Developing Thermodynamic Radionuclide Sorption Models: Experimental and Modeling Results

by

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Acknowledgment

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Outline of Presentation

- Sorption Model Abstraction in Performance Assessment
- Sorption Experiments and Key Geochemical Parameters
- Surface Complexation Modeling
- Potential Future Performance Assessment Abstractions
- Summary

Radionuclide Sorption in Performance Assessment

- Sorption Processes Can Delay Radionuclide Transport to the Biosphere

- Example
  - Sensitivity to K_d values of calculated breakthrough of ^{237}Np from Yucca Mountain unsaturated zone*

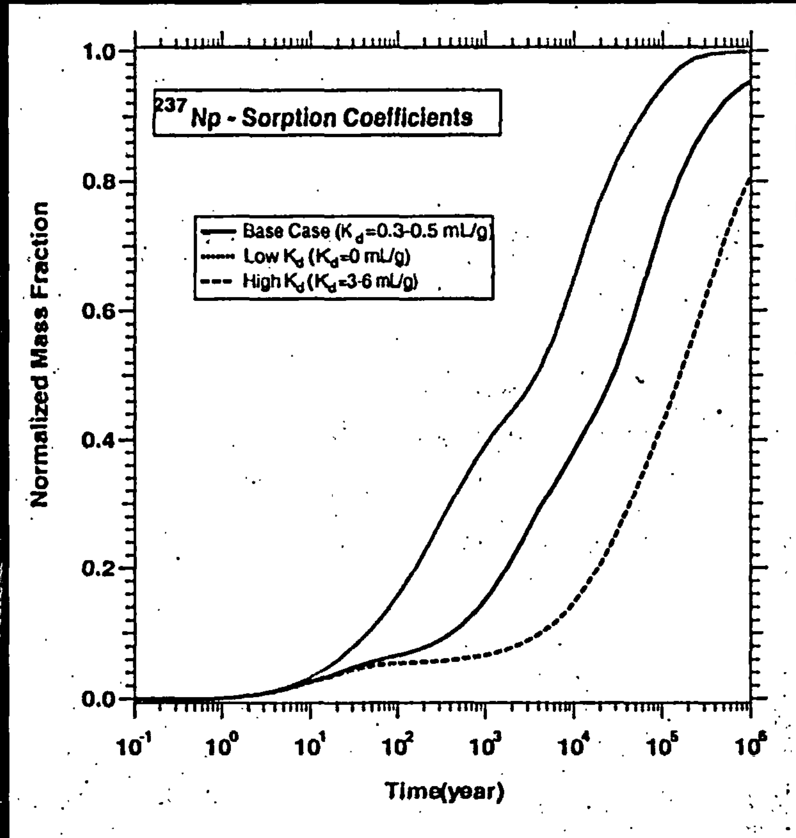

*Figure taken from G. Moridis (LBNL) presentation to the Nuclear Waste Technical Review Board. March 9-10, 2004, Las Vegas, NV. (http://www.nwtrb.gov/meetings/march%202004/moridis.pdf)

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Abstracting Radionuclide Sorption For Performance Assessment

- Sorption Is Important Aspect of Natural Barriers
- Sorption (and K_d) Is a Function of Site-Specific Mineralogy and Groundwater Chemistry
- Mineralogy and Groundwater Chemistry at Disposal Sites Can Vary Spatially (and Temporally)

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Thermodynamic Sorption Models: Performance Assessment Abstractions

- Conduct Radionuclide Sorption Experiments
- Develop Surface Complexation Models
- Use Site-Specific Data
- Generate Parameters for Sorption Model Abstraction in Performance Assessment Code

Sorption Experiments: U(VI) and Np(V)

- Single Mineral, End-Member Experiments
- Variables
  - Mineral sorbent
  - Radionuclide concentration
  - pH range
  - Ionic strength
  - Solid-mass to solution-volume ratio
  - P_{CO2} (carbonate concentration, C_T)

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Sorption Experiments: Sorbents

Minerals Used	*Type of Sorption Site*[a]	*pH_{ZPC}*	*N_2-BET Surface Area (m^2/g)*
Quartz	>$SiOH^0$	~2.5	0.03 0.5
Clinoptilolite[b]	>$SiOH^0$ & >$AlOH^0$	~3	10.1
Montmorillonite[b]	>$SiOH^0$ & >$AlOH^0$	~6.1	97
α-Alumina	>$AlOH^0$	~8.9	0.23

a Sorbents treated to remove carbonates and Fe-Ox
b Clinoptilolite and Montmorillonite exchanged to Na-end member

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Sorption Experiments: Results

- Key Geochemical Parameters
  - pH
  - Complexing ligands (e.g., carbonate)
  - Site concentration (sorbent concentration/surface area)

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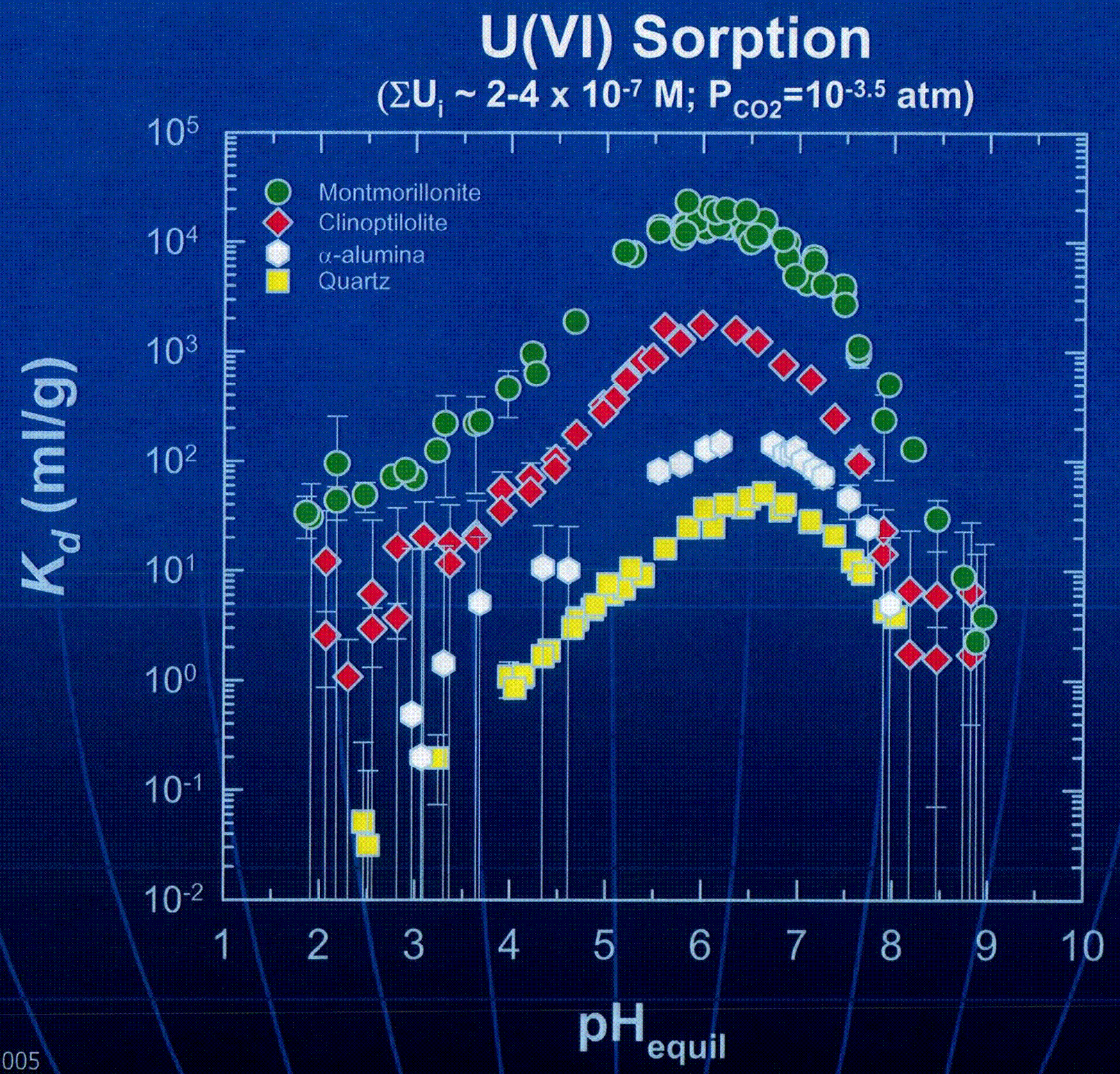
Effect of pH on U(VI) Sorption



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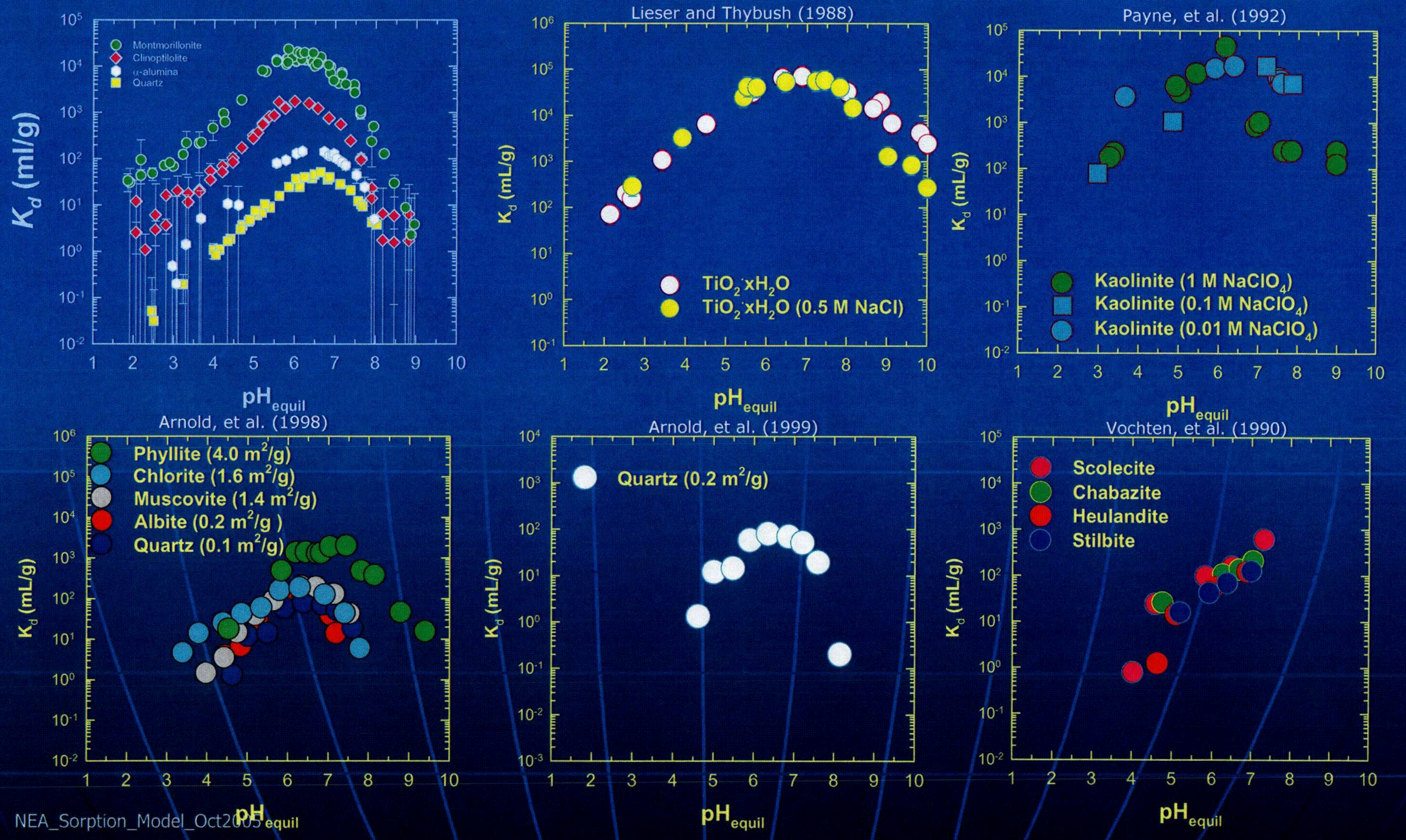
Effect of pH on U(VI) Sorption: Literature Data



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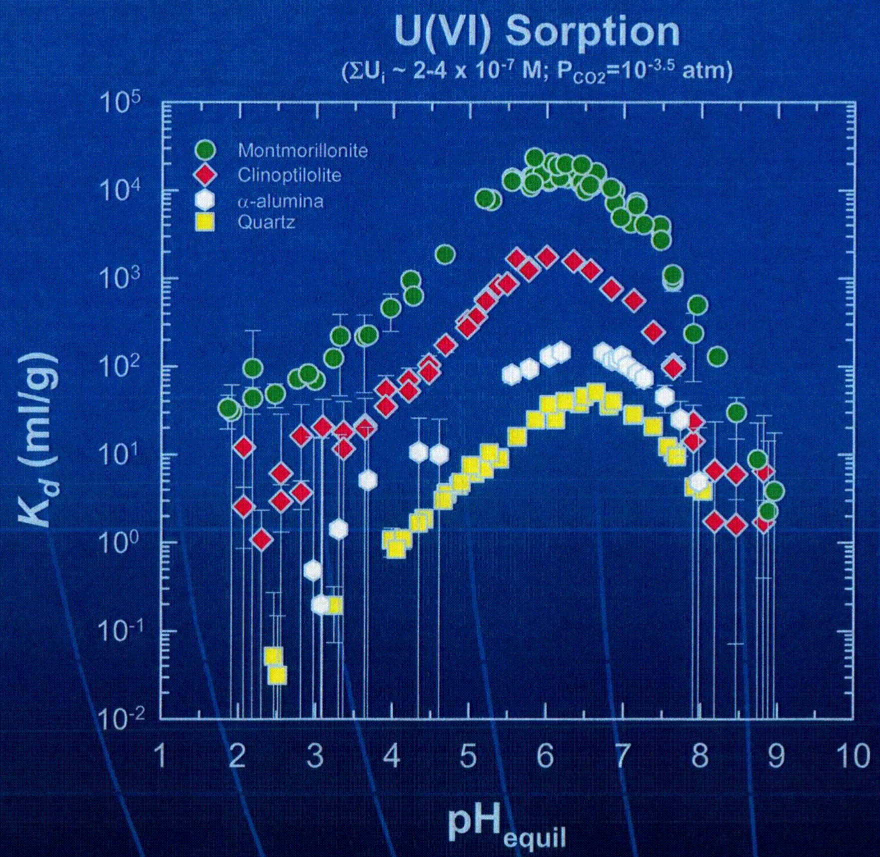
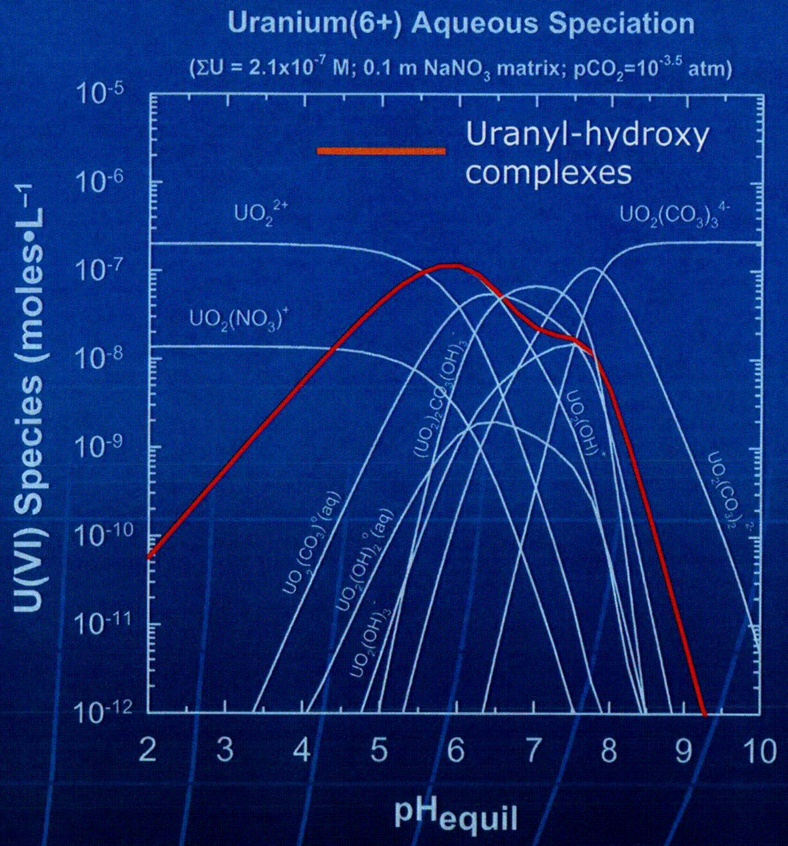
U(VI) Sorption and Aqueous Speciation





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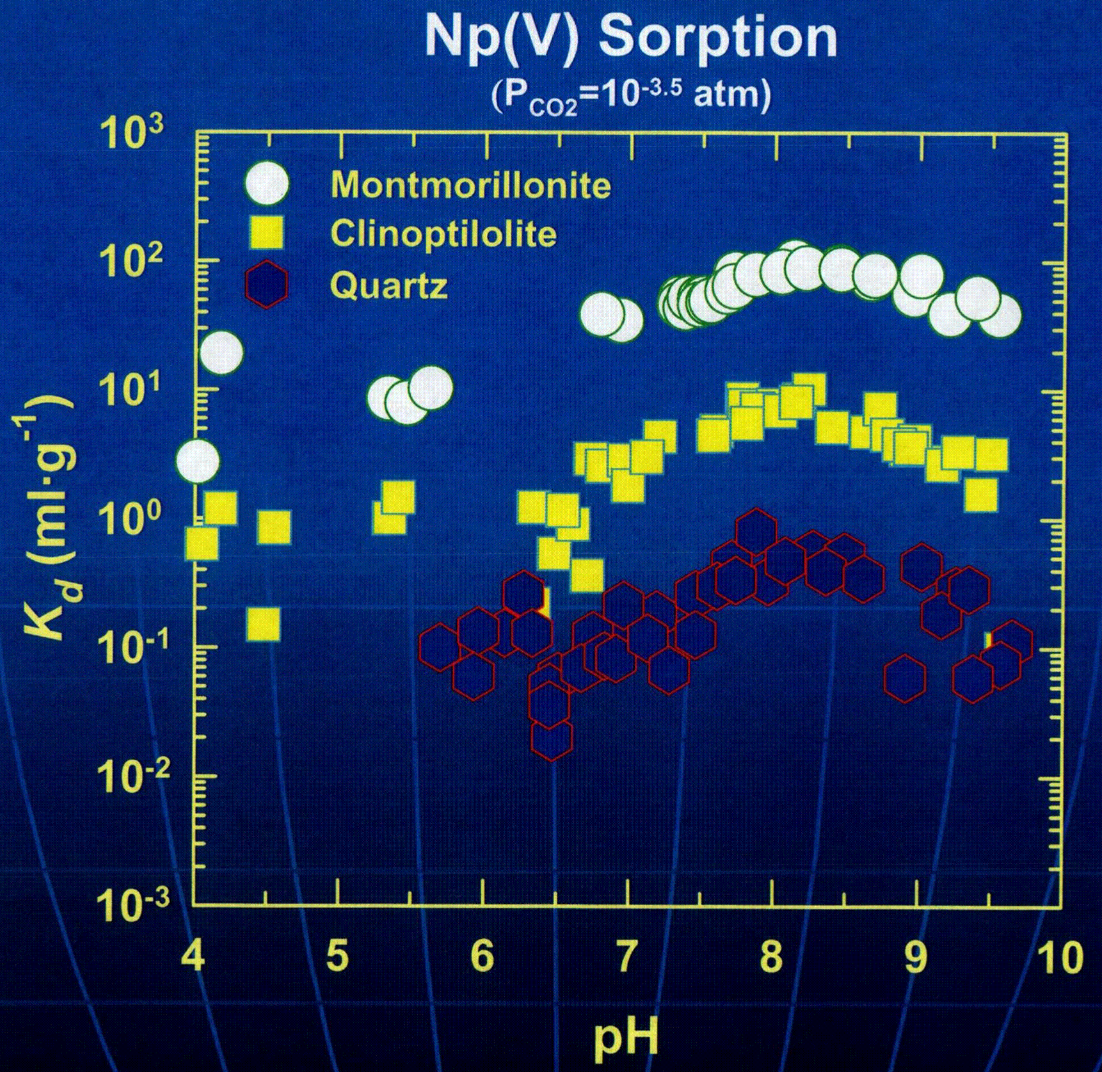
Effect of pH on Np(V) Sorption



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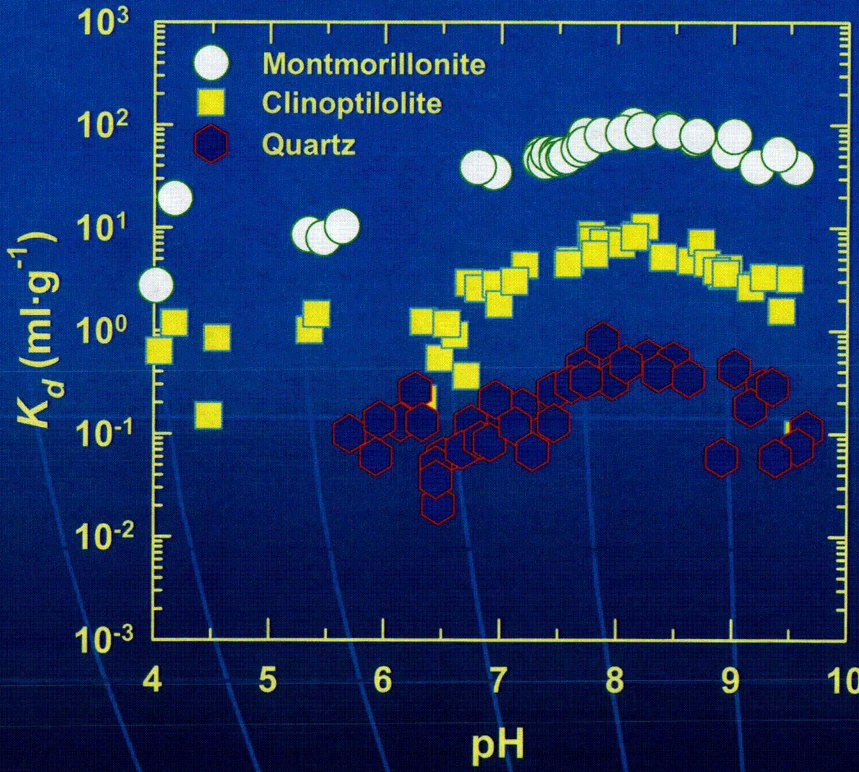
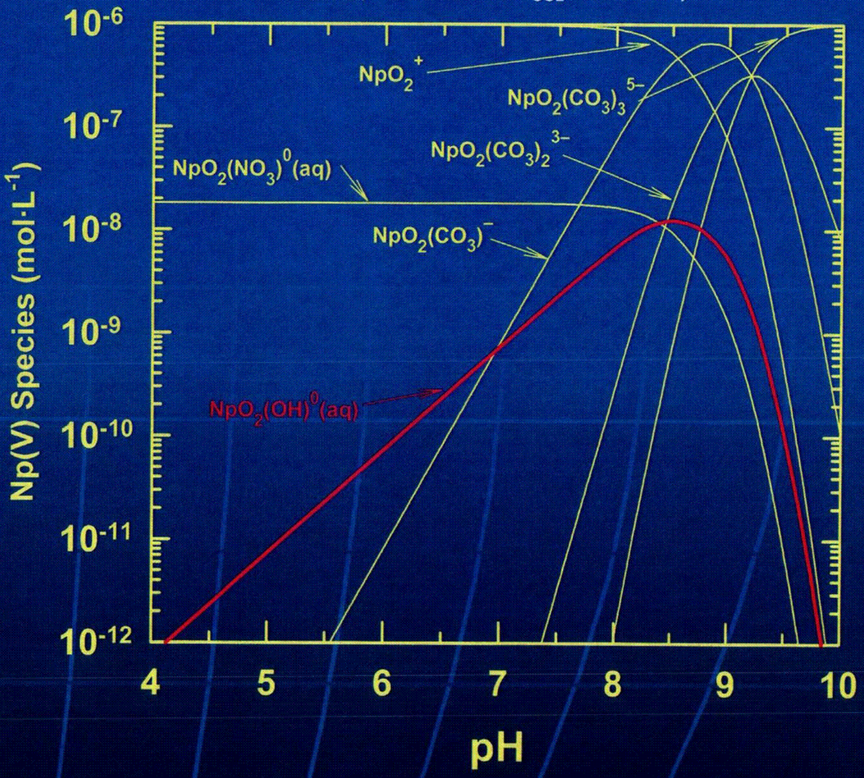
Np(V) Sorption and Aqueous Speciation

Np(V) Sorption
($P_{CO2}=10^{-3.5}$ atm)



Np(V) Aqueous Speciation
(ΣNp_i ~ 1 x 10^{-6} M; $P_{CO2}=10^{-3.5}$ atm)



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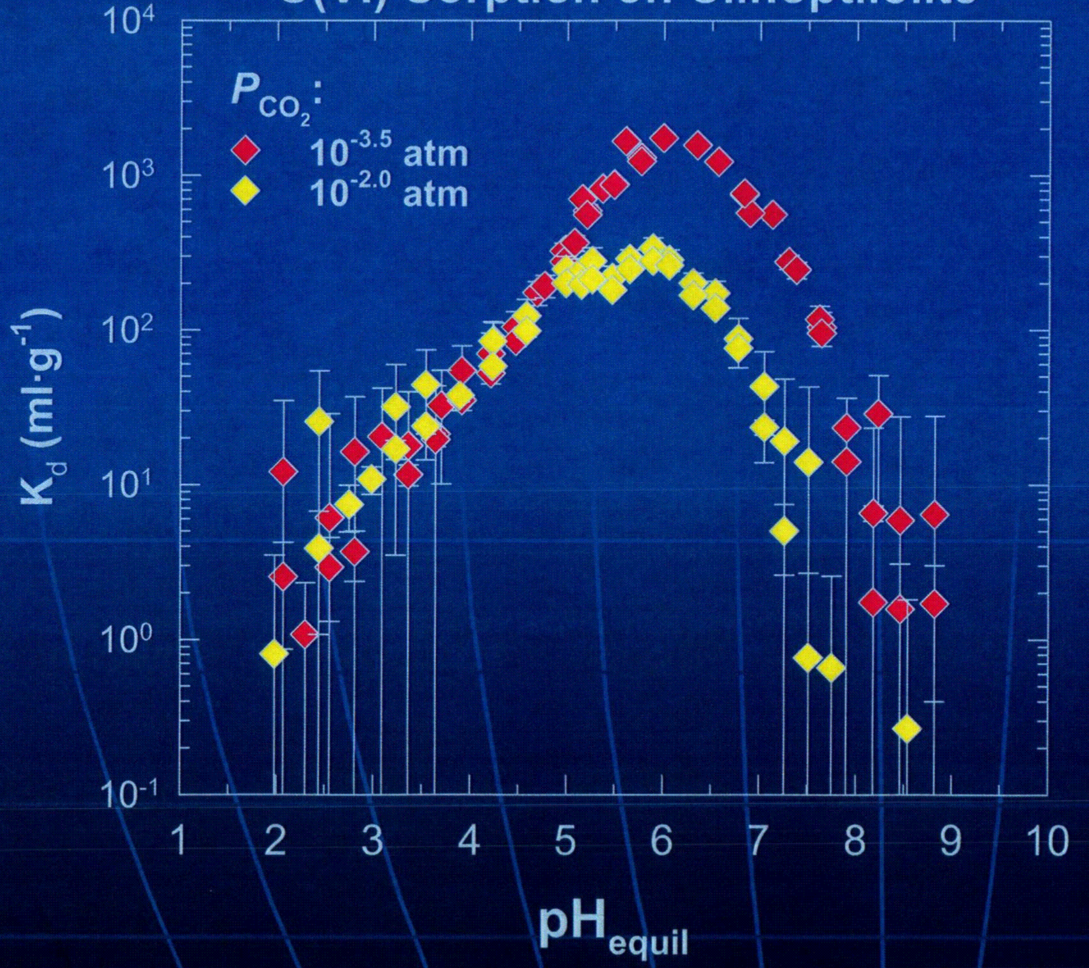
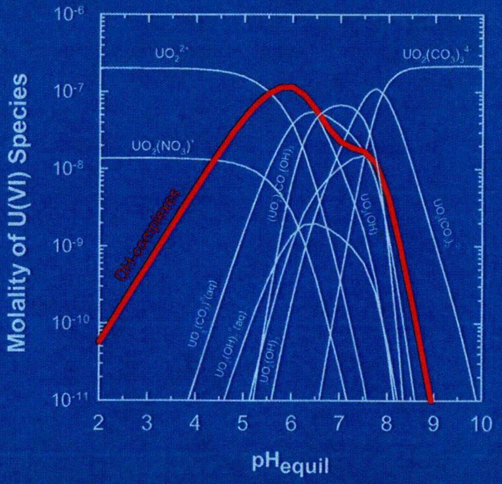
U(VI) Sorption: Effect of P_{CO2} (C_T)

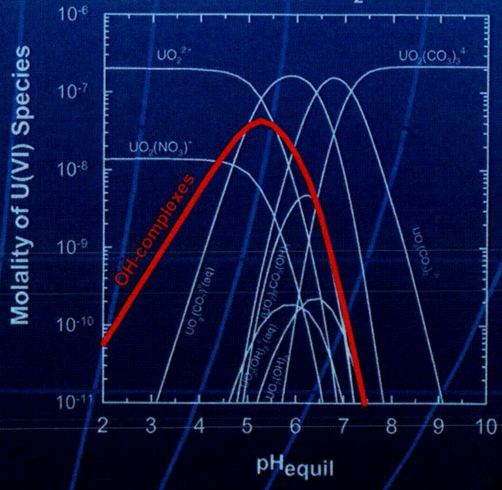
U(VI) Sorption on Clinoptilolite



U(VI) Speciation, $PCO_2=10^{-3.5}$ atm



U(VI) Speciation, $pCO_2=10^{-2.0}$ atm



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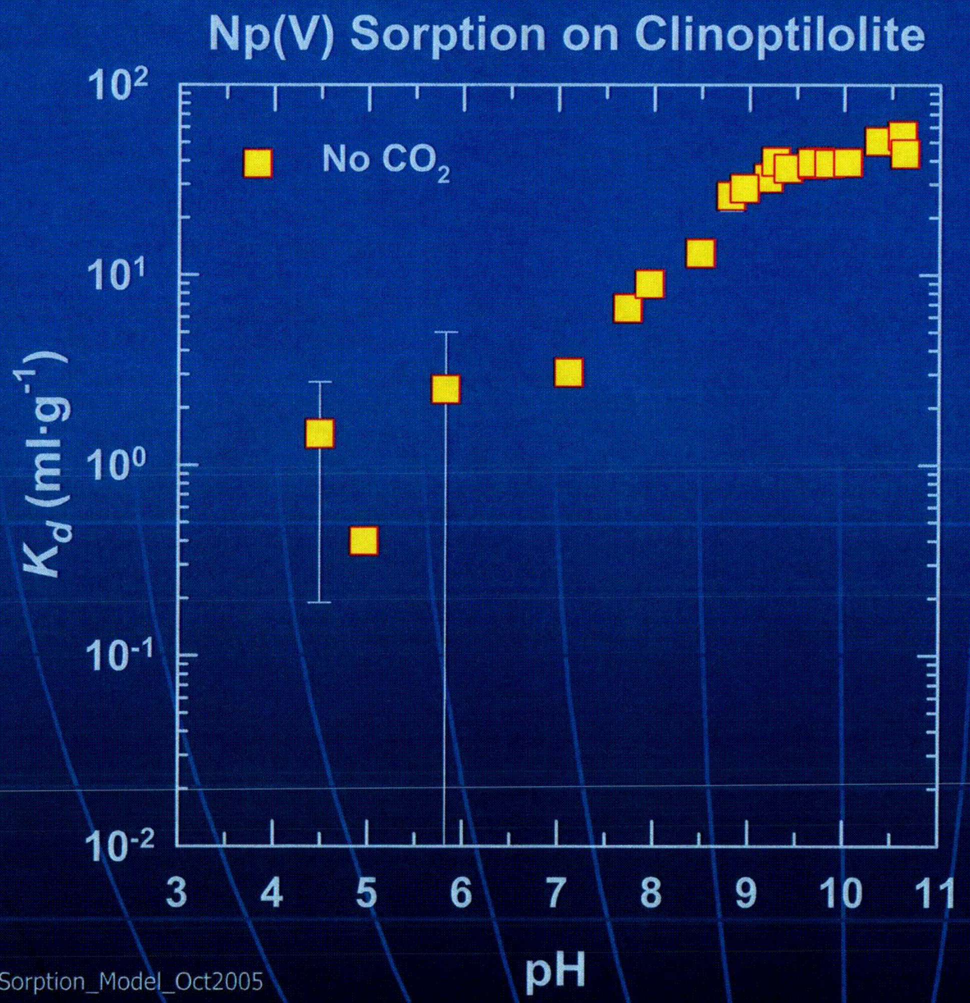
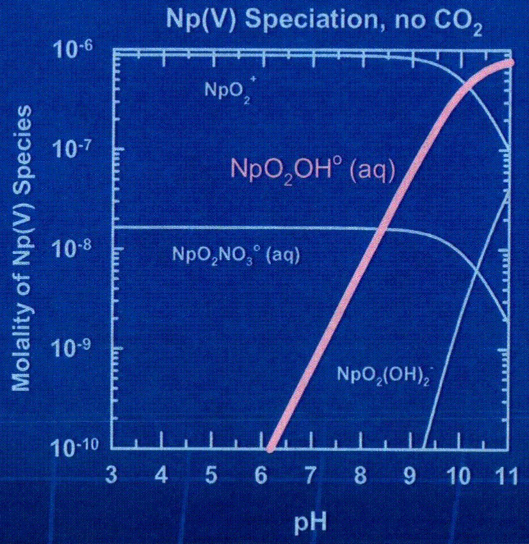
Np(V) Sorption: Effect of P_{CO2} (C_T)





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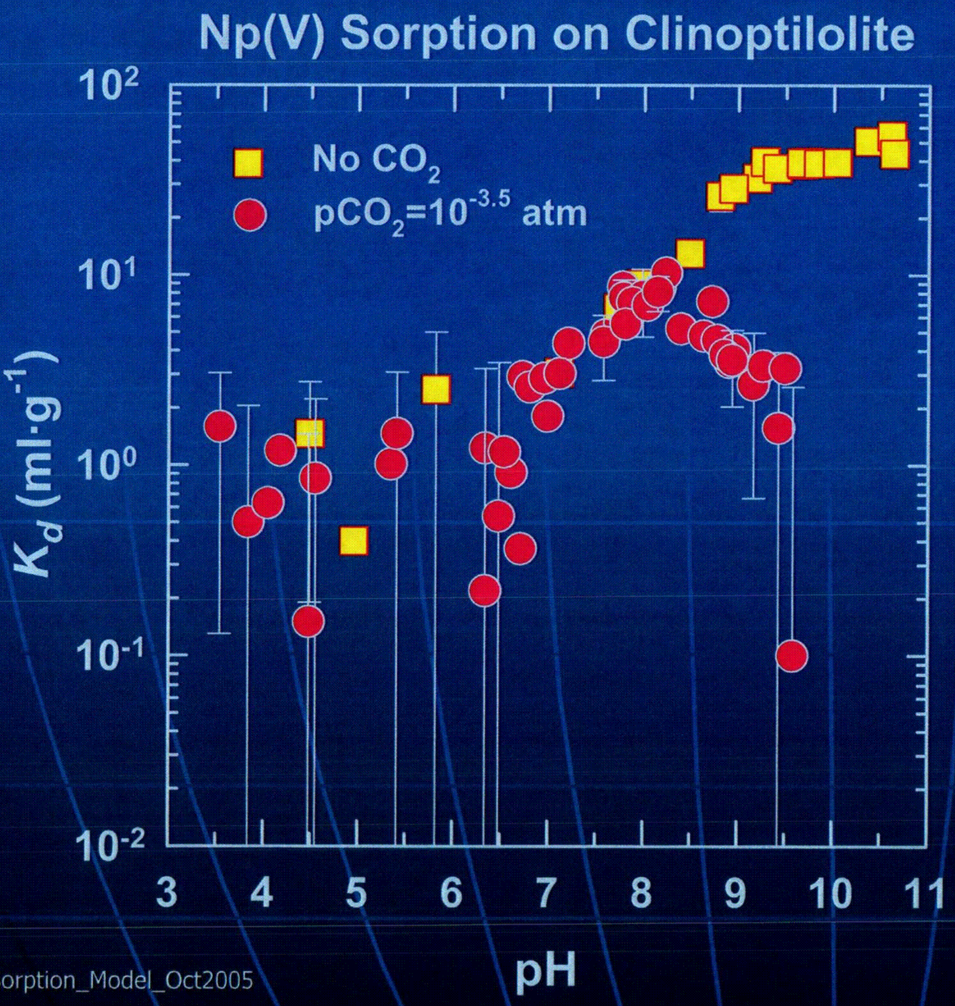
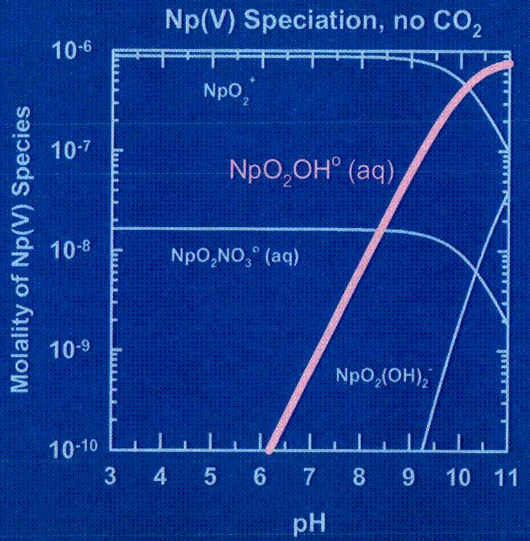
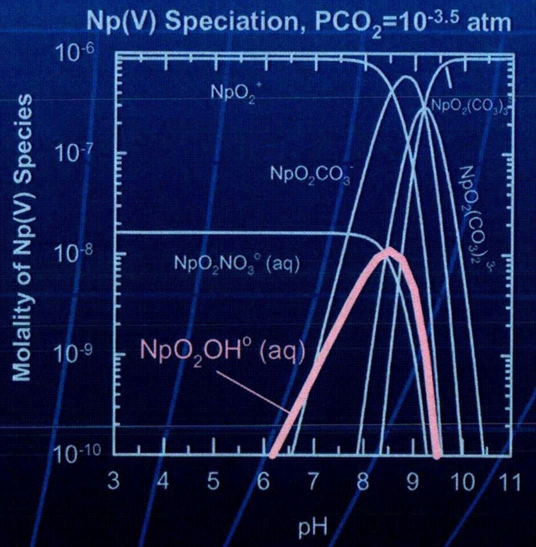
Np(V) Sorption: Effect of P_{CO2} (C_T)







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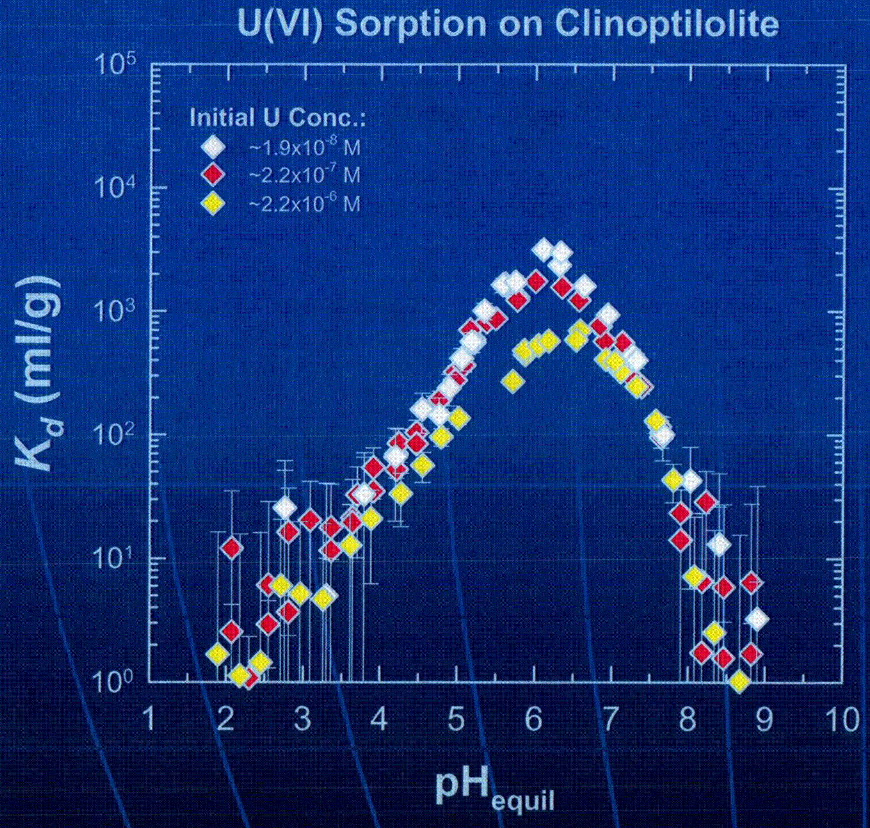
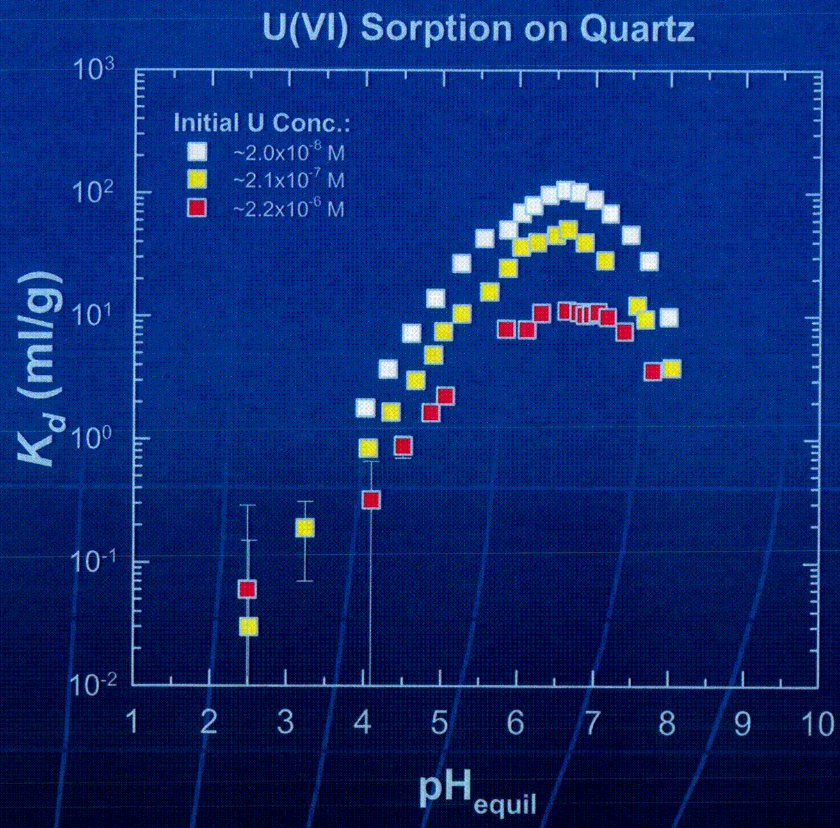
Effect of Sorbate Concentration





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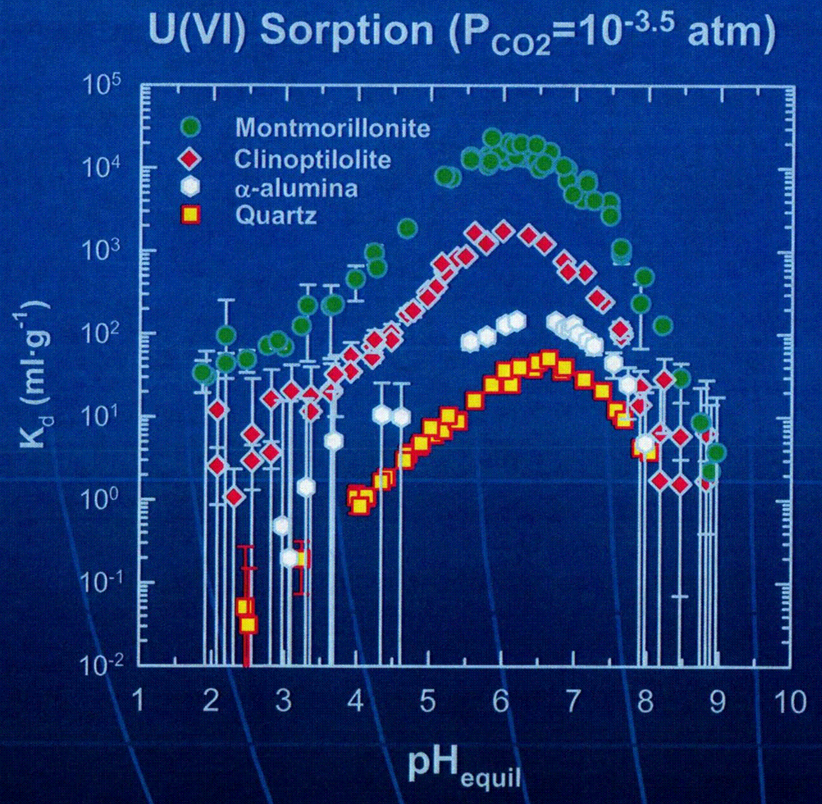
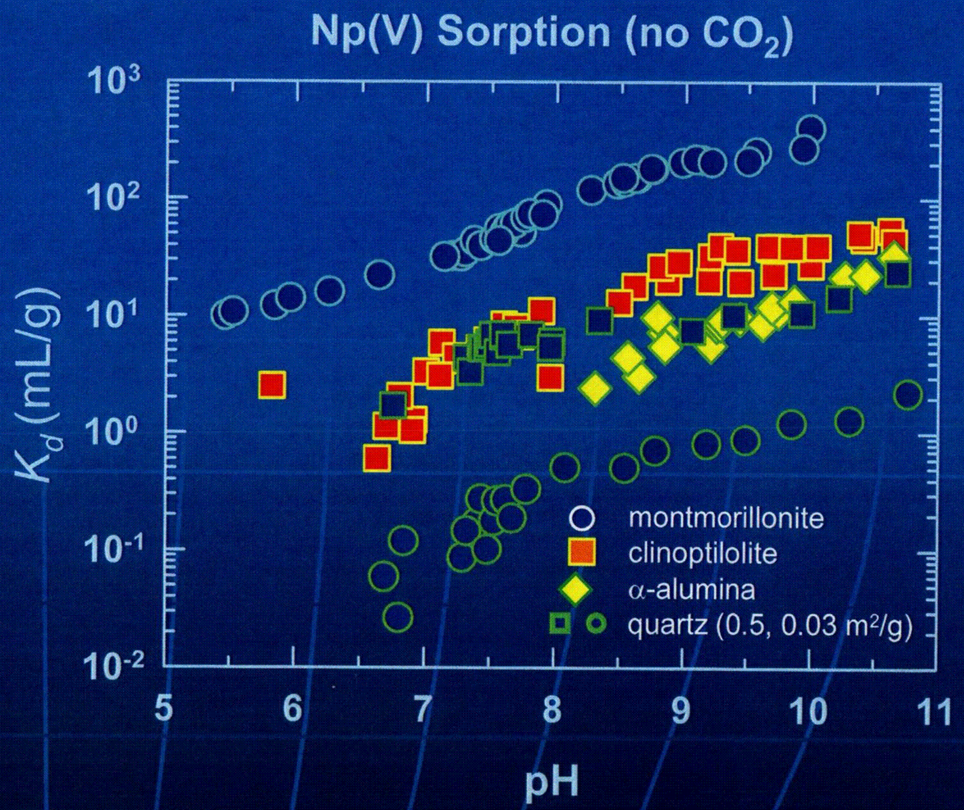
Effect of Surface Area: K_d (mL/g)

$SA_{Mont} > SA_{Clinop} > SA_{\alpha\text{-}Al2O3} > SA_{Quartz}$





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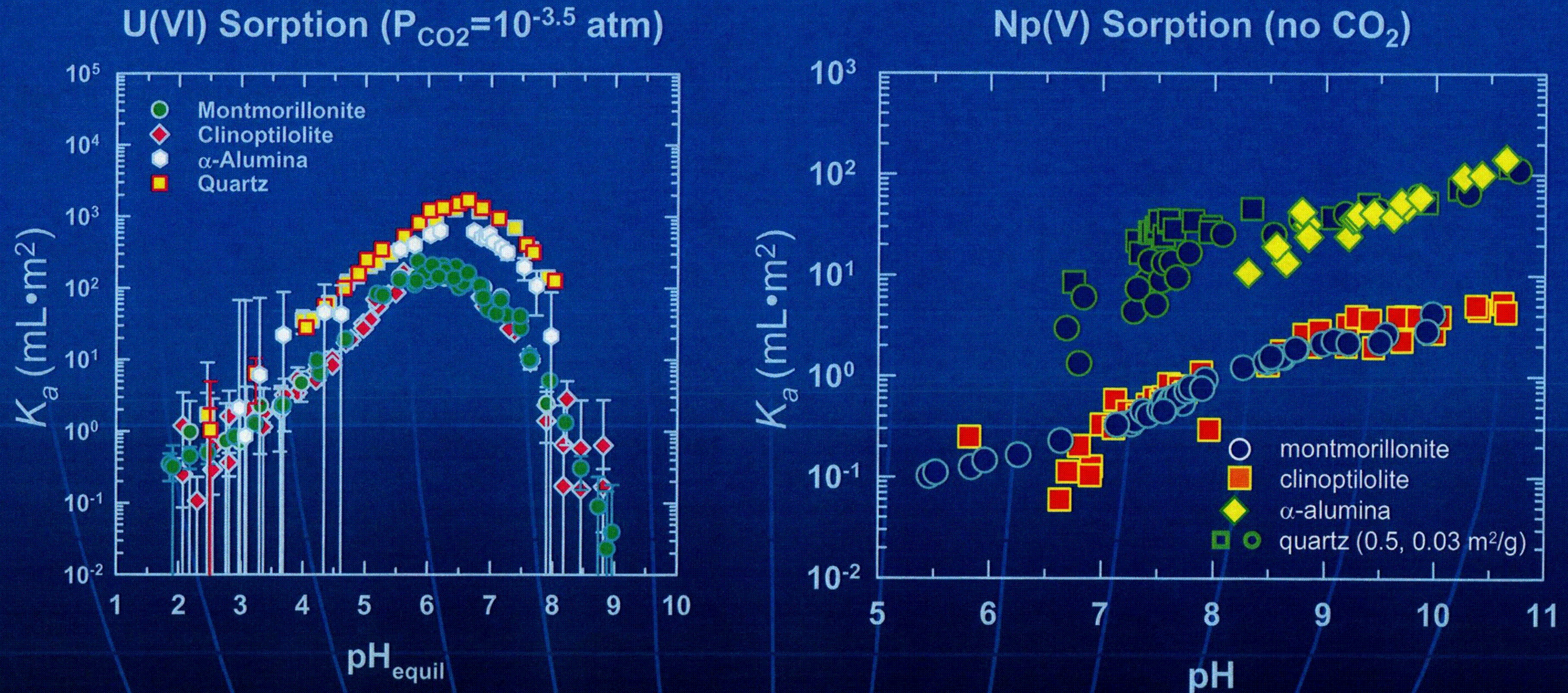
Effect of Surface Area (cont'd.)

$$K_a\ (mL/m^2) = K_d/SA$$



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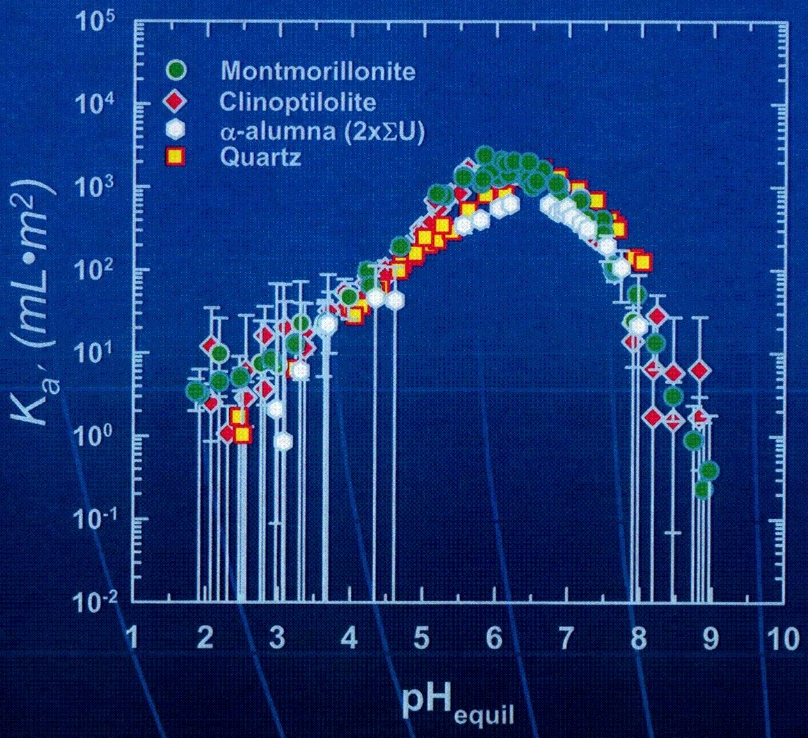
Effect of Surface Area (cont'd.)

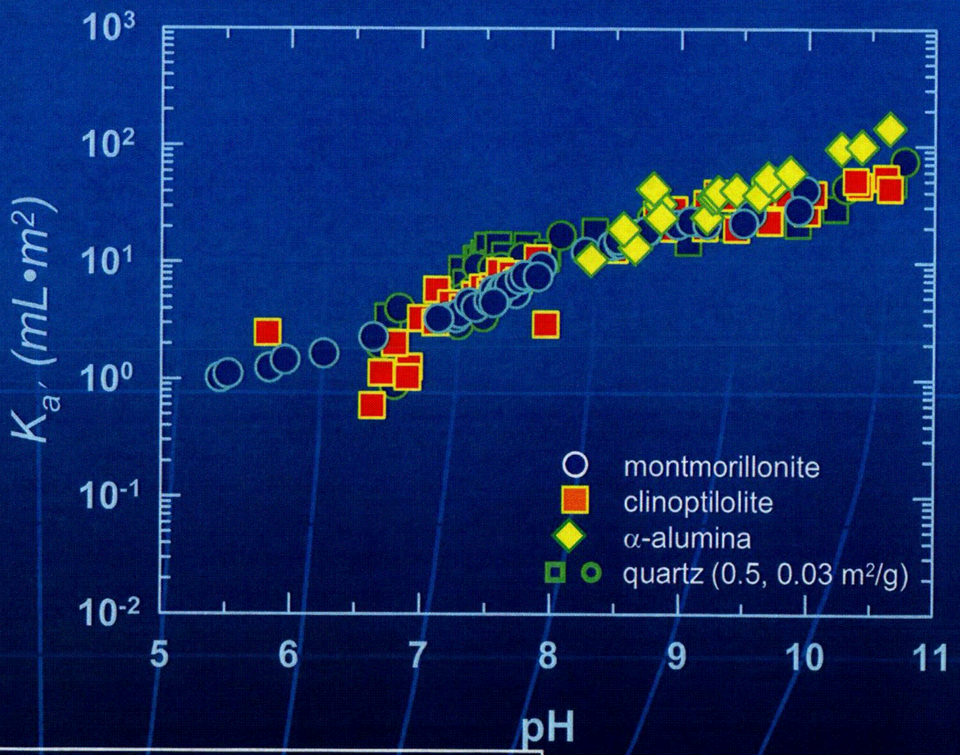
$K_{a'}$ (mL/m^2) = K_d/SA_{eff}

(For clinop & mont, $SA_{eff} = 0.1 \times SA$)

U(VI) Sorption ($P_{CO2}=10^{-3.5}$ atm)



Np(V) Sorption (no CO_2)



∴ $K_{a'}$ useful for PA abstraction

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Surface Complexation Modeling

- Experimental Data from CNWRA, Open Literature
- Electrostatic Diffuse Layer Model (DLM)
  - $>SiOH^0$ & $>AlOH^0$
  - Component additivity for aluminosilicates
    - Si:Al ratios fixed *a priori*
  - Parameters derived using FITEQL
  - Uniform site density (2.3 sites/nm^2)
  - Monodentate surface species
  - Thermodynamic data from NEA TDB and LLNL EQ3/6 database
  - No ion exchange
- Limited to Silicate and Aluminosilicate Sorption. Fe-(hydr)oxides and Calcite to be Handled Separately Where Abundant

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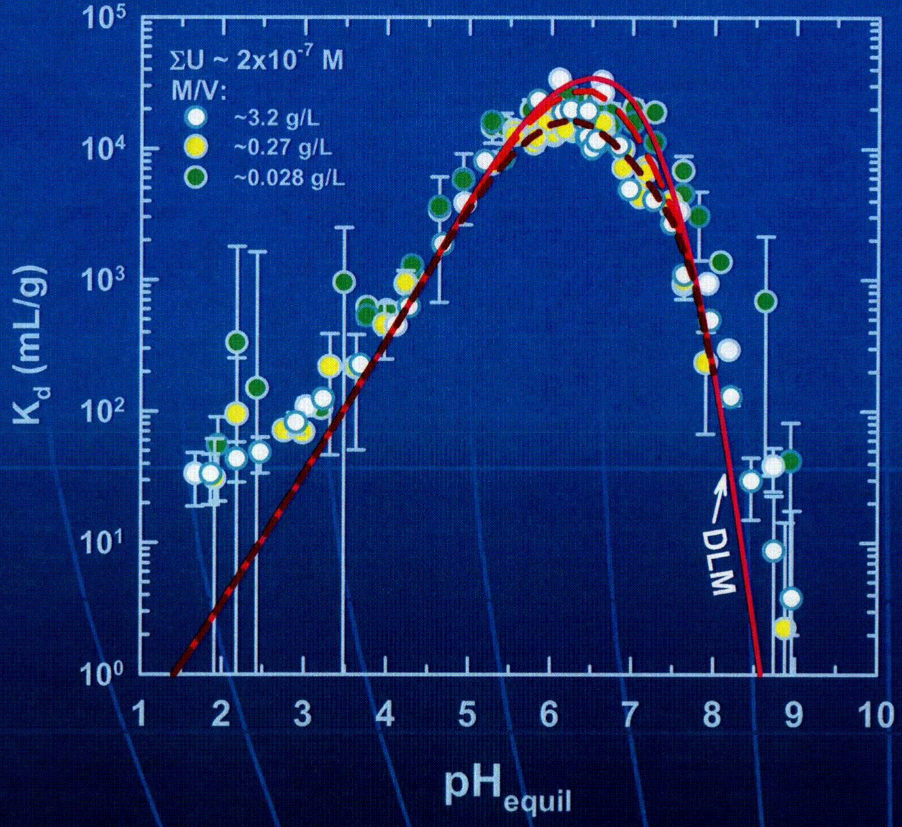
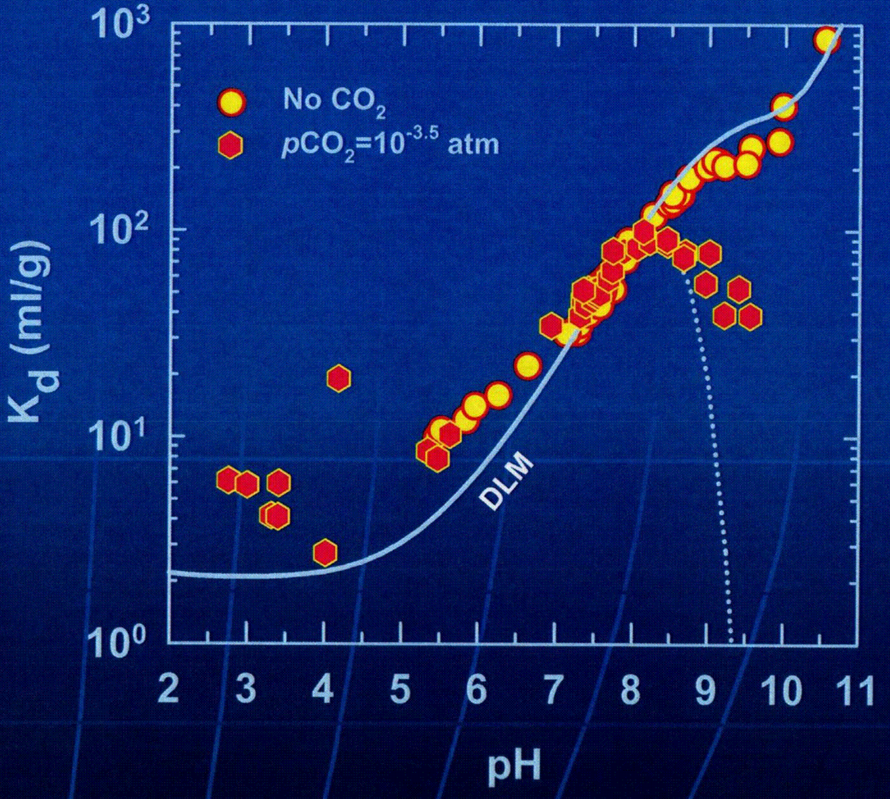
Surface Complexation Modeling: Calculated vs. Experimental Data

U(VI)-montmorillonite



Np(V)-montmorillonite



Data from Pabalan and Turner (1997) and Turner et al. (1998)

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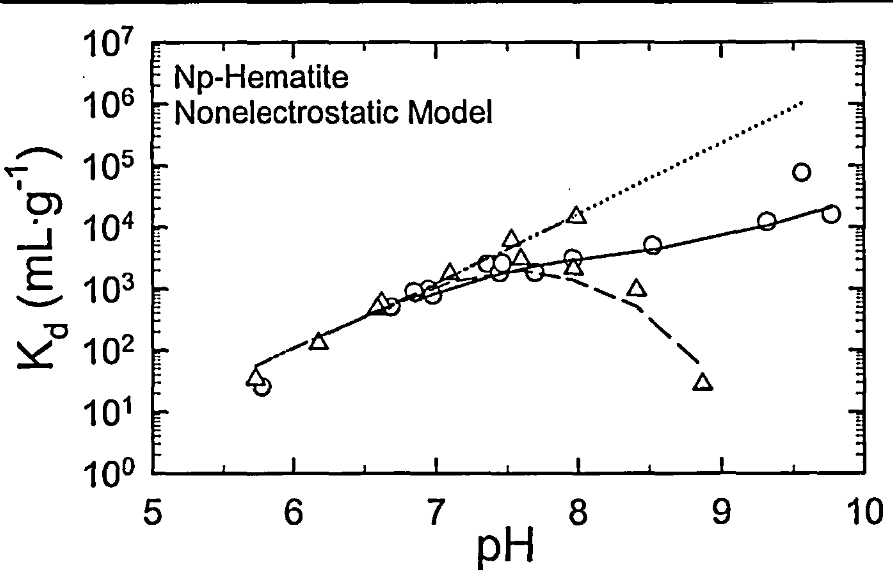
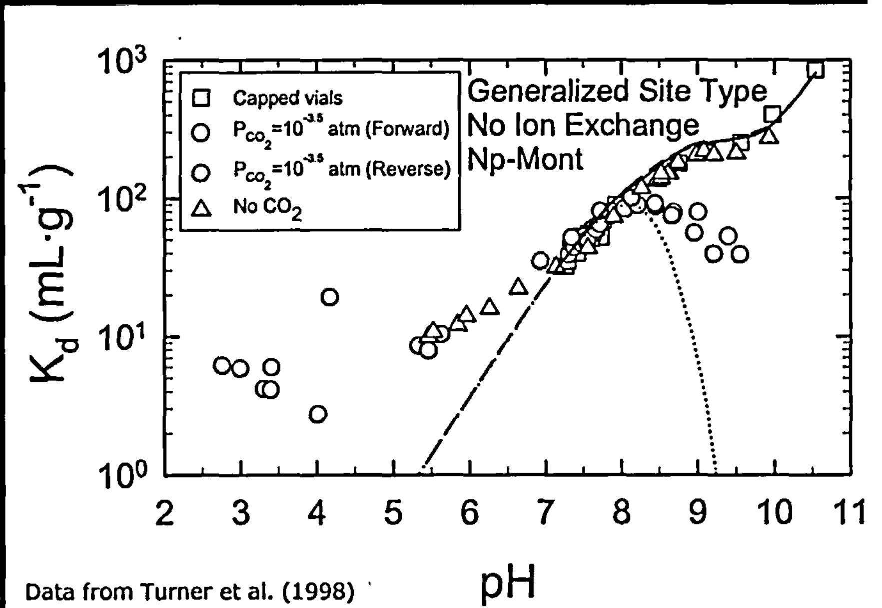
Potential Future Modeling Efforts

- Examine Non-Electrostatic Models (NEM) with Generalized Composite Model for Sites
- Include Ion Exchange



Data from Kohler et al. (1999)



Data from Turner et al. (1998)

- Can Be Used Off-Line to Further Refine TPA Response Surfaces
- Useful for Experiments with Composite Materials (In Process)

Summary

- Sorption Experiments to Identify Key Geochemical Parameters That Control Radionuclide Sorption Behavior
- Simplified Surface Complexation Models to Develop Uniform Parameter Set
  - Captures major aspects of sorption behavior
  - Focus on support for performance assessment abstractions

Applying Thermodynamic Radionuclide Sorption Models to Performance Assessment

by

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Outline of Presentation

- Geologic Disposal of High-Level Nuclear Waste (HLW) and Role of Performance Assessment
- Sorption Model Abstraction in Performance Assessment
- Approaches to Improving Sorption Model Abstraction
- Summary

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Geologic Disposal of U.S. HLW

- Potential Geologic Disposal of HLW at Yucca Mountain, Nevada
- 70,000 MTHM for Disposal
  - ~90% commercial spent nuclear fuel (by radiation content)
  - ~10% defense HLW, Naval reactor fuel, U.S. Department of Energy (DOE)-owned reactor fuel

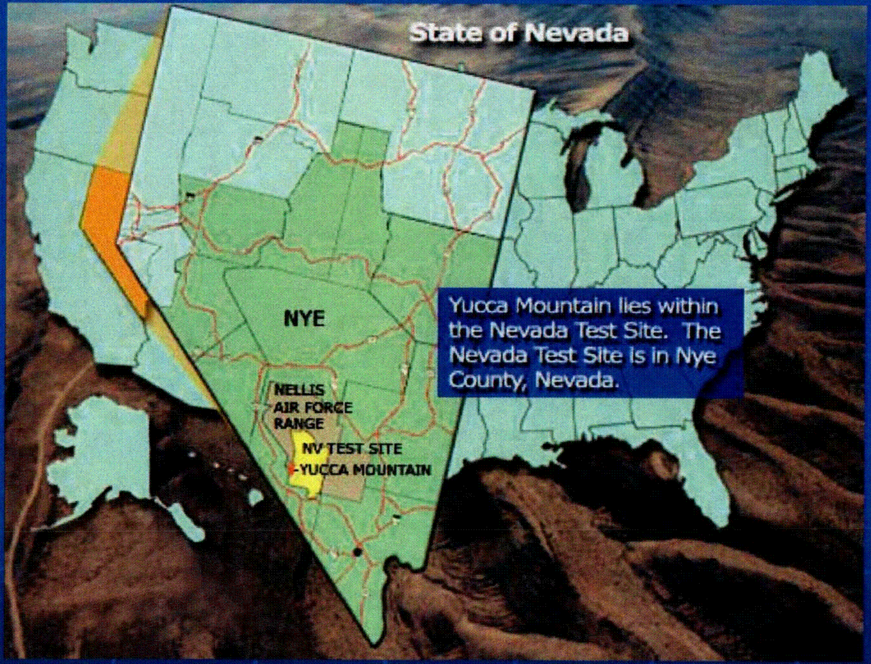

Figure taken from http://www.ocrwm.doe.gov/ymp/about/tour/index.shtml

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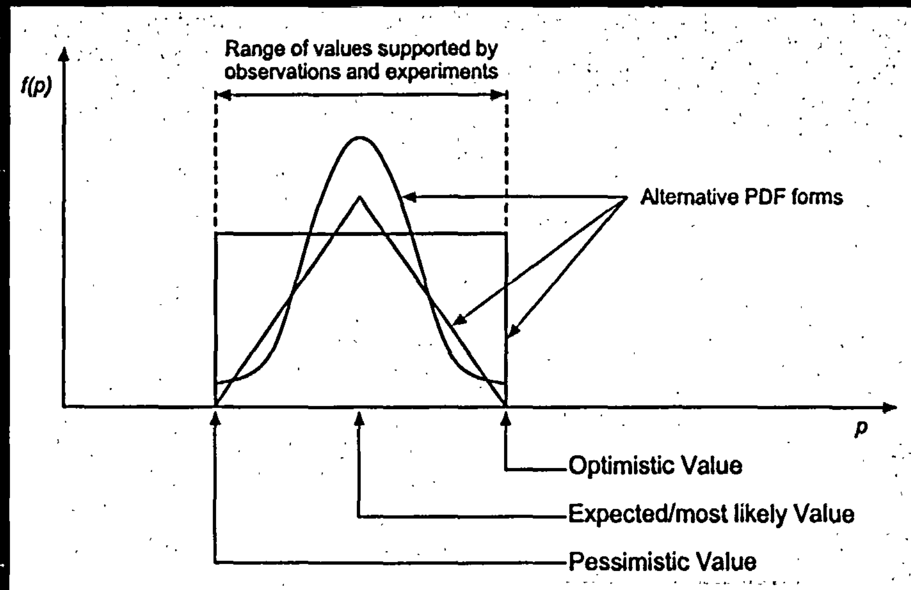
Role of Performance Assessment in HLW Disposal

- Performance Assessment
  - Used to estimate how a specific system and all of its components evolve over time
  - Required by regulation
  - Provides a tool for determining whether a system meets regulatory requirements
- Total-system Performance Assessment (TPA) Links Conceptual/Numerical Models Of System Components
  - Simplifies, or abstracts, key attributes of process level modeling
  - Iterative process as models, data, and computer codes are added and refined

Abstraction of Radionuclide Sorption in TPA

- Performance Assessment Codes Use Distribution Coefficients, or K_ds, to Represent Sorption
  - Constant K_d for each radionuclide and each hydrostratigraphic unit over the time of the realization
  - Probability distribution functions (PDFs) represent variability in K_d
  - PDFs based on
    - Laboratory experiments
    - Expert judgment
    - Process models



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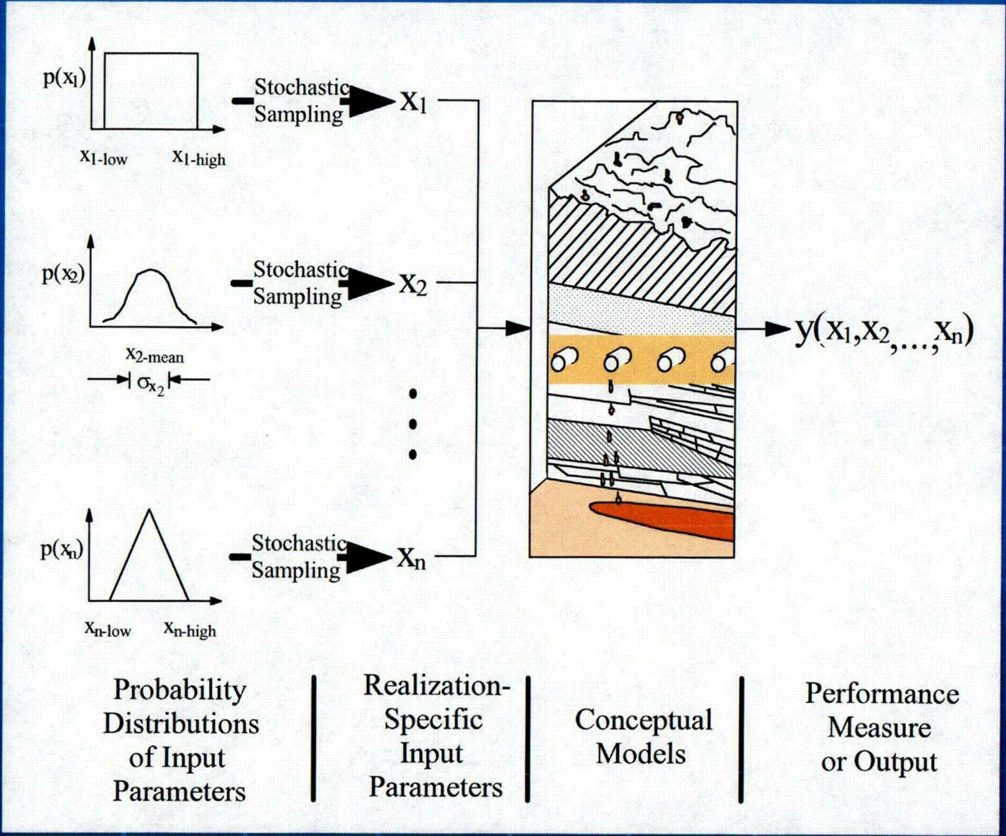
Abstraction of Radionuclide Sorption in TPA (cont'd.)



NRC TPA Code

- Transport Modeled with K_d Approach $\mathbf{R_f} = \mathbf{1} + \frac{\rho_b}{\theta}\mathbf{K_d}$
  - 16 radioelements
  - 9 stratigraphic units
  - >250 transport parameters
- Transport Treated as Uncertain—Parameter PDFs
- Single K_d Throughout Simulation Time for Each Realization and Each Stratigraphic Unit

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Considerations for Improving Sorption Abstractions in TPA

- Sorption (and K_d) Is A Function Of Site-Specific Mineralogy And Groundwater Chemistry
- Mineralogy And Groundwater Chemistry At Disposal Sites Can Vary Spatially (and Temporally)
- K_d Is Well Established In Existing TPA Transport Models
  - Improvements focused on support for transport parameter PDFs

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Improving Sorption Model Abstractions in TPA: Objectives

- Develop Abstractions Considering Effects Of Chemistry On Radionuclide Sorption Coefficients ('smart K_d')
- Develop Abstracted Models Based On Site-Specific Information
  - Groundwater chemistry
  - Rock properties
- Improve Transparency And Traceability Of Sorption Models In TPA

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Improving Sorption Model Abstractions in TPA (cont'd.)

- Practical Considerations
  - Availability of data and models
  - Limits on computational requirements and other resources
  - Flexibility

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Improving Sorption Model Abstractions in TPA: Approach

- Conduct Radionuclide Sorption Experiments
- Identify Sorption Experimental Data from Open Literature
- Develop Surface Complexation Models
- Use Site Specific Data
- Generate Parameters For Sorption Model Abstraction in TPA Code

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Sorption Experiments: Results

- Key Geochemical Parameters
  - pH
  - Complexing ligands (e.g., carbonate)
  - Site concentration (sorbent concentration/surface area)

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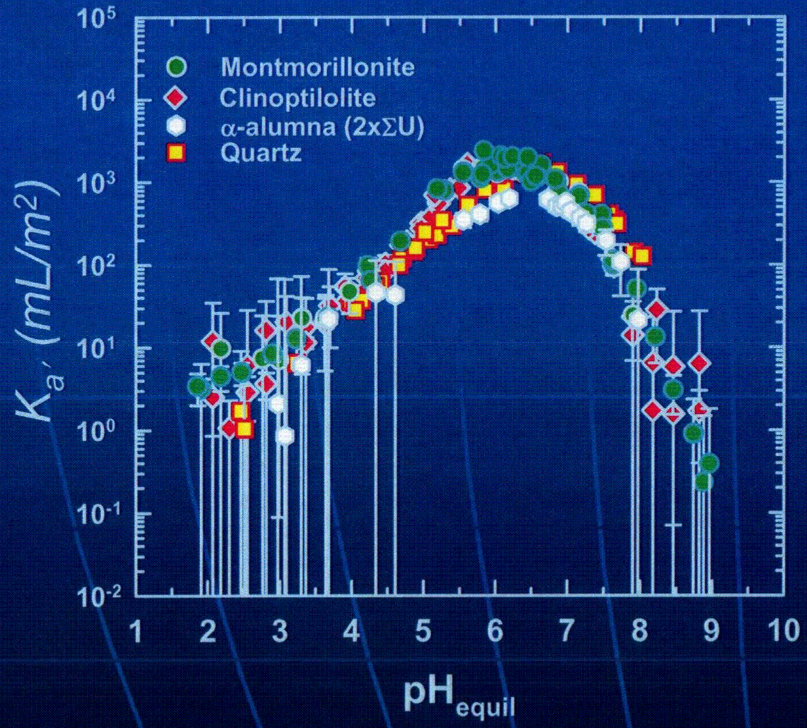
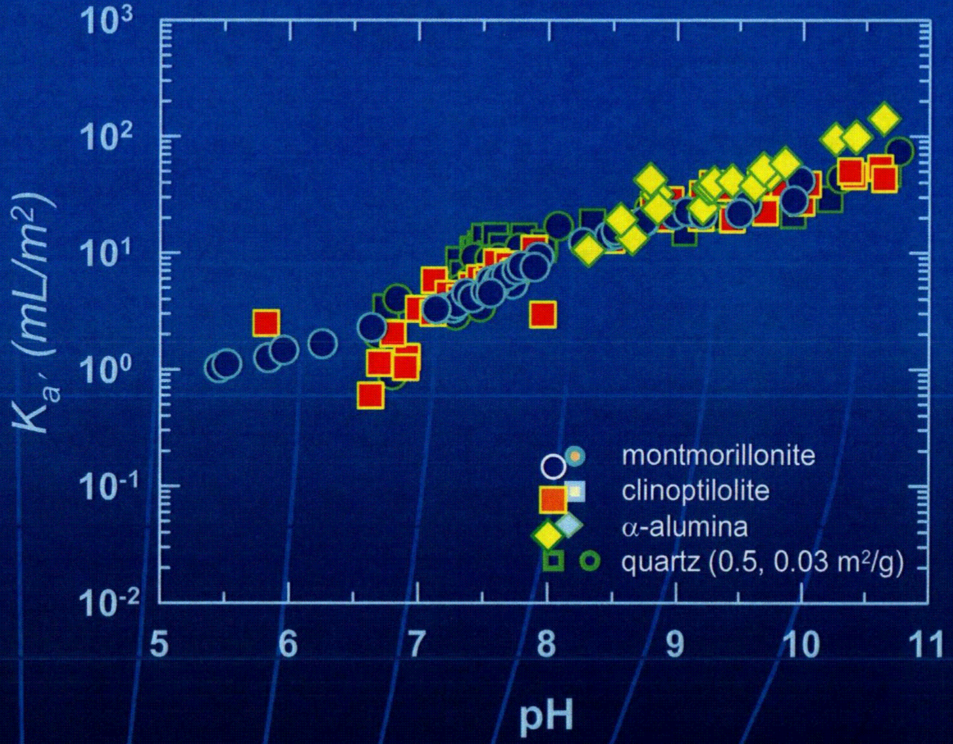
Effect of Surface Area

$K_{a'}$ (mL/m^2) = K_d/SA_{eff}

(For clinop & mont, $SA_{eff} = 0.1 \times SA$)





∴ $K_{a'}$ useful for PA abstraction

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Surface Complexation Modeling

- Experimental Data from CNWRA, Open Literature
- Electrostatic Diffuse Layer Model (DLM)
- Np(V), U(VI)—Montmorillonite (CNWRA Data)
- Am(III), Pu(V), Th(IV)—α-Alumina (Literature Data)

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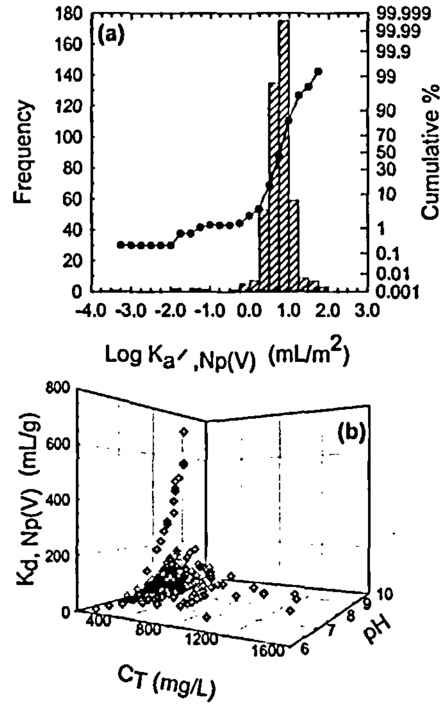
Process Model Abstraction for TPA: Refining K_d Parameter Distributions

- DLM For Five Actinides Computed with Regional Water Chemistry Data (n = 460)
- Frequency Histograms and Parameter Correlations for Calculated $K_{a'}$, K_d
- Distributions Roughly Log Normal
  - Low calculated K_d values correspond to low pH and high HCO_3^- groundwaters
  - Most calculated K_d values fall within 2 to 3 orders of magnitude



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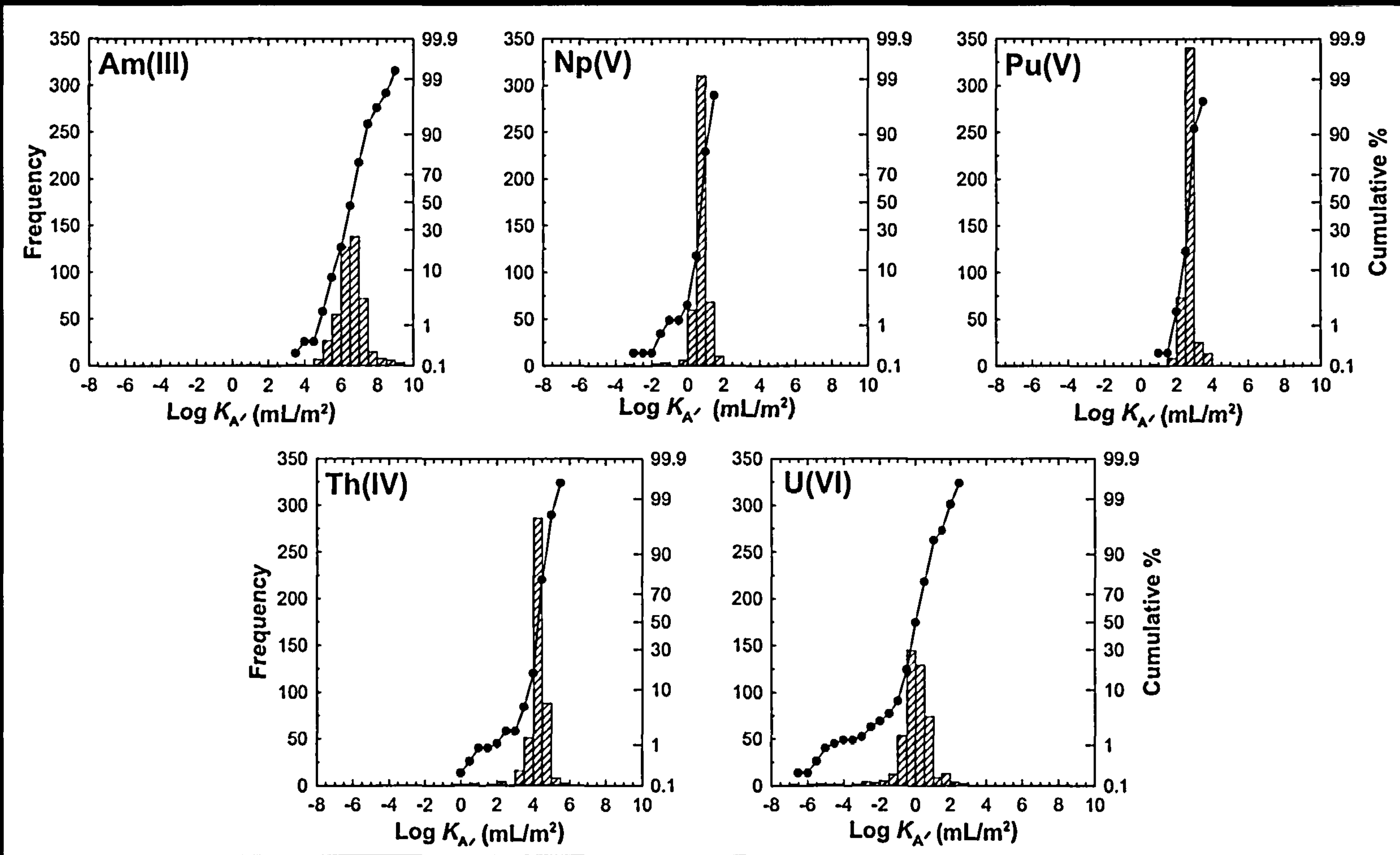
Process Model Abstraction for TPA: Actinide Sorption



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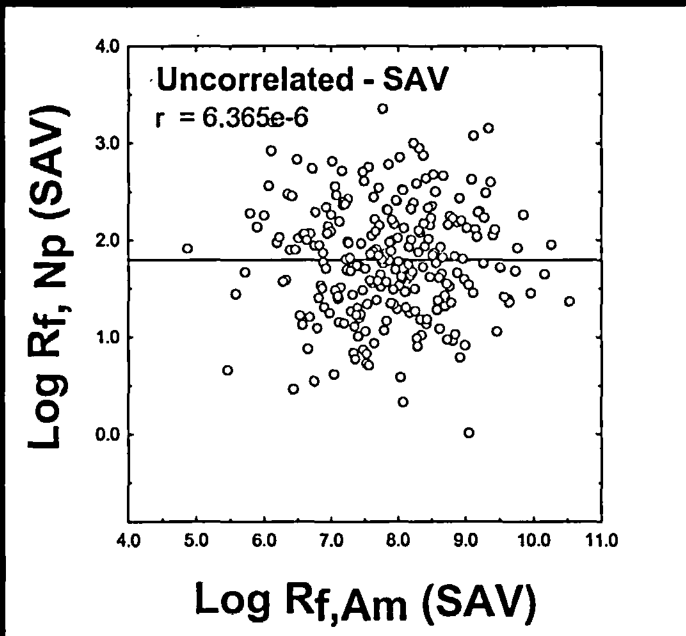
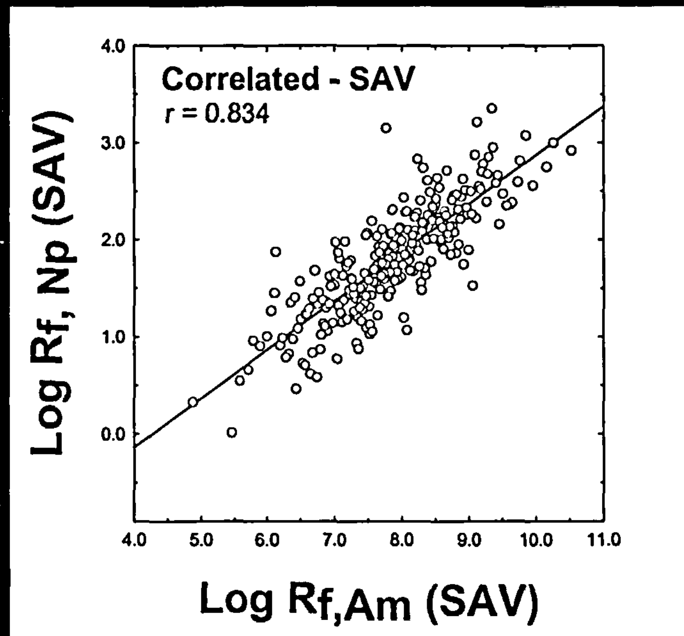
Process Model Abstraction for TPA: Actinide Sorption

- Calculated Sorption Parameters Linked Through Water Chemistry
- Correlation Coefficients Implemented In TPA
  - Indirect incorporation of geochemical effects
  - Computationally intensive





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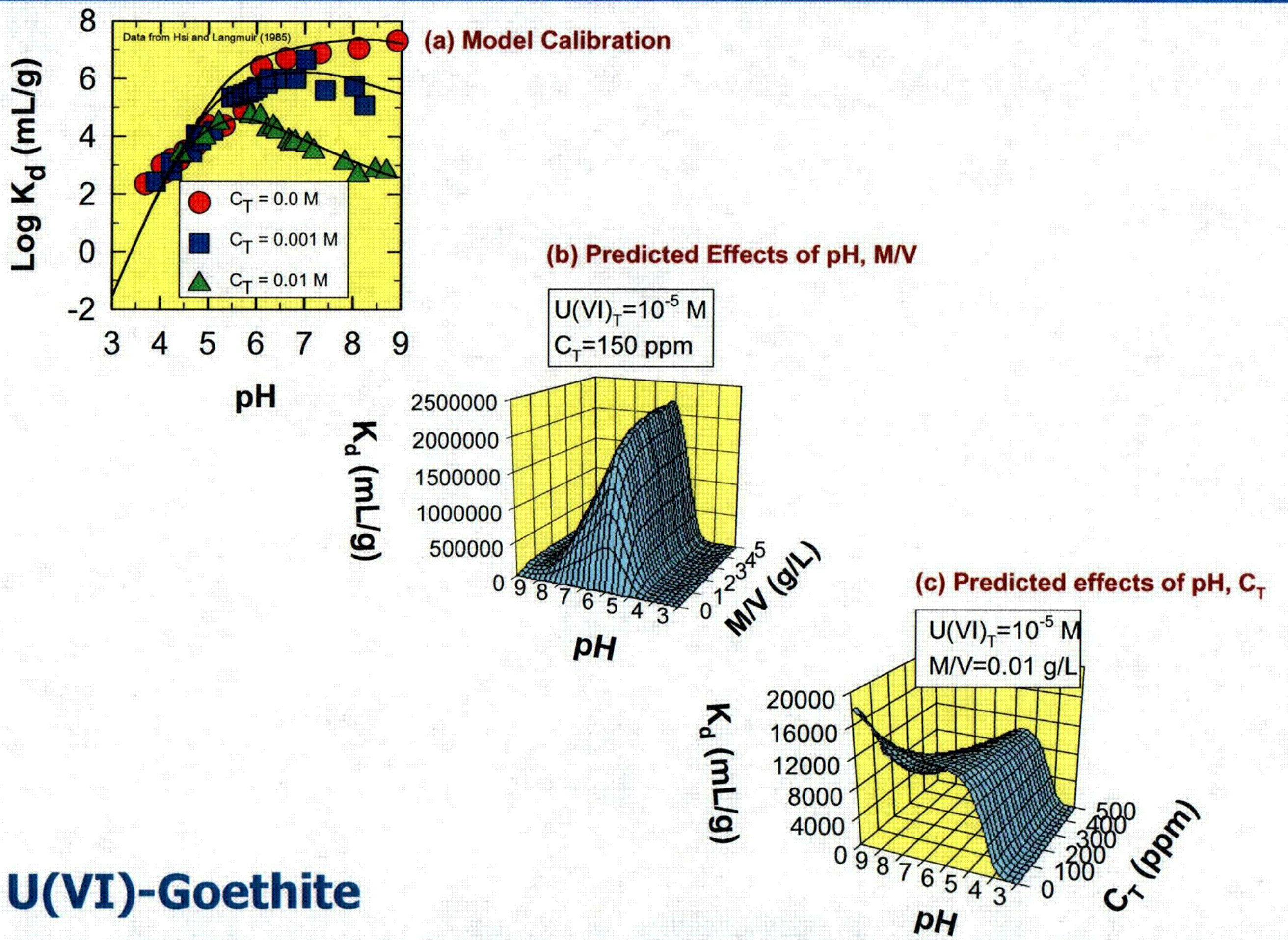
Further Refinements: Developing Response Surfaces



U(VI)-Goethite

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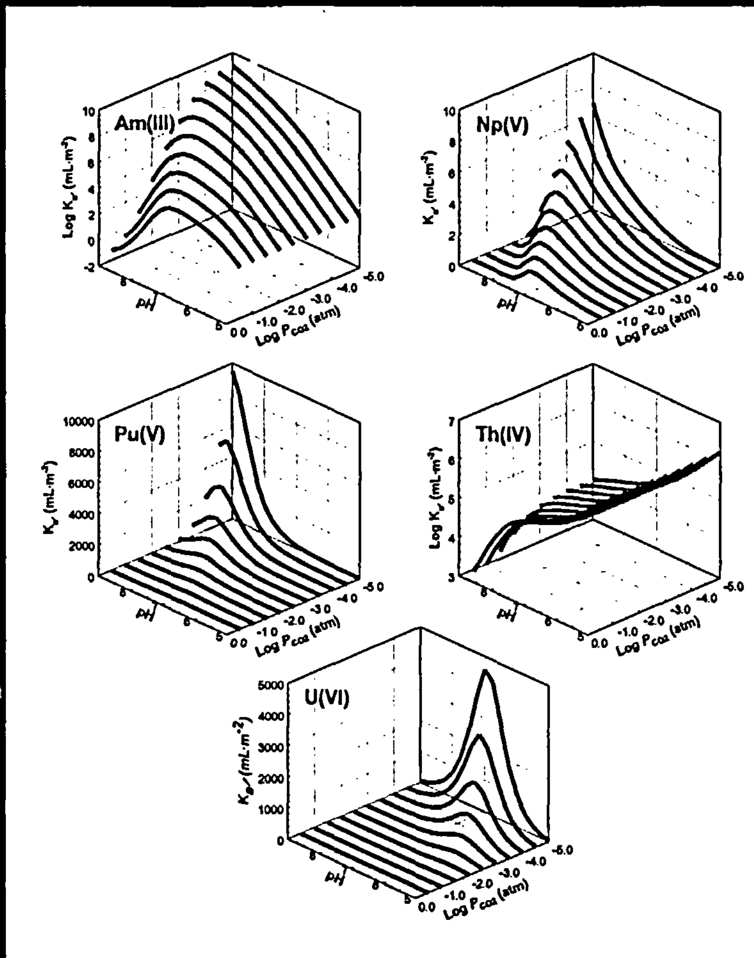
Further Refinements: Response Surfaces



- Sorption Response Surfaces (K_a vs pH, P_{CO2})
  - Electrostatic DLM
  - MINTEQA2 with NEA and EQ3/6 thermodynamic data
- Advantages
  - Increased flexibility
  - Reduces number of sampled transport parameters
  - Allows stochastic sampling of measured hydrochemical parameters
  - Provides direct link to site-specific geochemical variability

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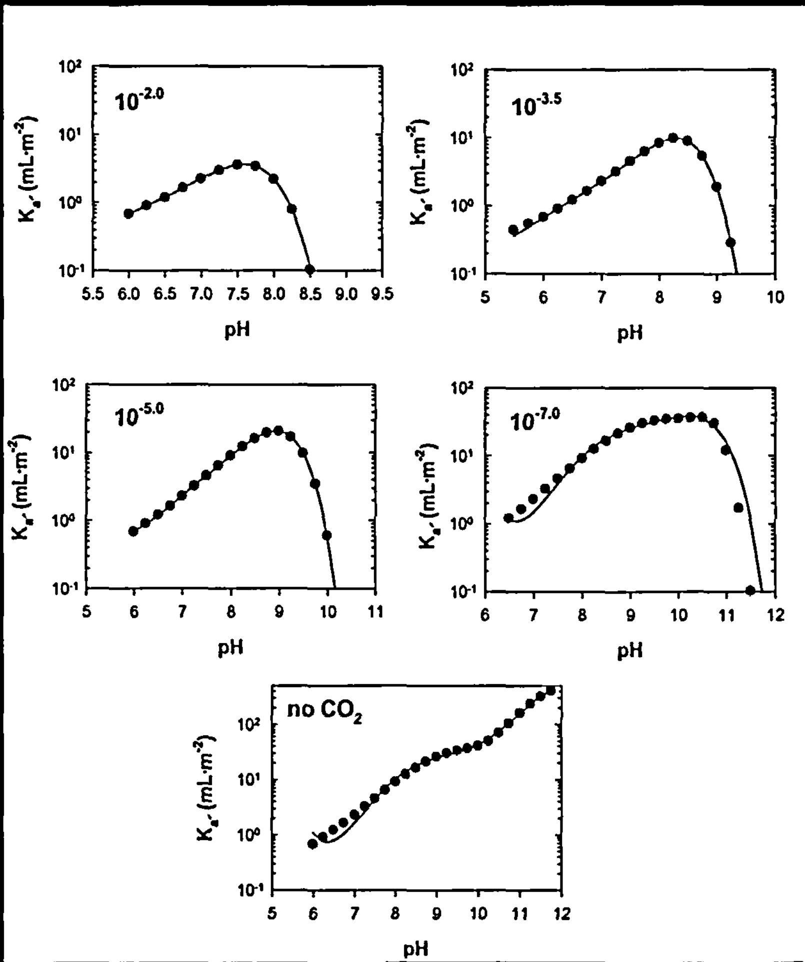
Implementation in TPA



- Offline Calculations
  - SCM run at discrete pH and P_{CO2}
  - K_a, calculated as function of pH for a fixed P_{CO2}
    - Polynomial fit to curves
- Implementation in TPA
  - pH and P_{CO2} selected from site-specific PDF for each realization
    - Interpolation as necessary
  - K_a, identified from response surface
  - K_a, converted to K_d based on estimated ESA
  - Run transport simulation

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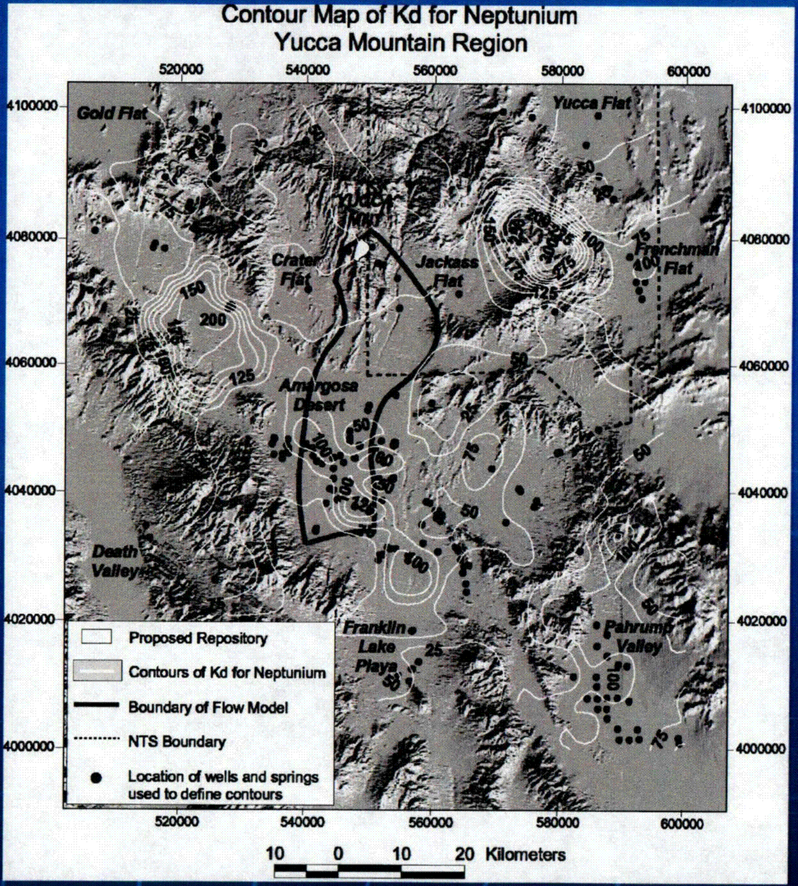
Process Model Abstraction for TPA: Effects of Geochemical Variability

- Process Modeling To Investigate Effects Of Geochemical Variability
- Trends In Calculated Sorption Parallel Trends In pH and P_{CO2}
- Data Limitations Include
  - Sparse data
  - Water sampling integrated over entire well bore
  - Does not include post-1994 data (Nye County EWDP wells)



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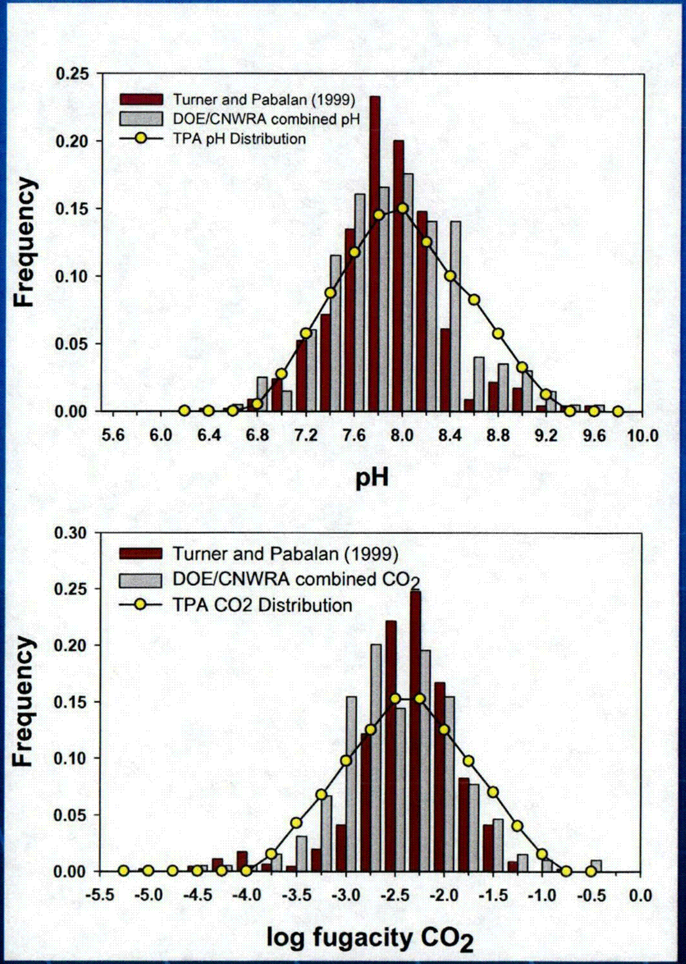
Refining Site-Specific Groundwater Chemistry Data



- pH/P_{CO2} Distributions Are Being Evaluated
- Original Pre-1994 Data Set Covered a Large Area
  - Revise for narrower focus on anticipated flowpaths
- Additional, More Recent Site-Specific Data Now Available
  - Revise to include newer data
  - Small changes in pH/P_{CO2} mean values

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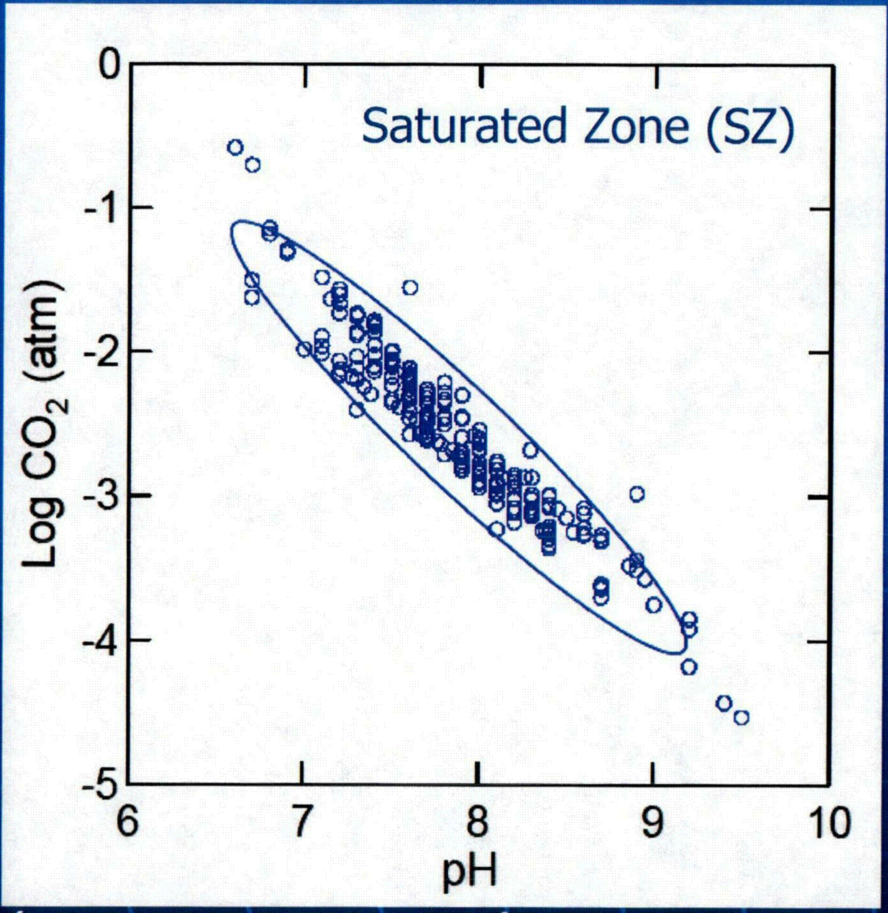
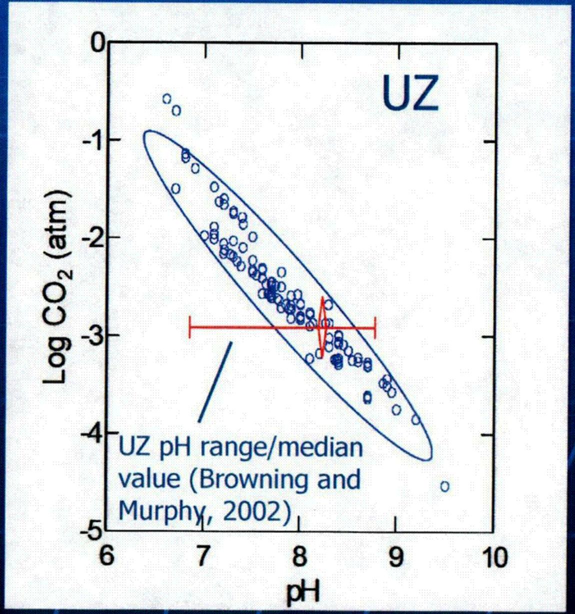
Correlating Key Geochemical Parameters



(From McMurry and Bertetti, 2005)

- New pH and P_{CO2} Data From Individual Flow Zones
  - Some outliers
- Negatively Correlated
  - Correlation factor about - 0.95
  - Used to correlate PDFs



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Summary

- Process Models Used to Support Sorption Parameter Distributions
- Experiments to Identify Key Parameters That Control Sorption Behavior
- Surface Complexation Models Were Applied
- Site-Specific Groundwater Chemistry Data and Rock Properties Were Used