 0.185 M Ca^{2+} + 0.00027 M SiO_4^{4-}	Tait and Luht, 1997
1.4×10^{-2} (^{90}Sr)	25	PWR, BWR and CANDU fuel, assumed SF particles	immersion SKB, NNWSI Canadian	Grambow et al., 1990, see also Forsyth, 1986 and Stroess-Gascoyne et al., 1985
0.35 ~ 1.8	25	BWR SF (Swedish)	immersion bent/ox, seq/ox log (p_{O_2}/p_{CO_2}) = -3.1 ~ -3.5	reviewed by Grambow, 1989
0.30 ~ 2.0 (Initial value)	25	UO_2, pellet 4.5 cm^2/9.8 g	immersion stat/ox synthetic groundwater log (p_{O_2}/p_{CO_2}) = -3.2 ~ -3.5	reviewed by Grambow, 1989 Ollila, 1997 (need confir.)
2.4×10^{-4} (Sr) (Slowed-down rate)	25	SIMFUEL 4 cm^2/8-grams (~ 1 cm particles)	immersion with and without replenishment Granitic, pH=8.2	Sandino et al., 1991
3.1 ~ 5.4 (Initial value)	25	SIMFUEL 50 ~ 315 μm	immersion synthetic groundwater	Garcia-Serrano et al., 1996

Dissolution Rate (mg/[m^2-day]) (U, otherwise specified)	Temperature (°C)	Sample Type	Test Method Solution	References
0.069	20 ~25	BWR (Swedish) fuel & clad 2 cm long segments (assumed SF particles)	immersion Allard synthetic groundwater	Forsyth 1986
0.028 (^{90}Sr)	25	CANDU 5 cm section fuel/ clad	immersion distilled water	Stroess-Gascoyne et al. 1985
0.14 ~ 0.69 (^{90}Sr)	25	CANDU 5 cm section fuel/ clad	Immersion tapwater DDH_2O	Stroess-Gascoyne 1997

Dissolution Rate (mg/[m²-day]) (U, otherwise specified)	Temperature (°C)	Sample Type	Test Method Solution	References
0.95 ~ 5.7 (Initial value) (Equivalent initial values that Gray derived should be lower.)	25	UO_2 - 100 ~ 300 μm - 900 ~ 1100 μm - pellet	immersion 0.01 M, pH=8 $NaClO_4$	Casas et al., 1993
0.17	25	SIMFUEL 100 ~ 300 μm	flow-through (comparable with Gray),pH = 8.6, $NaClO_4$	Bruno et al., 1995
0.005	25	UO_2 SIMFUEL 100 ~ 300 μm	batch pH = 8.6 $NaClO_4$	Bruno et al., 1995
0.23 ~ 3.3	25	SIMFUEL 100 ~ 300 μm	flow-through (comparable with Gray) pH = 8.4 ~ 8.6 $NaCl/NaHCO_3$	Bruno et al., 1995
0.21 ~ 1.27	25	UO_2 SIMFUEL 100 ~ 300 μm	batch pH = 8.5 $NaCl/NaHCO_3$	Bruno et al., 1995
0.84 ~ 2.40	25	UO_2 100 ~ 300 μm	flow-through (comparable with Gray) 10^{-4} ~ 0.05 M NaCl, 1mM $[HCO_3^-]$	de Pablo 1997