From: <Yueting_Chen@notes.ymp.gov>
To: TWD2.TWP7(TMA)
Date: 6/2/98 7:14pm
Subject: References

Dear Tae:

Here is the references cited in my slides. Please note that the rate data for Na-boltwoodite is guessed from uranophane data, since no kinetic study has been done on Na-boltwoodite yet. If you have any future questions, please feel free to let me know.

Best Regards!

Yueting

I. Casas, J. Bruno, E. Cera, R. Finch, R. Ewing, 1994, Kinetic and Thermodynamic Studies of Uranium Minerals --assessment of the long-term evolution of spent nuclear fuel, SKB Technical Report 94-16.

I. Perez, I Casas, M. Torrero, E. Cesa, L. Duro, J. Bruno, 1997, Dissolution Studies of Soddyite as a Long-Term Analogue of the Oxidative Alteration of the Spent Nuclear Fuel Matrix, Mat. Res. Soc. Symp. Proc. 465 , pp. 565-572.

J. Bruno, I. Casas, E. Cera, R.C. Ewing, R.J., Finch, L.O. Werme, 1995, The Assessment of the Long-Term Evolution of the Spent Nuclear Fuel Matrix by Kinetic, Thermodynamic and Spectroscopic Studies of Uranium Minerals, Scientific Basis for Nuclear Waste Management, Vol. 353, pp.633-639.

Spent Fuel Dissolution and Np Release from Secondary Phases

Yueting Chen, Eric Siegmann, Patrick Mattie,
Jerry McNeish, David Sevougian, Robert Andrews

Duke Engineering & Services
Performance Assessment of CRWMS M&O

Spent Fuel Workshop

May 19th, 1998
Las Vegas, Nevada

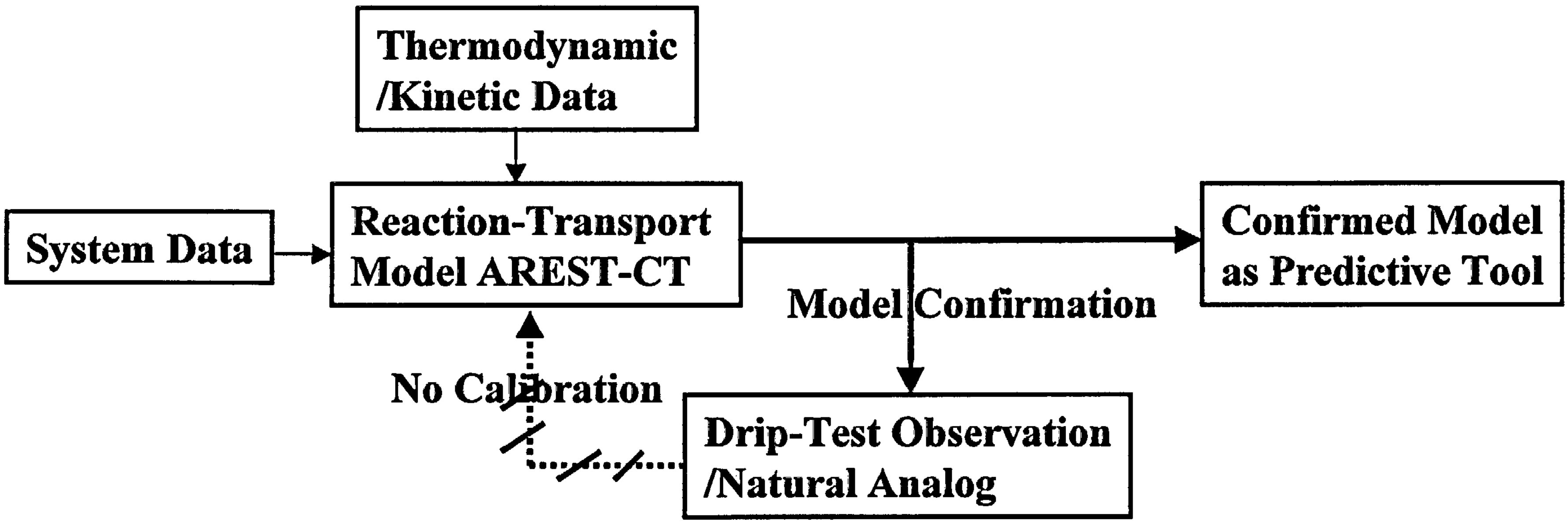
Acknowledgement

Various Helps Received from the Following Individuals

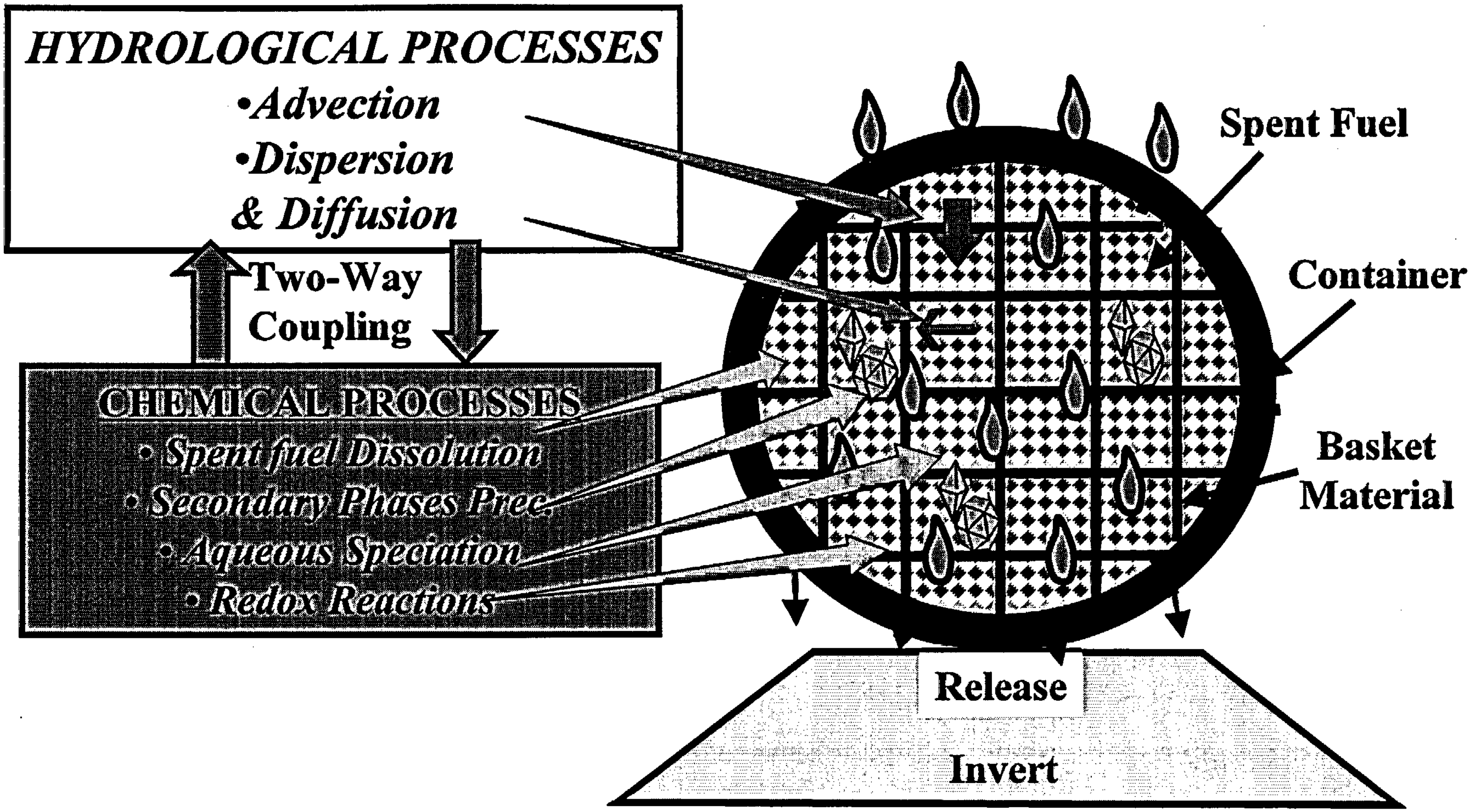
- Walt Gray (PNNL)
- John Bates, Pat Finn, Bob Finch, Edgar Buck (ANL)
- David Wronkiewicz (Univ. of Missouri)
- Christine Stockman (SNL)
- Bill Halsey, Bill Bourcier (LLNL)
- Vinod Vallikat, Kevin Mon (DE&S)

Overview

- **Objectives**
  - investigate long-term, in-situ dissolution of spent fuel and release of radionuclides
- **Approach**



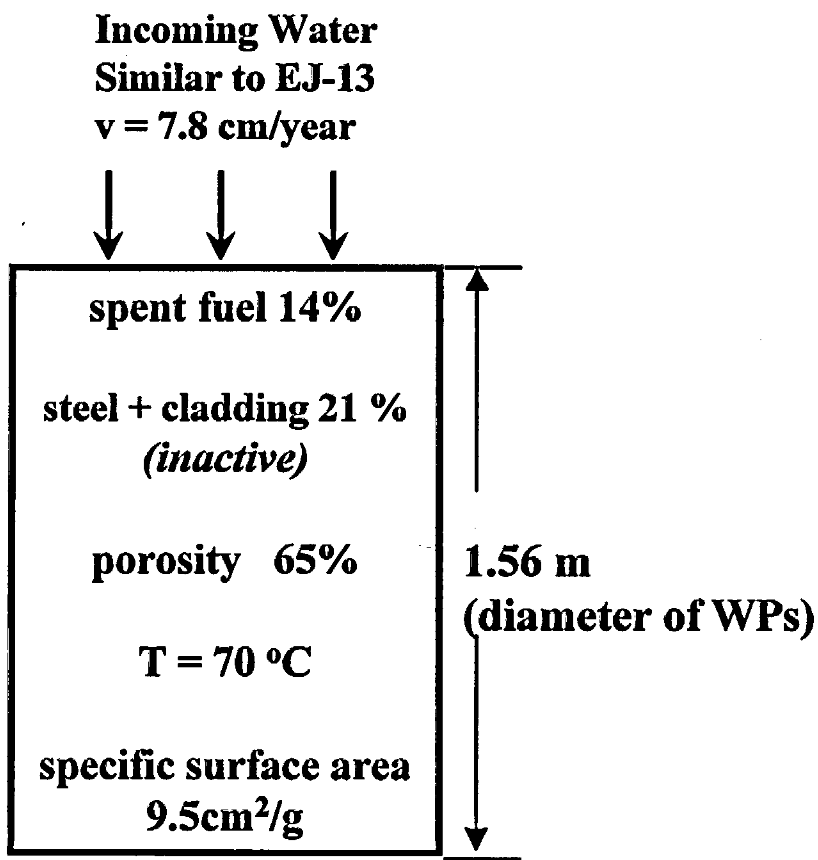
Processes within Waste Packages



Features of AREST-CT

- Developed at PNNL (Chen, McGrail, and Engel, 1995)
- General, user-defined reaction sets
- 1-D and 2-D domains
- Kinetic dissolution of solids
- Kinetic precipitation and dissolution of secondary phases
- Aqueous equilibrium reactions
- Gaseous-aqueous equilibria
- Advection, dispersion, and diffusion
- Non-isothermal or isothermal reactions
- Extended Debye-Huckle activity correction
- Nucleation threshold for precipitation of new solid
- Texture-dependent reactive surface

Physical Configuration of AREST-CT Simulations



Chemical Reactions

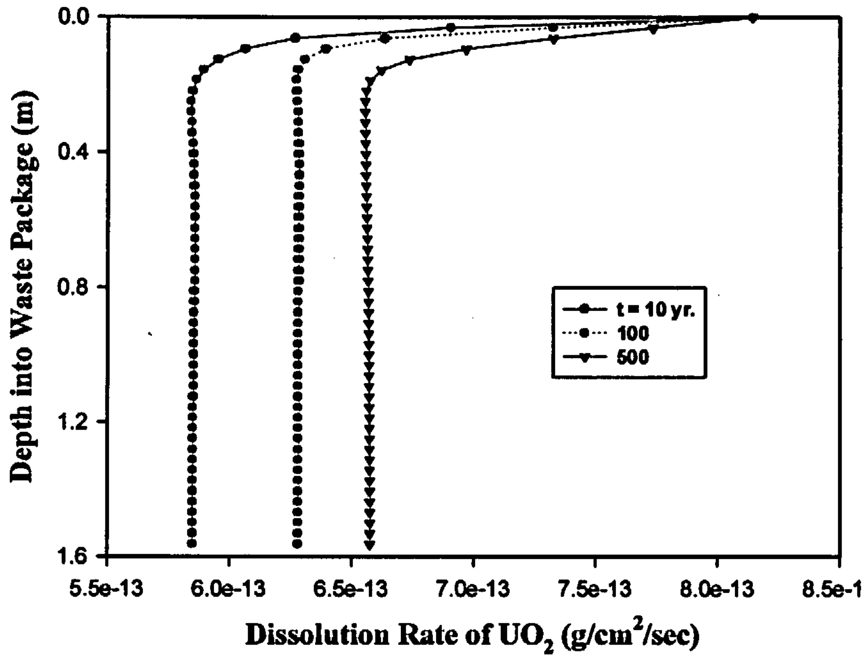
- **UO_2 dissolution**

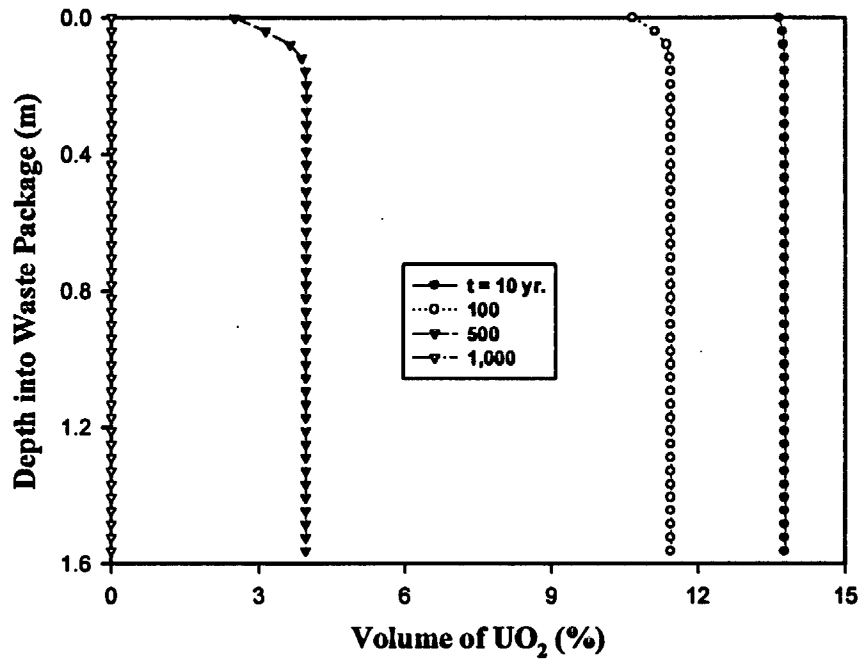
  $UO_2 + 2\,H^+ + 0.5\,O_2(g) = UO_2^{++} + H_2O$

  $$\log k = 7.45 + 0.258\log[\sum CO_2] + 0.142\log[H^+] - 1550/T \text{ (Gray, 1992)}$$

- **4 secondary minerals (kinetic reactions)**
  - **Schoepite, Uranophane, Soddyite, Na-boltwoodite**
  - **Kinetic data from Casas (1994), Bruno (1995), and Perez (1997)**
- **8 components: H, O, CO_2, SiO_2, Ca, Na, Cl, and U**
- **16 aqueous equilibrium reactions**
- **2 gaseous-aqueous equilibrium reactions**
  - **f_{CO_2} = 0.0003 atm.**
  - **f_{O_2} = 0.209 atm.**

Simulation Results (Dissolution of UO_2)





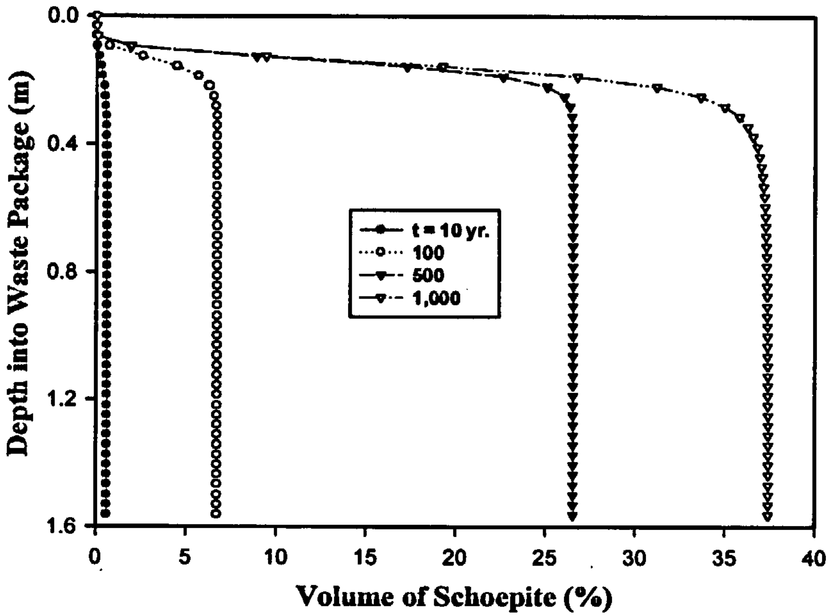
- the dissolution rate of UO_2 does not change much
- <u>observation from drip tests:</u>

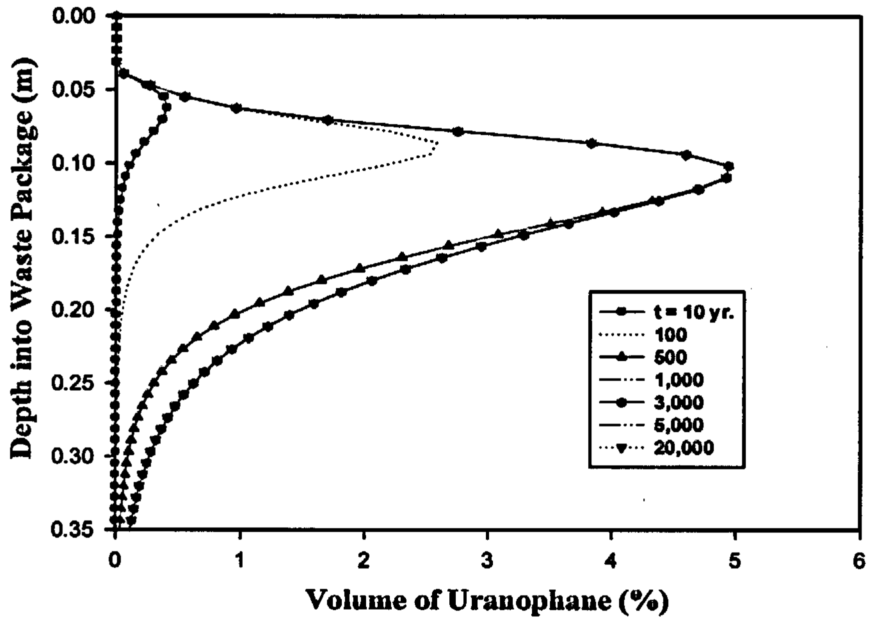
" the reaction pathways have been constant ... or that the contribution from multiple reaction pathways has not varied over time" Finn et al., 1997)

- UO2 was totally dissolved after 1,000 years.
- <u>observation from drip tests:</u>

" 3% of the Tc99 inventory is released after 3.7 years " (Finn et al, 1997)

Simulation Results (Schoepite & Uranophane Formation)





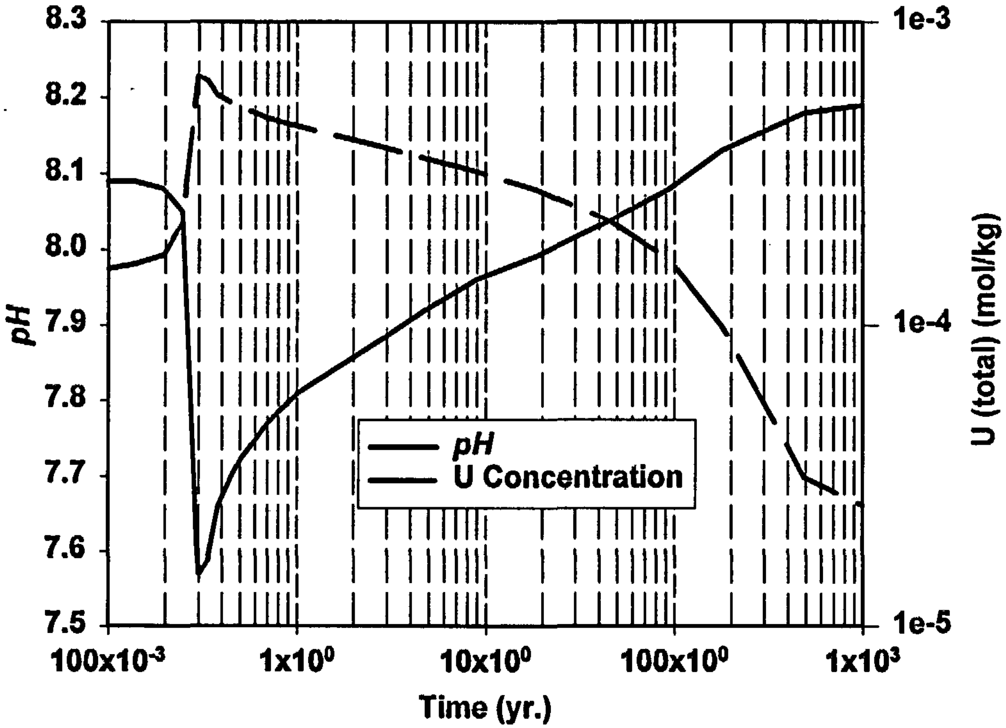
- **Schoepite is the major secondary phase, which controls U concentration in aqueous phase**
- **<u>observation from drip tests:</u>**

"... dehydrated schoepite is the dominant alteration phase." (D. Wronkiewicz et al., 1992)

- **Uranophane precipitates within the top portion of the waste package**
- **<u>observation of drip tests:</u>**

" Uranophane is the most common phase observed on the top surface ... but is conspicuously absent from the sides and bottoms of these samples" (D. Wronkiewicz et al., 1992)

pH and U(total) at the Exit



Note: NO data manipulation was done to match lab results. The above predictions are done blindly.

- **U initially has a rapid pulse release, followed by decrease**
- **<u>Observation from drip tests:</u>**

"The initial increase was followed by a transient decline.."
The average U conc. is 1.34 x *10^{-5} mol/kg.*
(D. Wronkiewicz et al., 1992)

- **pH drops from 8.1 to 7.6 at the very beginning, followed by a raise**
- **<u>Observation from drip tests:</u>**

"Solution pH values decrease from 8.2 for injected EJ-13 water, to 6.9±0.5" (D. Wronkiewicz et al., 1992)

Summary (Step-1)

- A UO_2 dissolution and secondary phase precipitation model, which is based on mechanistic dissolution/precipitation models, has been built
- The model qualitatively reproduced drip-testing results and observations at Pena Blanca
- Gray's dissolution rate equation is applicable to the repository conditions
- Spent fuel disappears in 10^2 -10^3 years and forms secondary phases in waste packages
- Discrepancy between lab observations and simulation results
  - Na-boltwoodite vs. uranophane
    - Na-boltwoodite, instead of uranophane, was observed in ANL's high-drip tests
    - reason: thermodynamic data of uranophane and Na-boltwoodite

Np Release: Assumptions & Their Basis

- **Spent fuel alters to secondary phases in 10^2 - 10^3 years**
  - ANL's drip tests show 3% SF altered in 3.7 years
  - model calculation predicts SF has a lifetime of 10^2 - 10^3 years
- **Assume no pure Np phases formed during SF alteration**
  - no Np phases were observed in lab experiments
  - no Np phases were observed in natural analog
- **Assume all Np remains in secondary phases, according to inventory Np:U ≅ 0.0005 : 1**
  - U-O bond length (0.18 nm) is similar to Np-O bond length (0.165-0.181) (Burns, et al., 1997)
  - Np is observed in schoepite formed at ANL's drip tests (Buck et al., 1997)

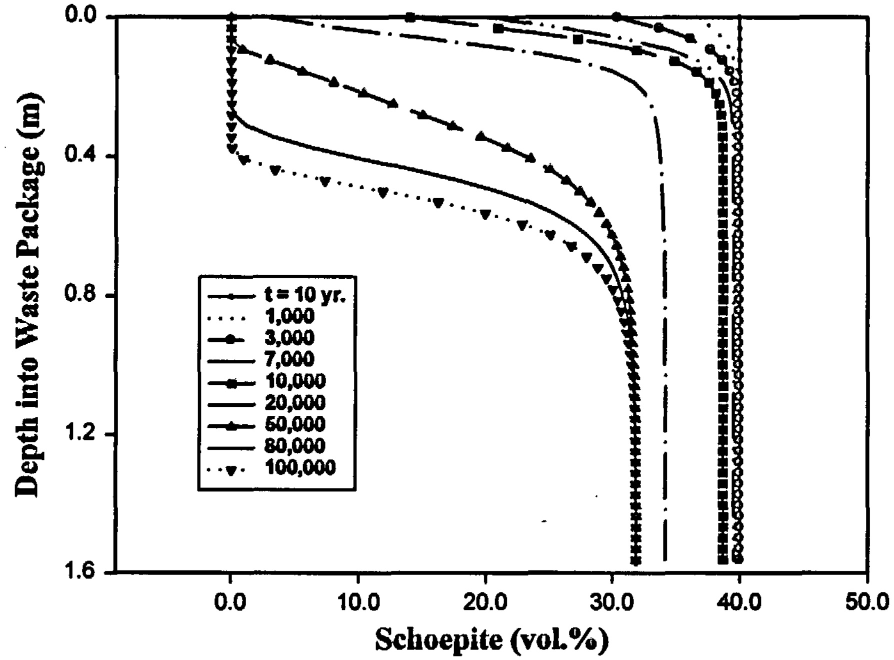
Np Release: Assumptions & Their Basis(con't)

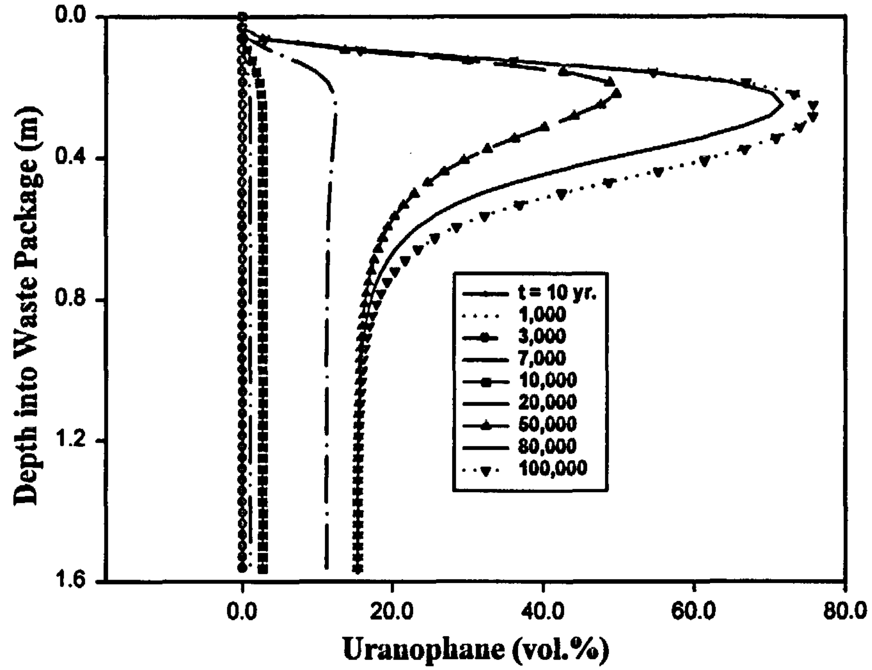
- Using schoepite as a surrogate of secondary phases
  - Np release is congruent with schoepite dissolution
    - schoepite-0.0005Np + $2H^+ = UO_2^{2+} + 0.0005\ NpO_2^+ + 3H_2O$
- Schoepite is replaced by uranophane, soddyite, and Na-boltwoodite
- No change on K^{eq} of schoepite due to Np doping
  - conservative

Simulation Conditions

- Same 1-D column, but with schoepite replaced SF
- Schoepite dissolution
  - schoepite-0.0005Np + $2H^+ = UO_2^{2+}$ + 0.0005 $NpO_2^+ + 3H_2O$
- Precipitation/dissolution of uranophane, soddyite, and Na-boltwoodite (K^{eq} from Nguyen et al., 1992)
- 9 components & 29 aqueous equilibrium reactions
- 2 gaseous species and 2 gaseous-aqueous equilibria
  - $f_{CO_2} = 0.0003$ atm.
  - $f_{O_2} = 0.209$ atm.

Schoepite Replaced by Uranophane



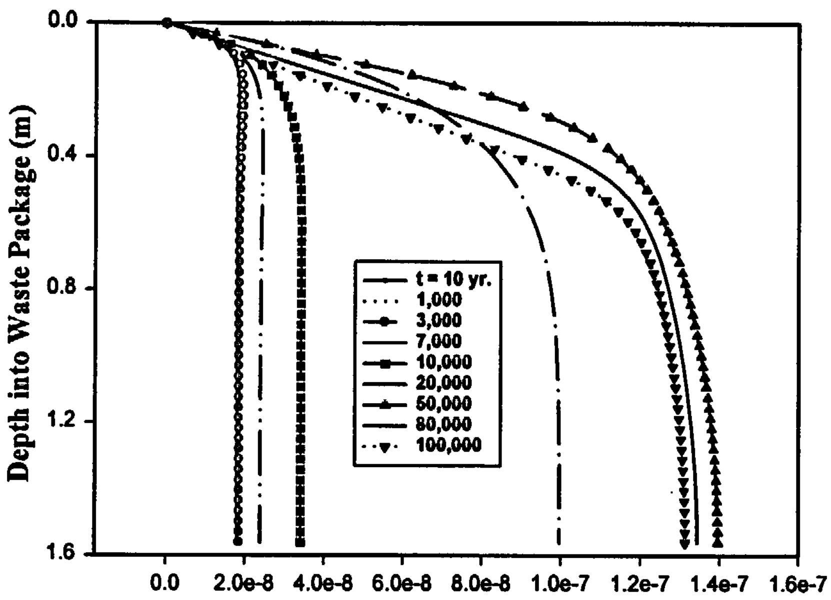


- Schoepite dissolves at both the top of WPs and downstream
- Downstream dissolution stops after 20,000 years

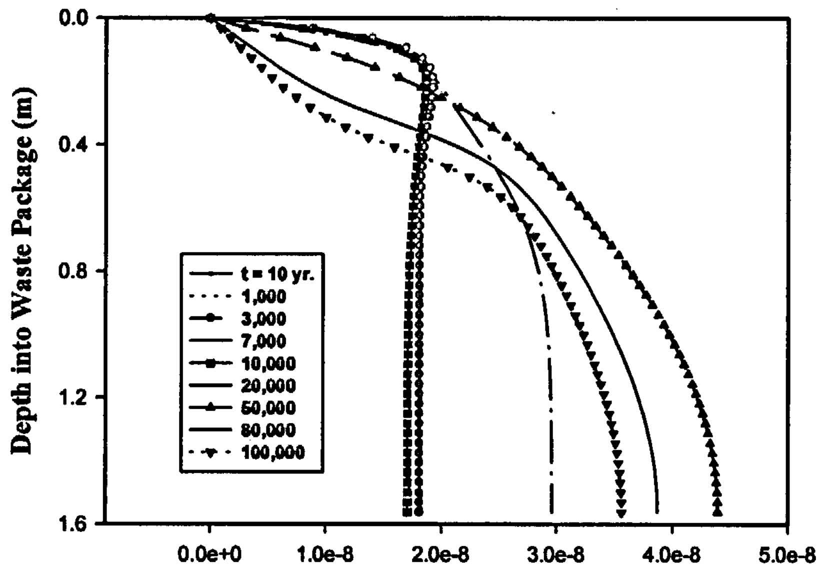
- Uranophane precipitates at both the top of WPs and downstream
- Downstream precipitation stops after 20,000 years

Np Concentration

Case I: All Np released from schoepite dissolution goes into water

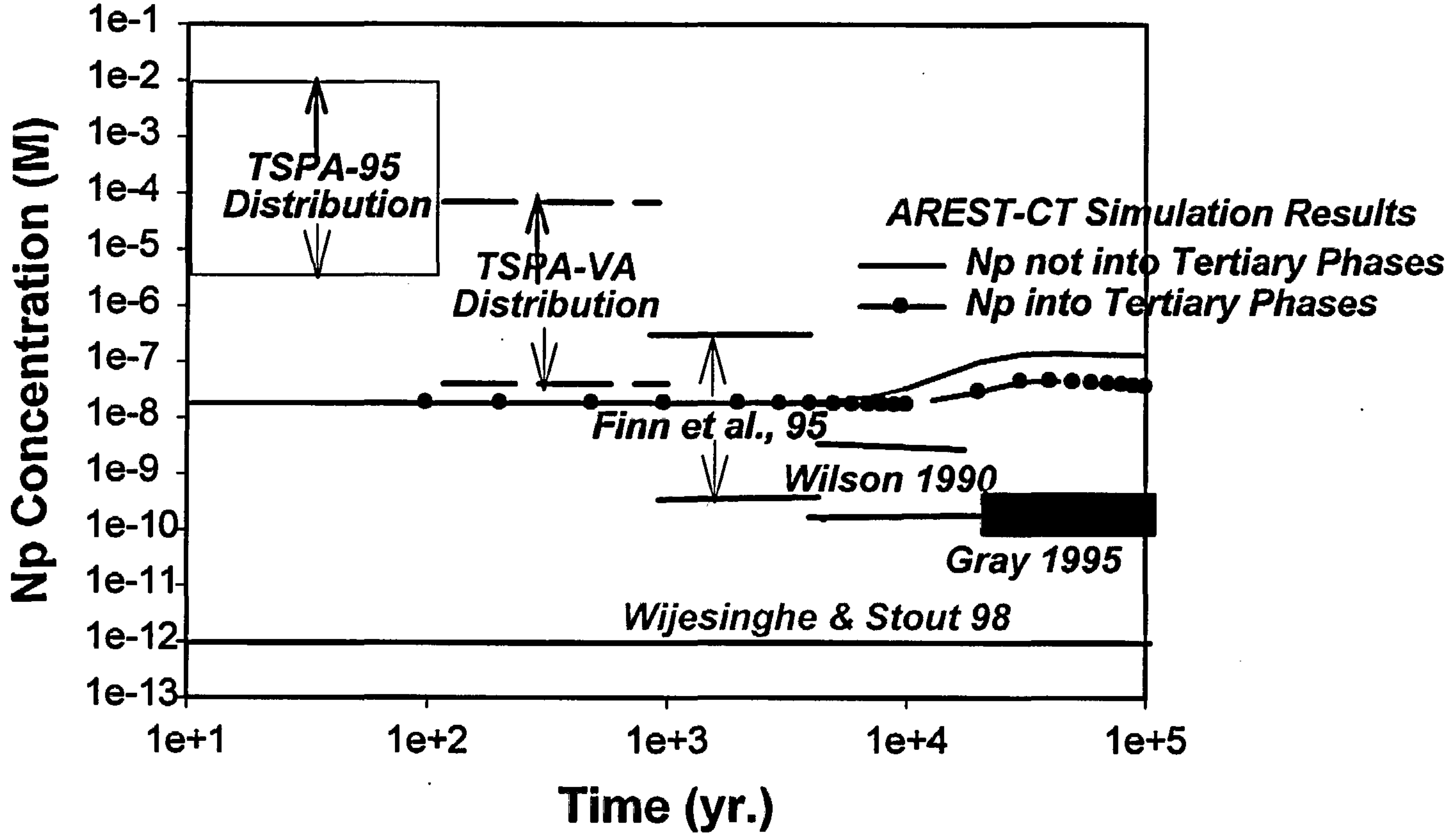


Case II: Np released from schoepite dissolution goes into tertiary phases congruently with U



- Np concentration increase with time followed by decrease
- Np has the highest concentration at the bottom of WPs
- Case II has lower Np concentration than Case I

Comparison of Np Values



Conclusions

- After spent fuel is consumed, the release rate of radionuclides may be controlled by the dissolution rate of secondary phases
- Due to the low dissolution rate of secondary phases, Np concentration may be significantly below the solubility limit
- Low Np concentration means low release
  - natural reactor of Oklo, Gabon shows Np is "most retained; some local redistribution" (J. Smellie, 1995)
- Current Np distribution for TSPA-VA may be too conservative, which could be replaced with well-justified realism
- We need more and better data