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Management System**

**Management & Operating  
Contractor**



**TRW Environmental Safety  
Systems Inc.**

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# In-Package Geochemistry

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Las Vegas, NV**

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# **In-Package Geochemistry: Outline**

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**(1) Purpose of Calculations**

**(2) Review of Waste Packages (Commercial vs. DOE SNF, MD)**

**(3) Methods**

**(4) Example (FFTF)**

**(5) Needs and Work in Progress:**

- Couple Geochemistry/Transport of Package and Near-Field**
- Evaluate Models for Variably-Saturated WP Degradation and Flow**
- Address Thermodynamic Data Needs**
- More Realistic Rate Models**
- Evaluate Effective Package/Near Field  $fO_2$**
- Cr example: Thermo data vs.  $fO_2$  modeling**

# (1) Purpose of Calculations

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**(a) Develop configurations/compositions for "internal" criticality calculations (within WP). Package degrades from water influx.**

Probability of internal criticality increases if neutron absorbers are removed and fissile materials remain in package. Conservative to assume most insoluble forms of fissile materials; e.g.  $\text{PuO}_2$  vs.  $\text{Pu}(\text{OH})_4$ .

**(b) Develop configurations for external criticality (outside WP). U & Pu-bearing water leaves package and flows through drift materials and fractured tuff. Assess masses of U, Pu & absorbers deposited ex-package.**

Probability of external criticality increases if neutron absorbers remain in the package, and fissile materials are released. NOT conservative to assume most insoluble forms of fissile materials in package.

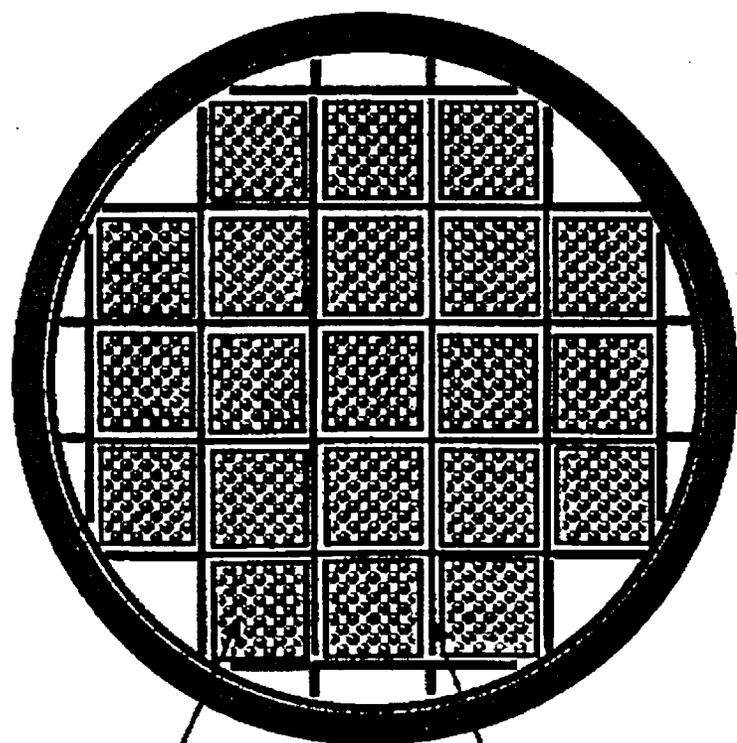
**(c) Recent change in scope: provide chemistry and source term for PA transport calculations. Add nuclides such as  $^{237}\text{Np}$ .**

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## (2) Codisposal Package Will Have High Glass/Fuel

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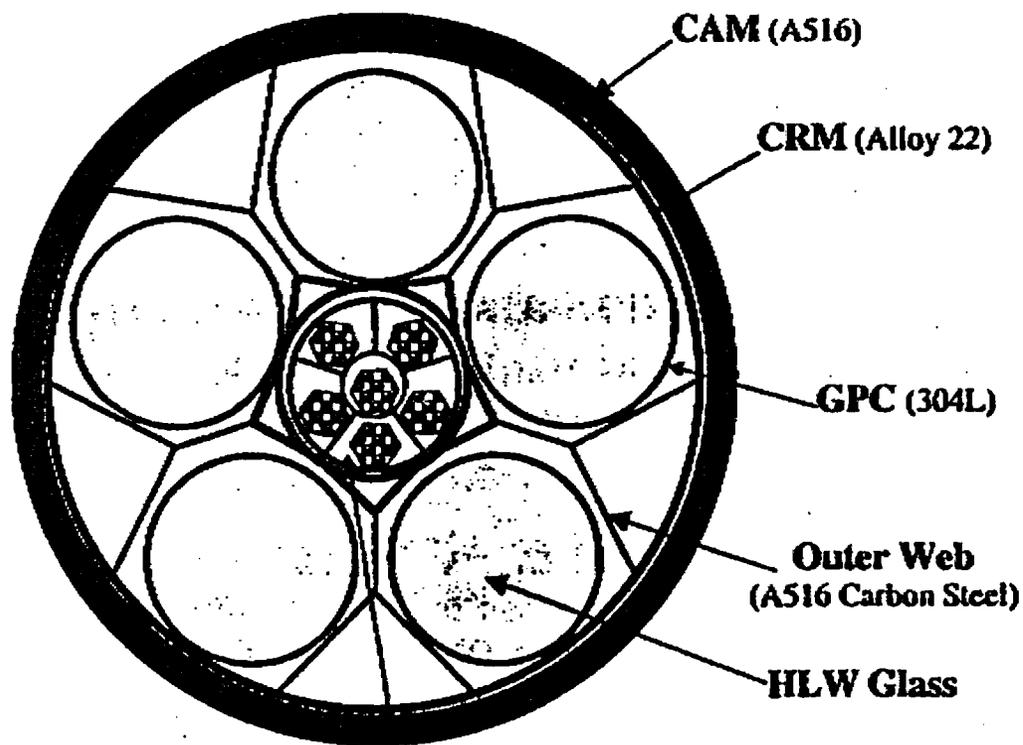
### Commercial



Boron Stainless Basket

Fuel in Carbon Steel Tube

### Codisposal



CAM (A516)

CRM (Alloy 22)

GPC (304L)

Outer Web  
(A516 Carbon Steel)

HLW Glass

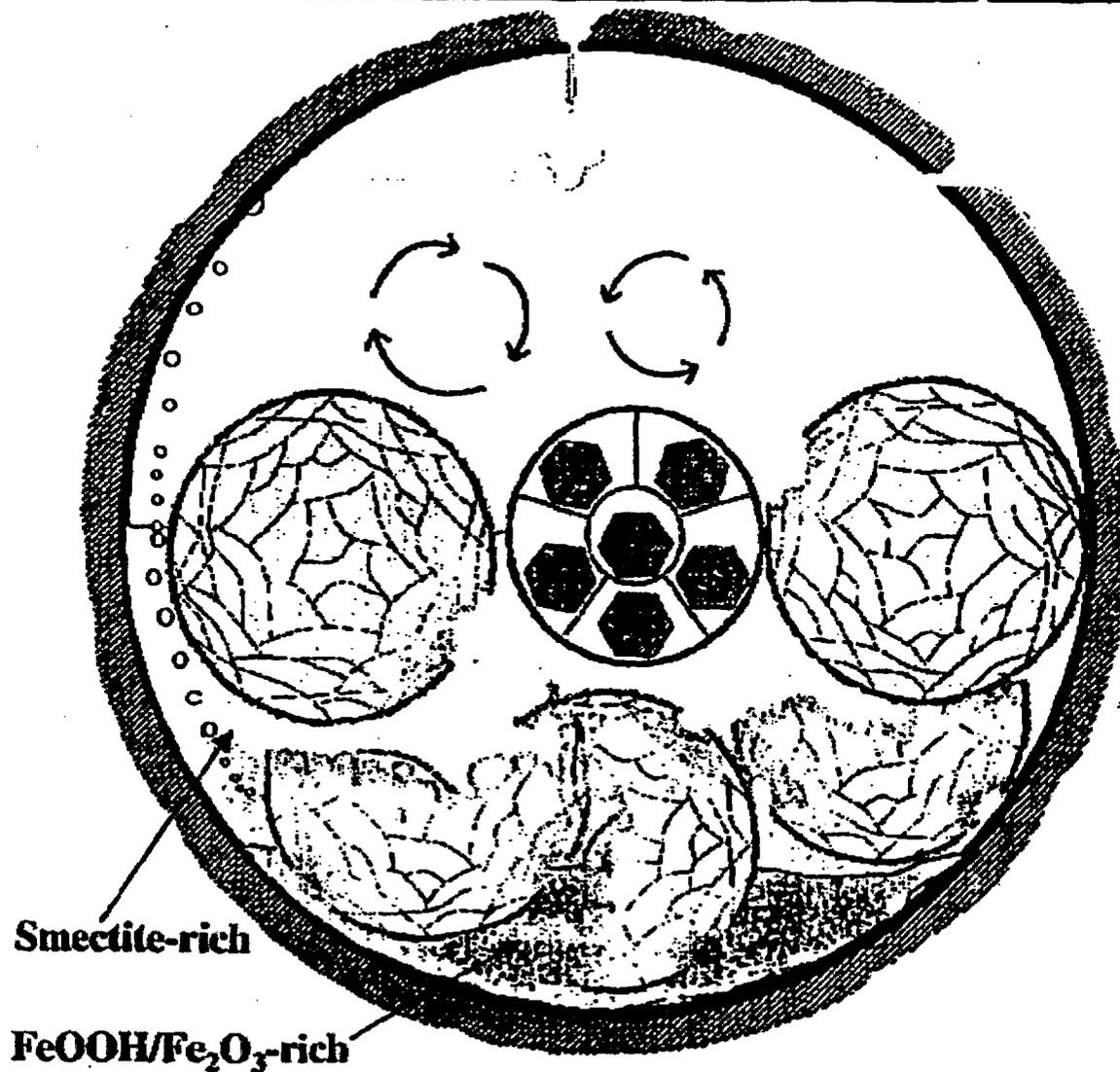
DOE SNF Canister (316L) & Fuel Assemblies;  
Basket Doped with GdPO<sub>4</sub>

## **(3a) Methods for In-Package Geochemistry Calculations**

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- Use modified (and qualified) version of EQ6 code, with solid-centered flow-through (SCFT) mode. “Bathtub” has influx of J-13-like water, mixing with water in package; outflow=inflow rate.**
- Set up matrix of conditions: vary rates of J-13 flux, corrosion rate of steel, glass and fuel. Typically use 20 to 40 runs.**
- Some runs broken into stages, with sequential exposure of package components.**
- Runs produce: time-resolved pH and compositions (e.g. Cl<sup>-</sup>, SO<sub>4</sub><sup>=</sup>, dissolved Fe) and volumes of aqueous phase (in and leaving package) and corrosion products.**
- Current qualified version of EQ6 has no radioactive decay; must post-decay <sup>239</sup>Pu (conservative for internal criticality).**

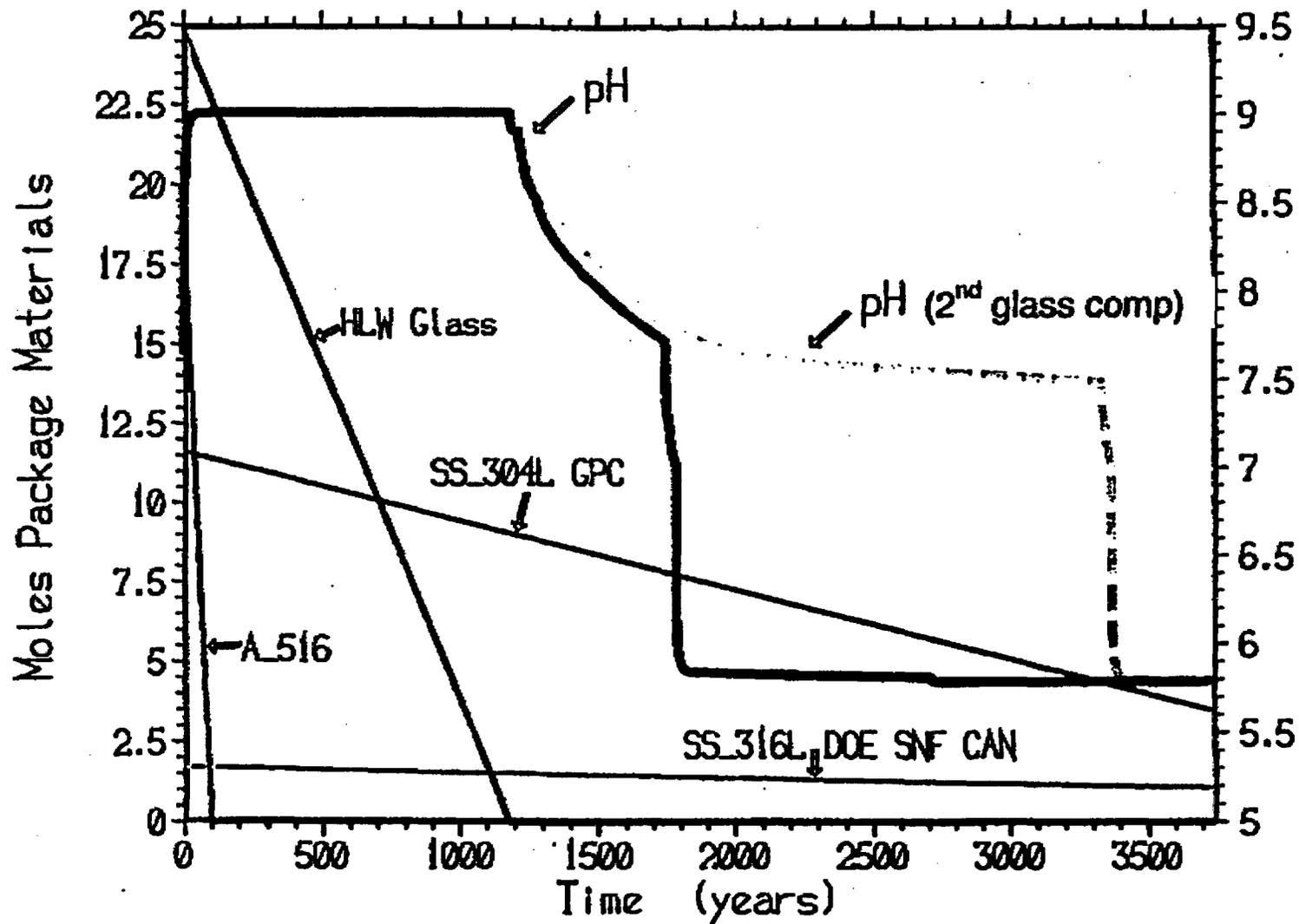
## (3b) Bathtub with SCFT (Solid-Centered Flow-Through)



- Constantly overflowing bathtub, causes continual dilution of aqueous phase → removal of neutron absorbers (e.g. Gd, B).
- Assume Alloy 22 CRM is ~inert.
- Remnant heat and gas bubbling allow some circulation.
- Calculation may be broken into stages, for greater realism or to achieve most extreme pH conditions.
- Calculation suite varies drip rates and corrosion rates of steel, glass, and fuel (~1 to 3 orders of mag. variation).
- Base case  $fO_2$  ~0.2 atm.
- Sensitivity studies to judge effects of lower oxygen potential,  $CO_2$ , "J-13" composition, glass composition, thermo data, Fe-oxides...

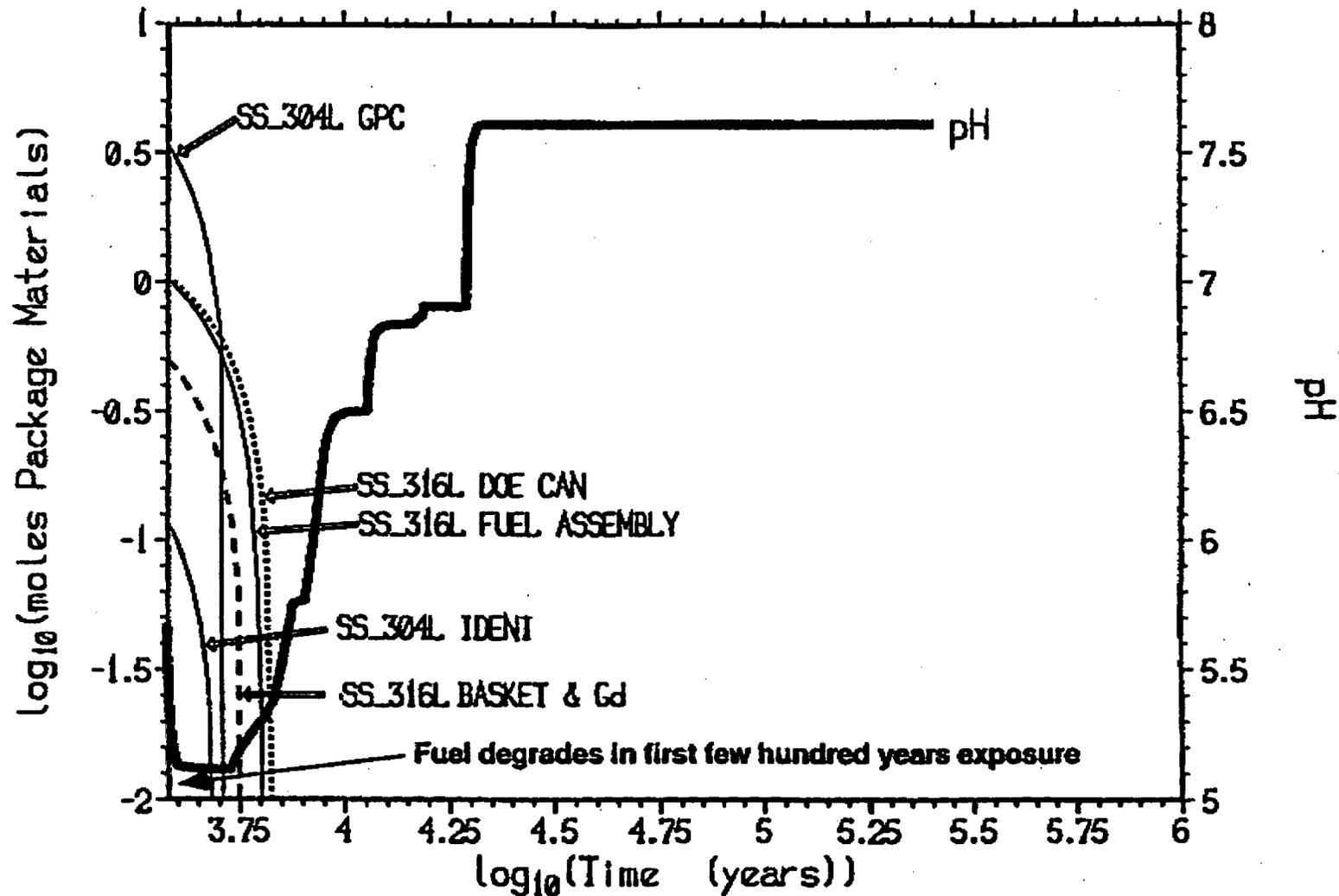
# (4a) 1st Stage of Calculation, Fast Drip & Glass Rates

(01g2204 / f00g2022 From BBA000000-01717-0210-00028 REV 00

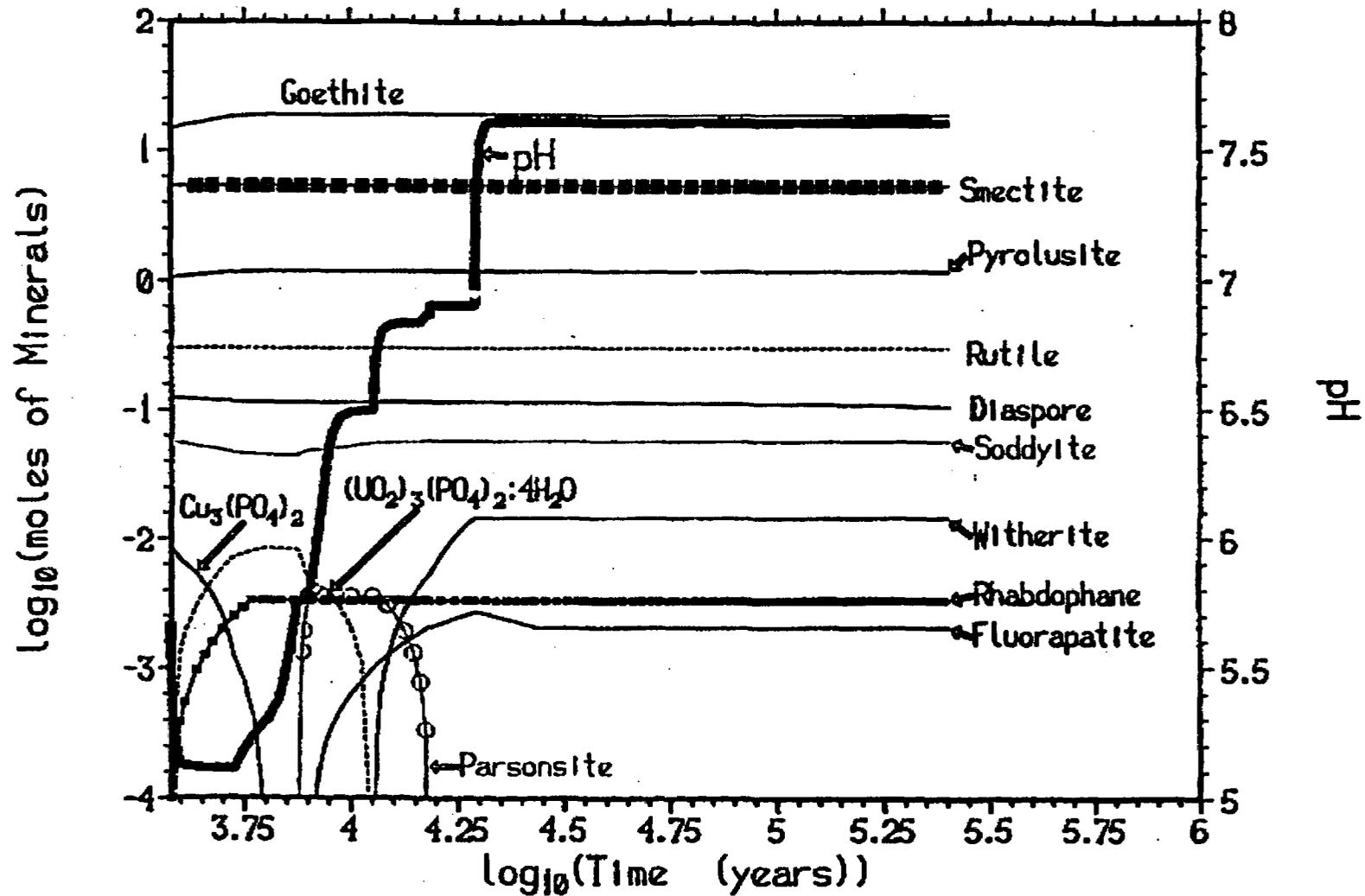


no radiolysis  
 no radioactive decay  
 drip rate?  
 • spense?  
 • spatial variation?

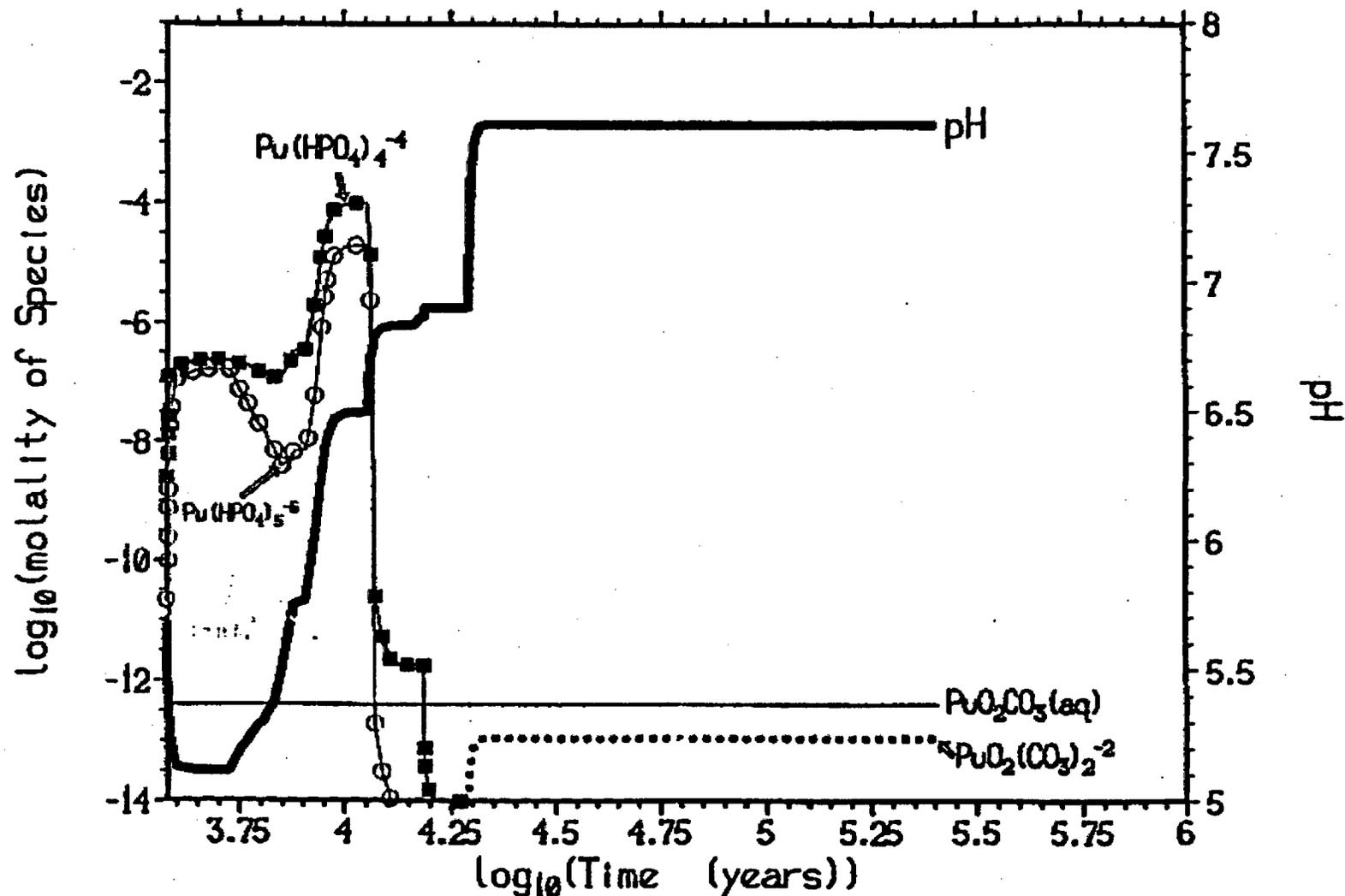
## (4b) 2nd Stage, Slow Drip Rate



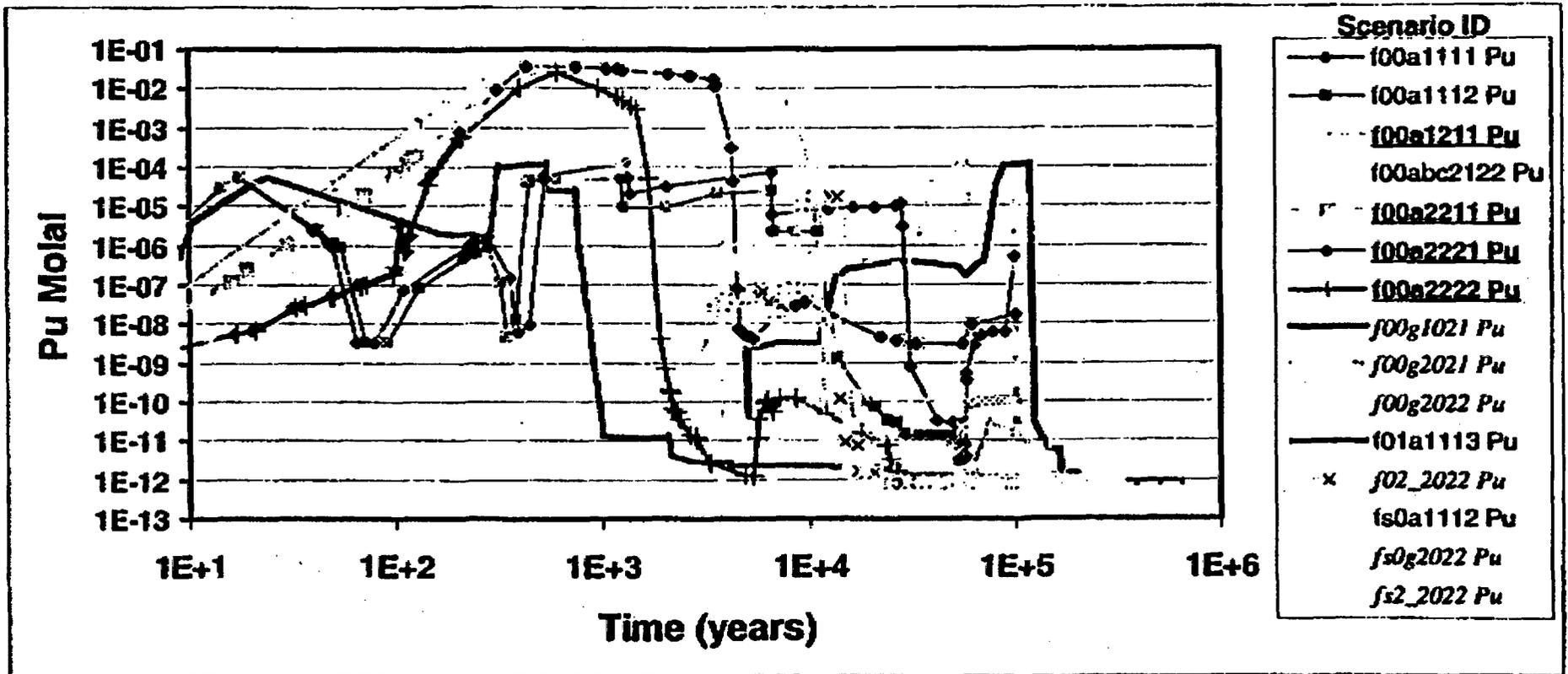
# (4c) 2nd Stage, Major Minerals Stabilize by ~5000 Years



## (4d) 2nd Stage, Pu Speciation (GdPO<sub>4</sub> Basket)



# (4e) All FFTF Scenarios: "Average" Aqueous Pu?



Aqueous Pu for FFTF DOE SNF models.  $\log_{10}(fCO_2) \sim -2.5$ . High Pu occurs mainly when glass canister degrades rapidly with fuel exposed. Drip rates vary 0.0015 to 0.15m<sup>3</sup>/year; SS from 0.1 to 1  $\mu$ /year; glass and fuel rates vary by ~2.5 orders. From output files for BBA000000-01717-0210-00028 REV 00. Code for file fxxxSGFW: S=Steel rate (1=low, 2=high); G=Glass rate (0=all reacted, 1=low, 2=high); F=Fuel rate (1=low, 2=high); W=drip rate(1=0.0015, 2=0.015, 3=0.15).

## **(5a) Couple Geochemistry of Package and Near-Field**

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Feed outputs of in-package calculations into near-field transport and chemistry.

Approaches:

- New EQ3/6: flow-through with variable saturation; passes output solution composition from one run to next. Each EQ6 "cell" sees a time-varying output from previous. Transmutes and tracks daughters (e.g.  $^{239}\text{Pu} \rightarrow ^{235}\text{U}$ ).
- GRIM code from Sandia – couples outputs/inputs from series of EQ3/6 runs, decays and sorbs between cells if desired, does all bookkeeping for DTN.
- PHREEQC v2 under qualification at M&O –dual porosity, solid solutions, dispersion (also has reactions, decay, sorption, 1D advective transport). Aids qualification of other codes; may be necessary for fractured material. EQ6 DB will be ported to PHREEQC.
- LaGrangian version of EQ3/6 under development at LLNL – like "adaptively gridded" version of PHREEQC, stronger ties to current EQ6 models.

Need consistency in Pu solubility control.

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## **(5b) Model "Drip-Through" Package (Variable Saturation)**

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**Consider possibility that no significant stagnant pools form in package; water drips through from inlet to outlet, intermittently contacting package components.**

**Consistency with VA/other M&O models?**

**Patch corrosion model  $\Rightarrow$  low probability of breaches  $\Rightarrow$  either partial bathtub or no water in package at all to  $\sim n \cdot 10^4$  years.**

**Need to iterate: PA must calculate probability of bottom breach based on calculations of in-package chemistry.**

**Will drips that run over package components reach saturation before hitting a stagnant pool (or leaving package)?**

**If *any* stagnant pools are present, will their effects overshadow drip-through?**

## **(5c) Address Thermodynamic Needs**

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### **Examples of Specific Needs:**

**PuO<sub>2</sub>·nH<sub>2</sub>O, Np solids, Th & Pu phosphate complexes, Cr compounds, U solid phosphate data, standardization on NEA actinide data.**

### **Temperature issues:**

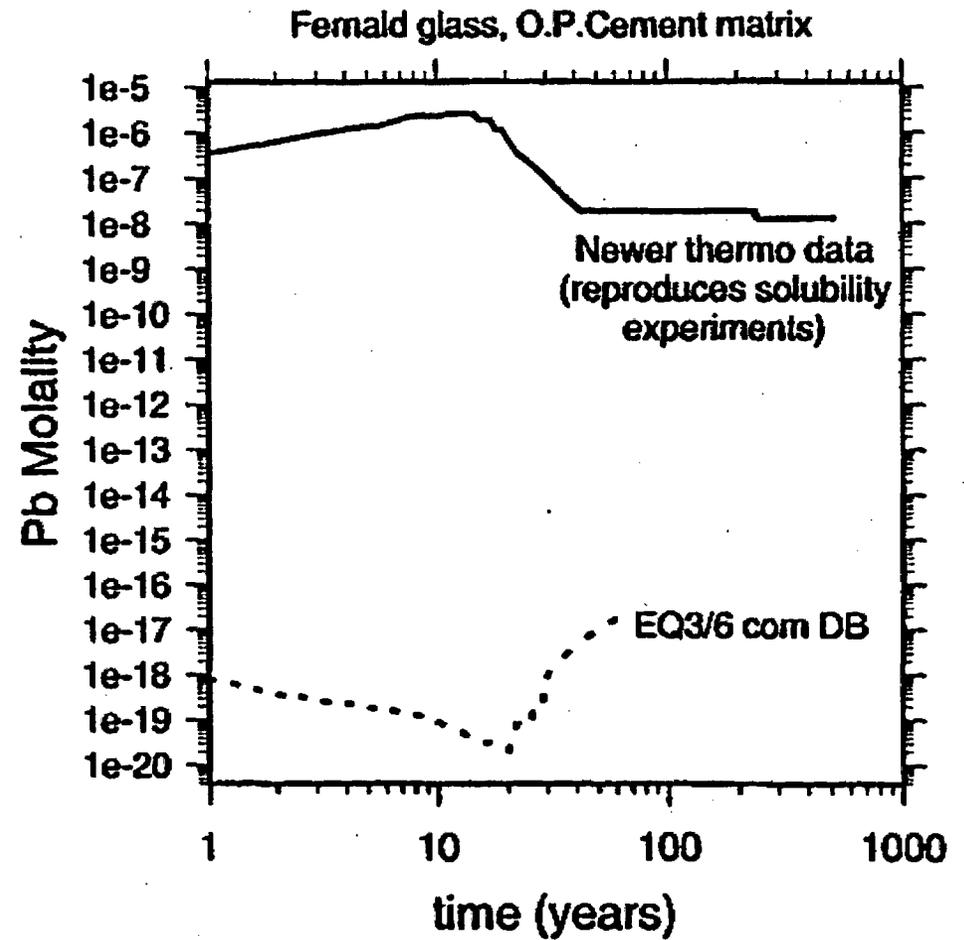
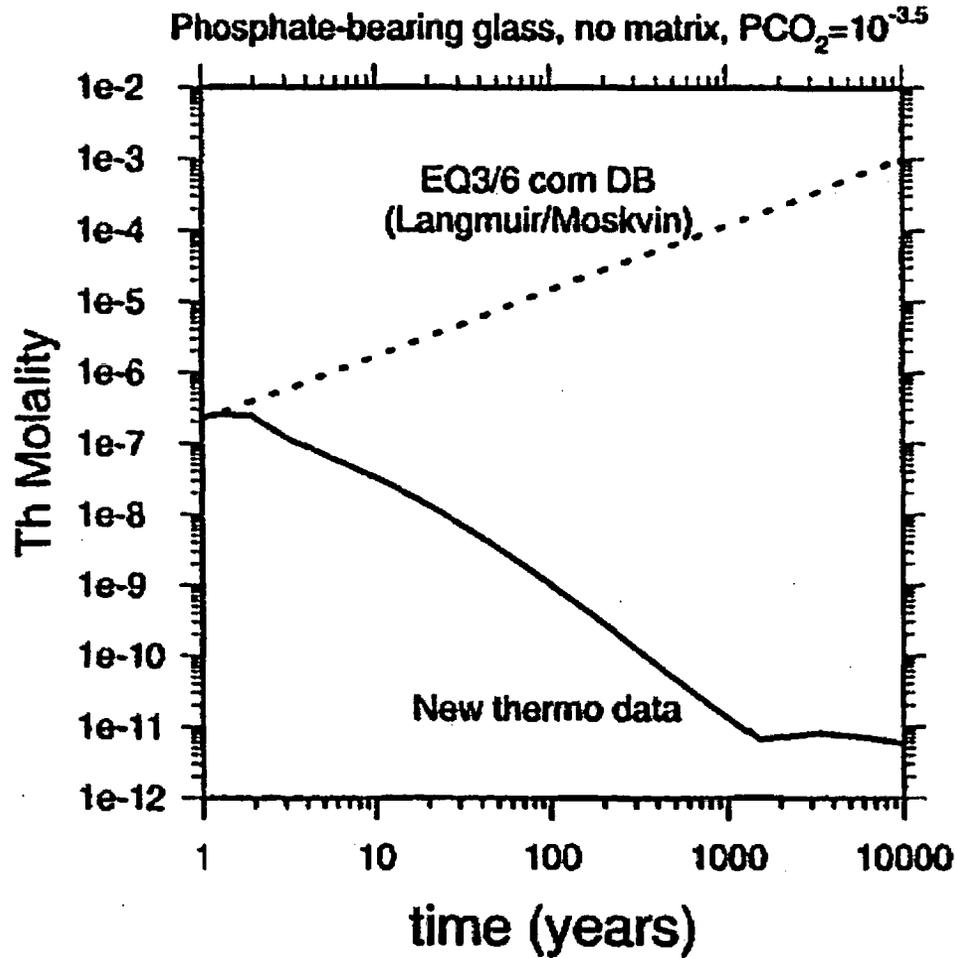
**Most data for 25C only; desirable to extrapolate to ~60C; in VA packages may not cool below 50C for ~30,000 years. With new thermal loading, this may be less of an issue.**

### **Qualification:**

**Need consistent databases across M&O. Most data additions & corrections performed for previous studies; must document via 3-15 or 3.12 process.**

# (5d) Example: Th and Pb Solubility in Glass Waste Models

"Old" = EQ3/6 com database (current). From SAND95-2730



## **(5e) More Realistic Rate Models**

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**Useful addition to EQ6: Composition dependence for “special reactants” -- rate laws with no saturation check, but pH dependence.**

**Glass rates probably very “conservative”; assume all cracks available as surface area. May greatly overestimate overall dissolution rate?**

**Importance: glass dissolution in DOE SNF can create conditions that dissolve all U and Pu.**

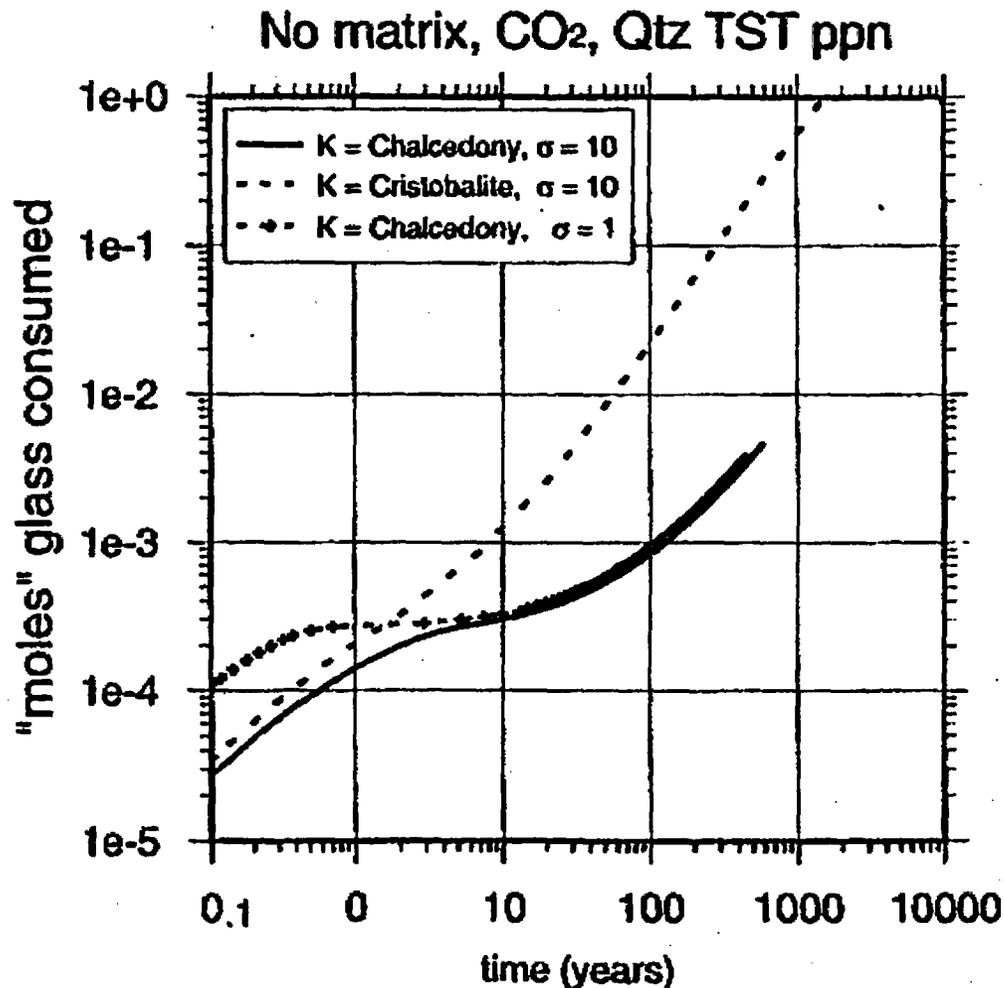
**Develop effective rates for intermittently wet solids in “drip through” model, *iff* the drip-through condition is shown to have significant effect on source term.**

**Do complicated rate laws (e.g. TST for dissolution and precipitation) add useful realism? (Answer: probably not, at current levels of uncertainty.)**

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# (5f) Worth it to Add TST Rate Laws?

From SAND95-2730



Transition State Theory Rate Law for Glass Dissolution:

Rate (in moles/sec) =

$$S \cdot k \cdot (a_1^{N_1} + a_2^{N_2}) \cdot (1 - (Q/K)^{1/\sigma})$$

$a = H^+$  activity;  $N_1 \sim -1$ ;  $N_2 \sim 0.4$ .

$K$  = quasi-solubility product for hypothetical SiO<sub>2</sub>-rich surface layer.

Model calculation: glass marbles ~1 cm diameter, with 0.04 cm diameter quartz sand in interstices, water-saturated, sand/glass 1/300 by weight; ppn law derived from TST dissolution law.

(New EQ6 mode to model glass dissolution described in SAND95-2730.)

## **(5g) Evaluate Effective Package $fO_2$**

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**Stagnant zones may control to lower  $fO_2$  (at later times, after radiolysis effects lessen). Surface waters (e.g. streams) and aerated ground waters have redox couples that suggest effective  $fO_2 \ll 0.2$  atm.**

### **Importance:**

**(1) pH control from chromium oxidation:**



**In Pu-ceramic WP calculations, dropping  $fO_2$  to  $10^{-10}$  reduces Gd loss (from  $\text{GdOHCO}_3$ ) from  $>50\%$  to  $<1\%$  (by preventing low pH extremes).**

**(2) At lower oxidation states, actinides can be much less soluble; e.g.  $\text{Pu}^{(V)}$  carbonate complexes much less stable than  $\text{Pu}^{(VI)}$ .**

### **Methods:**

**Sensitivity studies determine minimum  $fO_2$  for significant impact.**

**Detailed models of oxygen diffusion and consumption within package.**

## **(5h) Does it Help to Add Cr Thermo Data for Cr Solubility Control at 0.2 atm $fO_2$ ?**

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### **Added to date:**

New  $BaCO_3$  / Ba complex data (affects Cr concentration by stabilizing  $BaCrO_4$ ) in glass systems. Very limited effect.

$KFe_3(CrO_4)_2(OH)_6$  and  $KFe(CrO_4)_2 \cdot 2H_2O$ ,  $Fe_3(OH)_7CrO_4$ ,  $FeOHCrO_4$ ,  $FeCrO_4^+$  (solids undersaturated in most runs; no effect, only significant under acid conditions, and when Fe activity is kept high, as before  $Fe(OH)_3$  ripens to  $FeOOH$ ).

$NiCrO_4(Ni(OH)_2)_3$  and  $NiCrO_4(aq)$  (undersaturated in all runs; no effect).

$(Fe,Cr)(OH)_3$  solid solutions: very low Cr activity coefficients at low Cr content (~0.001). However, only significant when precipitation of  $FeOOH$  is suppressed, and  $Fe(OH)_3$  is orders of magnitude more soluble.

$(Fe,Cr)OOH$  (Cr-Goethite solid solution -- up to 11% Cr substitutes, but no published thermodynamic data exist -- contact Alex Navrotsky? ).

$CrO_4^{=}$  substitution for  $SO_4^{=}$  (Can infer thermo data, but the substitution is significant only when abundant, insoluble sulfates exist -- e.g.  $BaSO_4$ ).