Developing Thermodynamic Radionuclide Sorption Models: Experimental and Modeling Results

by

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NEA Workshop on Radionuclide Sorption
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Acknowledgment

The presentation documents work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC–02–02–012. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety. It is an independent product of CNWRA and does not necessarily reflect the view or regulatory position of NRC.

M. Almendarez, T. Dietrich, T. Griffin, A. Jain, P. Mueller, J. Prikryl, S. Sassman, and B. Werling helped with the experimental and modeling work.

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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

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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*

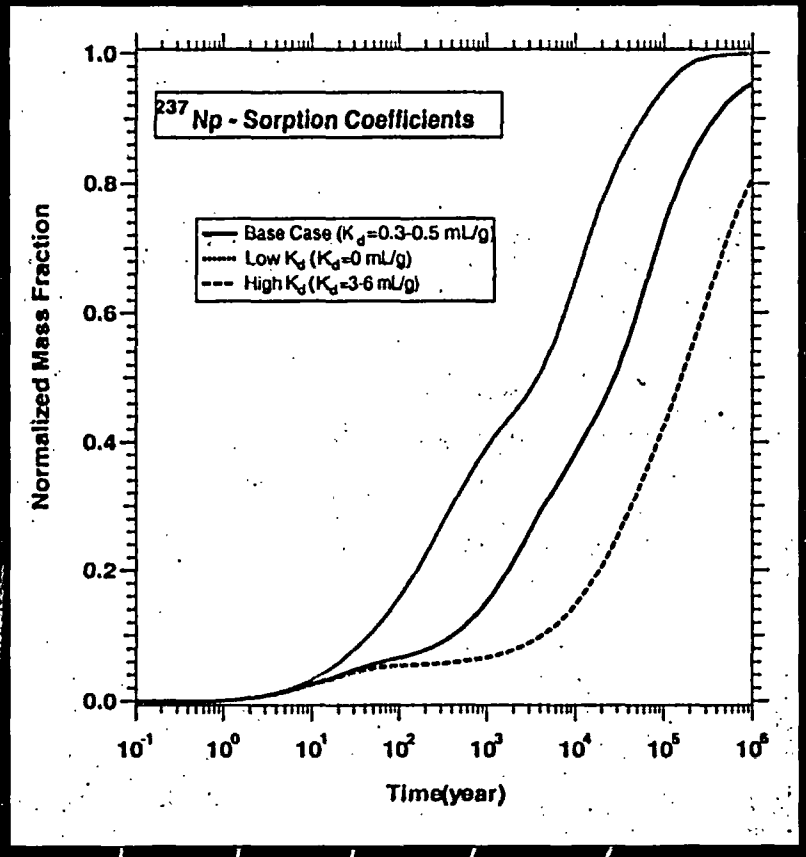

*Figure taken from G. Moridis (LBNL) presentation to the Nuclear Waste Technical Review Board. March 9-10, 2004, Las Vegas, NV. (http://www.nwtrb.gov/meetings/march%202004/moridis.pdf)

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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

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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)

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

Sorption Experiments: Results

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

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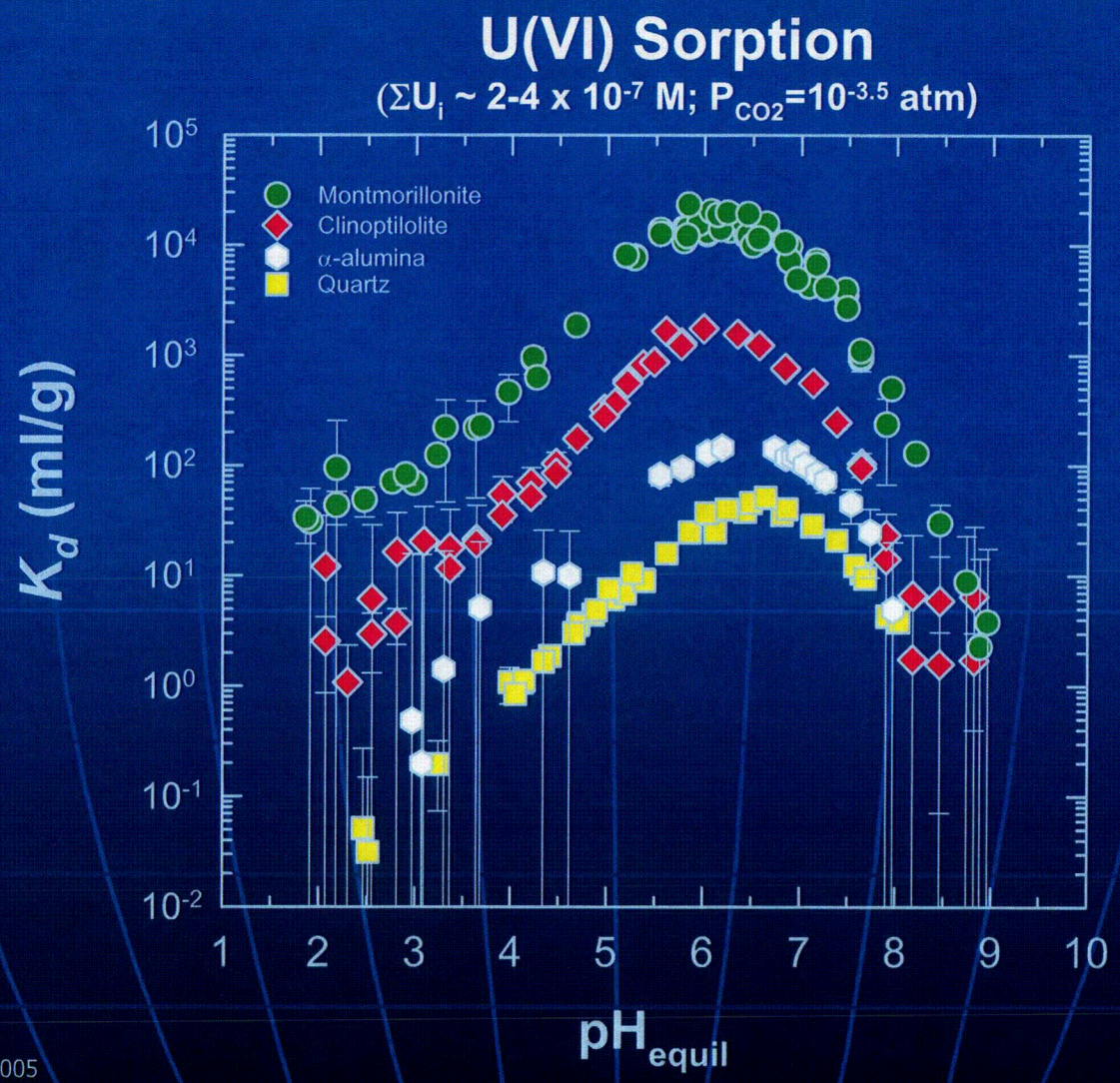
Effect of pH on U(VI) Sorption



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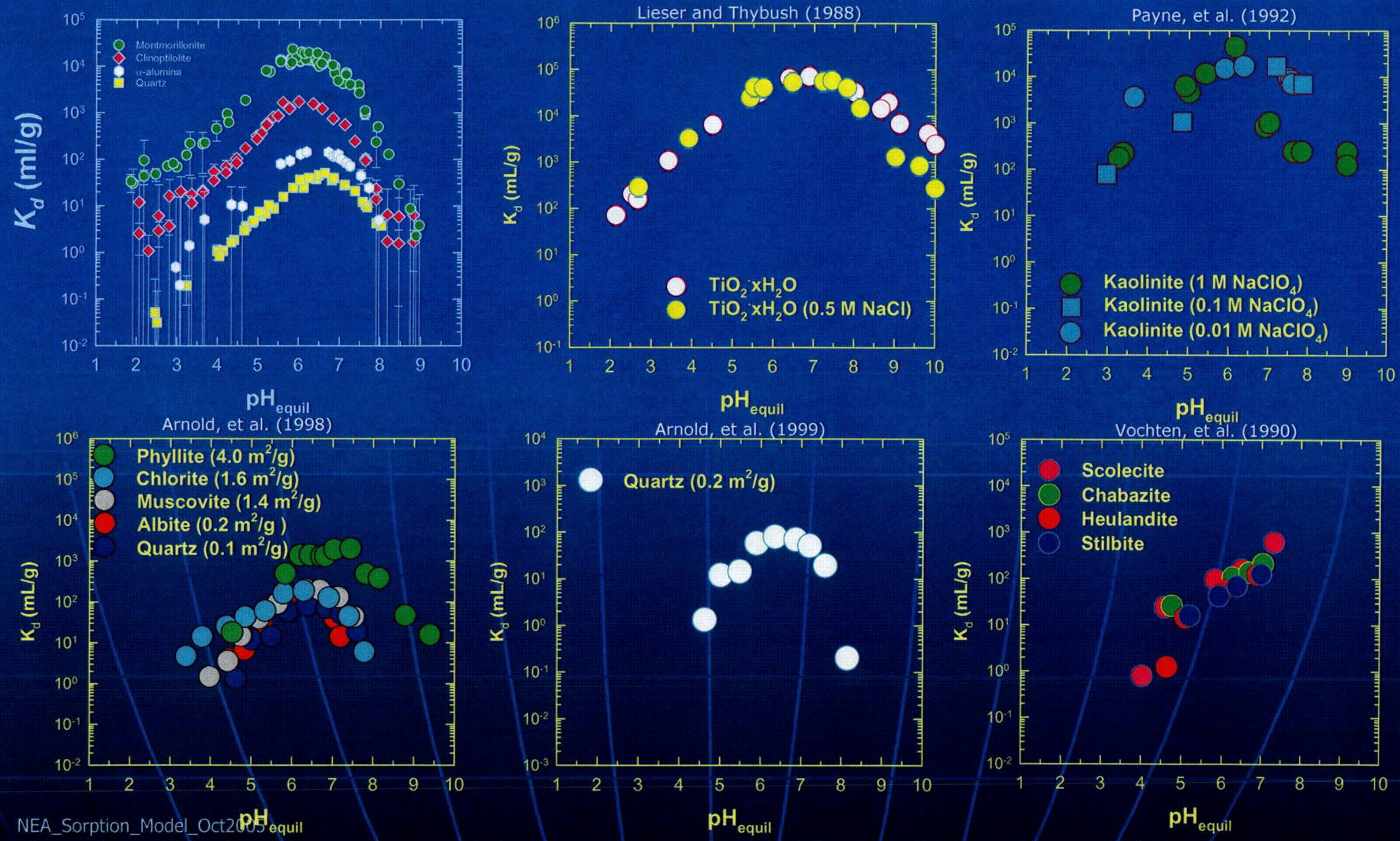
Effect of pH on U(VI) Sorption: Literature Data



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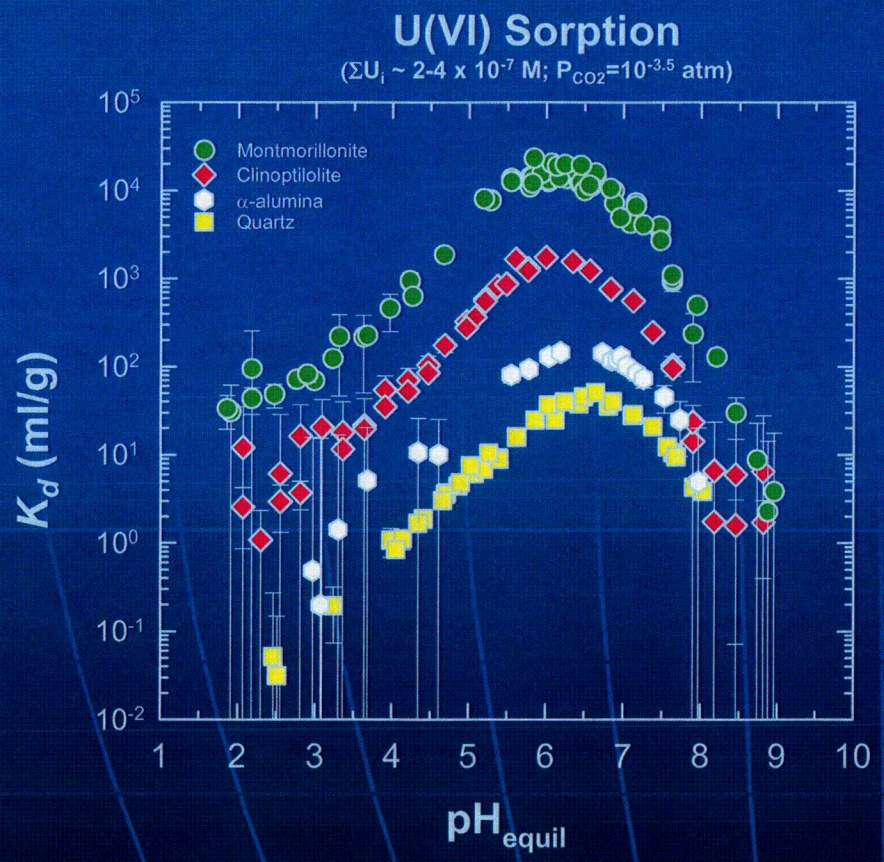
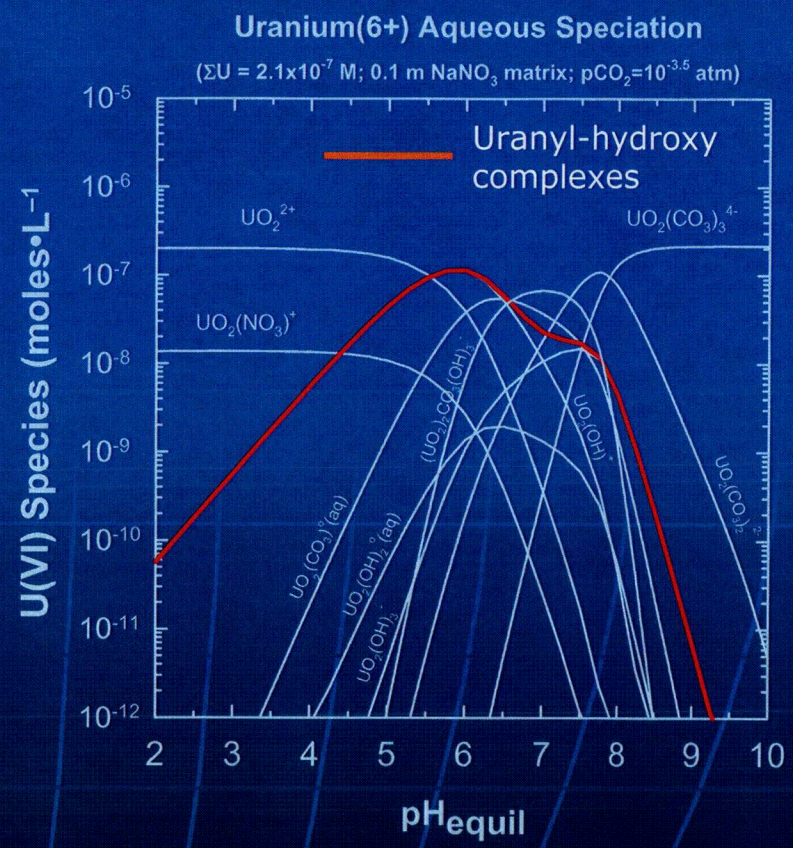
U(VI) Sorption and Aqueous Speciation





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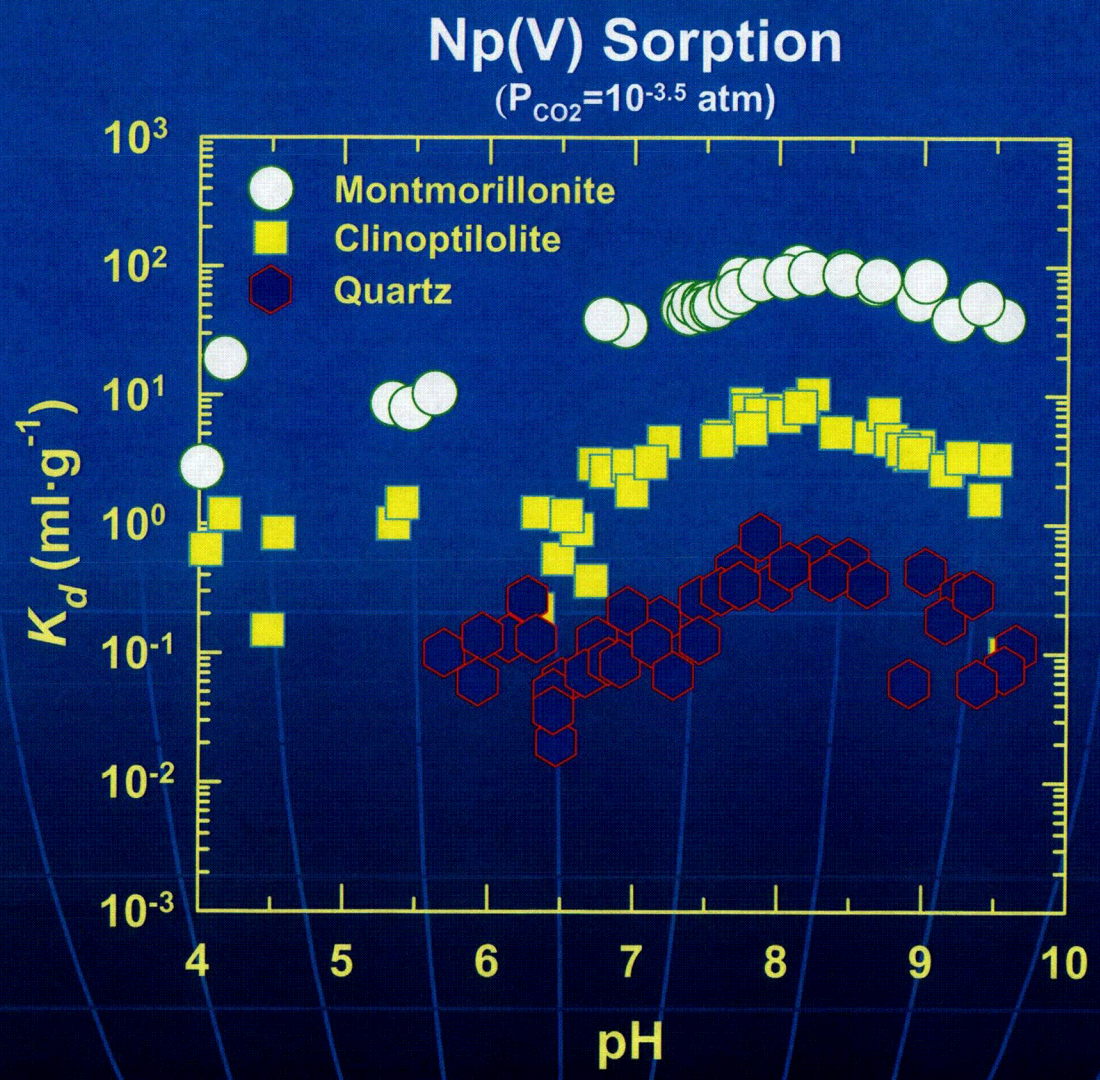
Effect of pH on Np(V) Sorption



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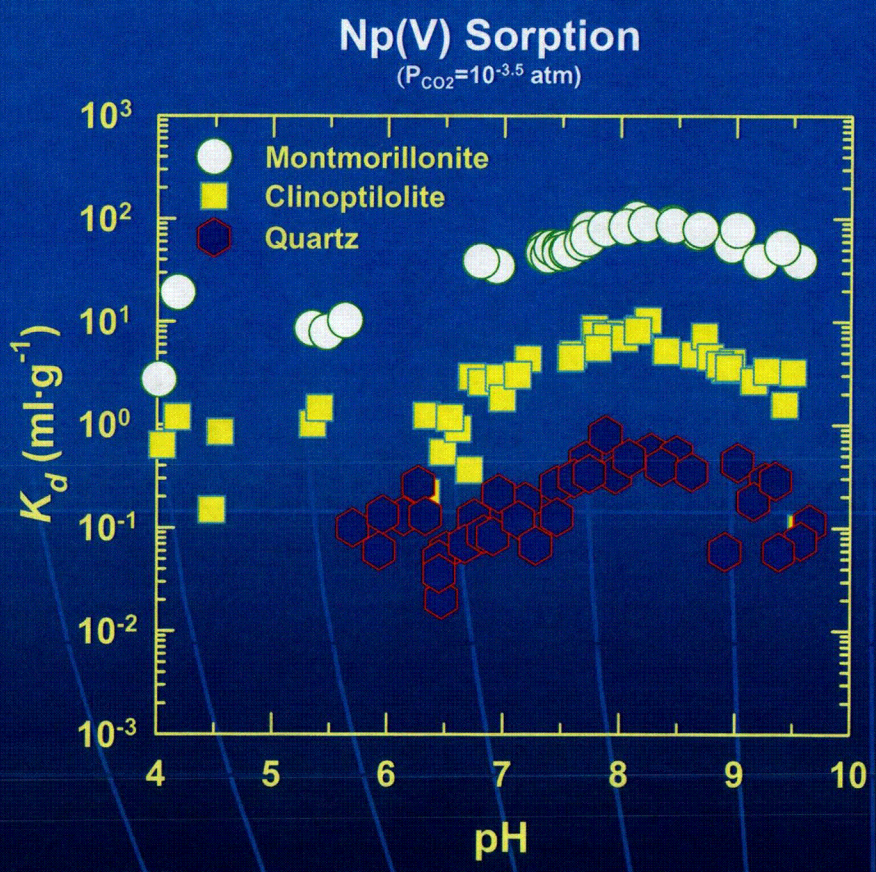
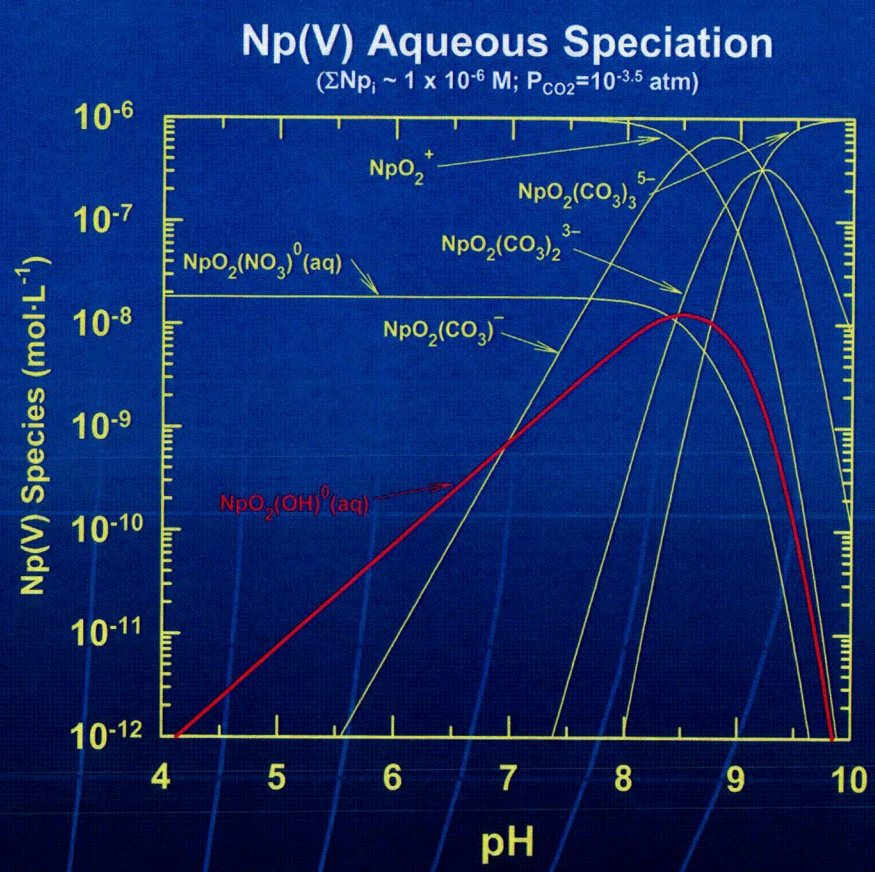
Np(V) Sorption and Aqueous Speciation





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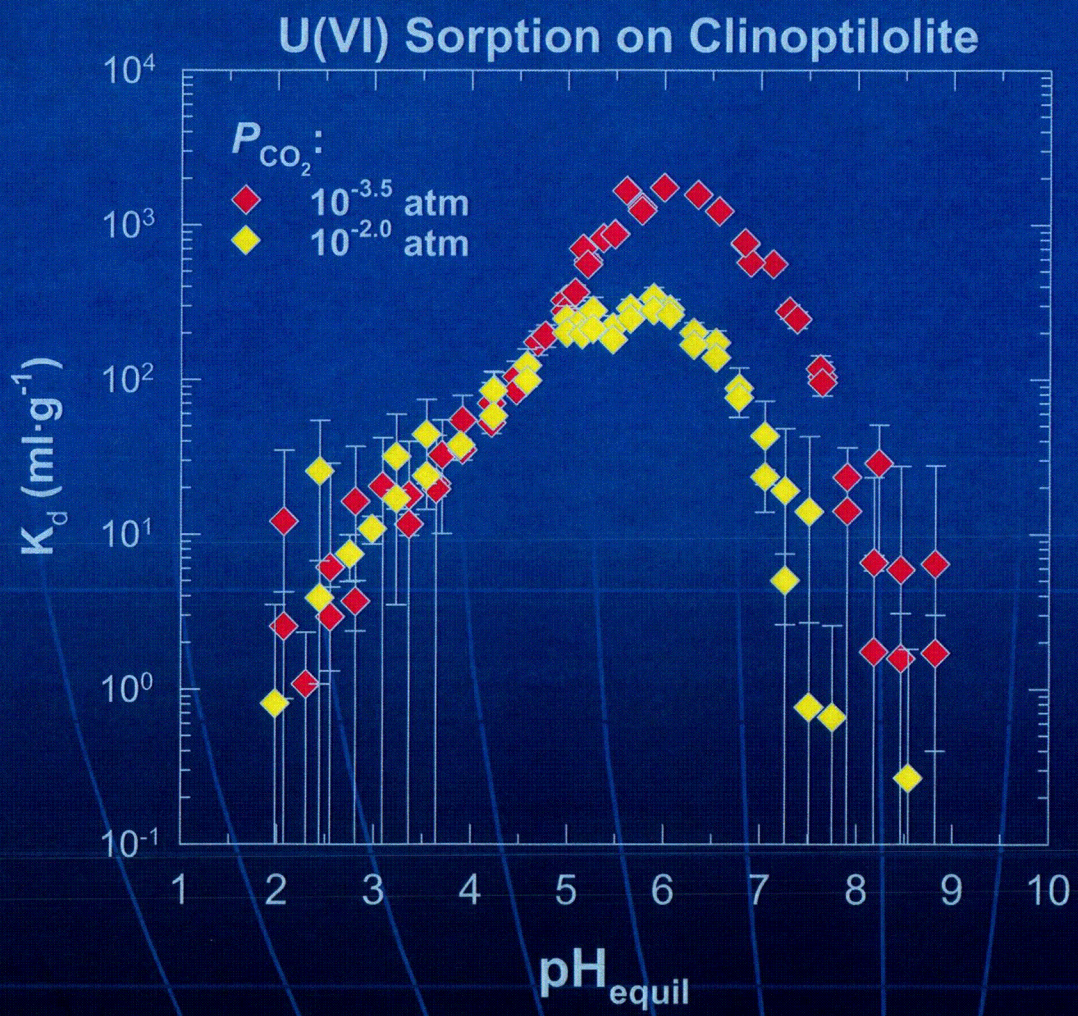
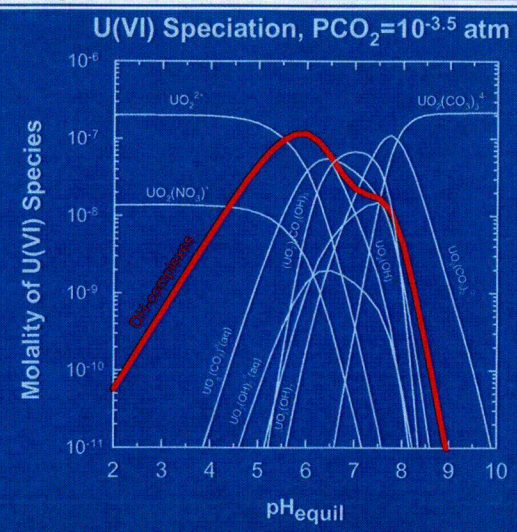
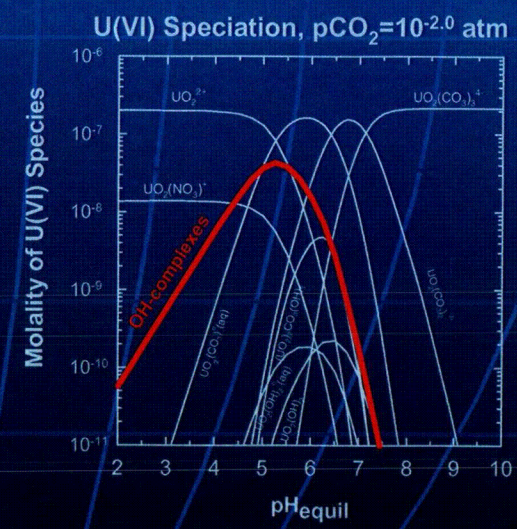
U(VI) Sorption: Effect of P_{CO2} (C_T)







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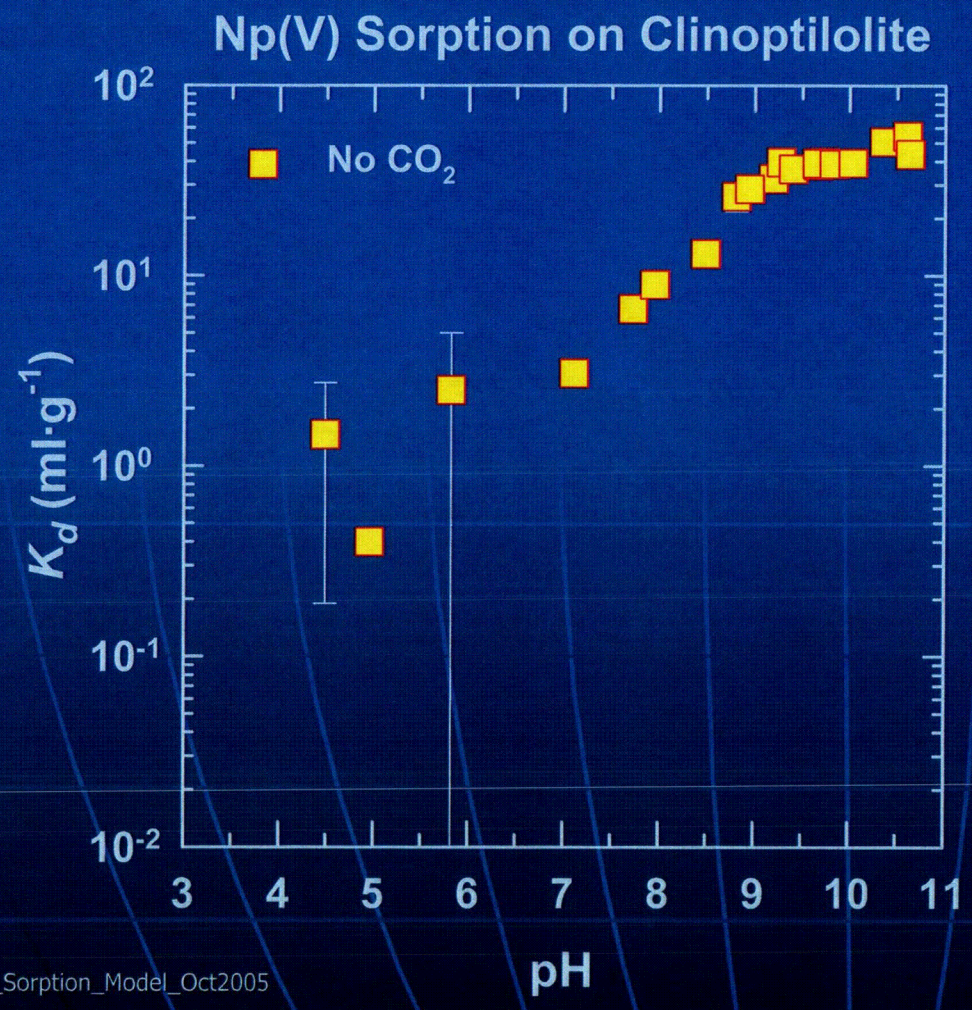
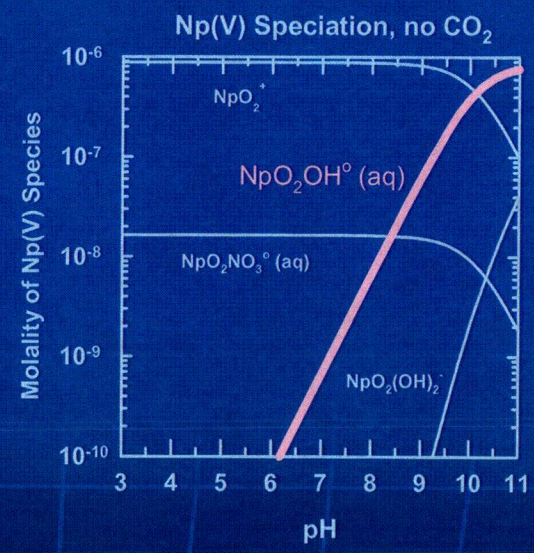
Np(V) Sorption: Effect of P_{CO2} (C_T)





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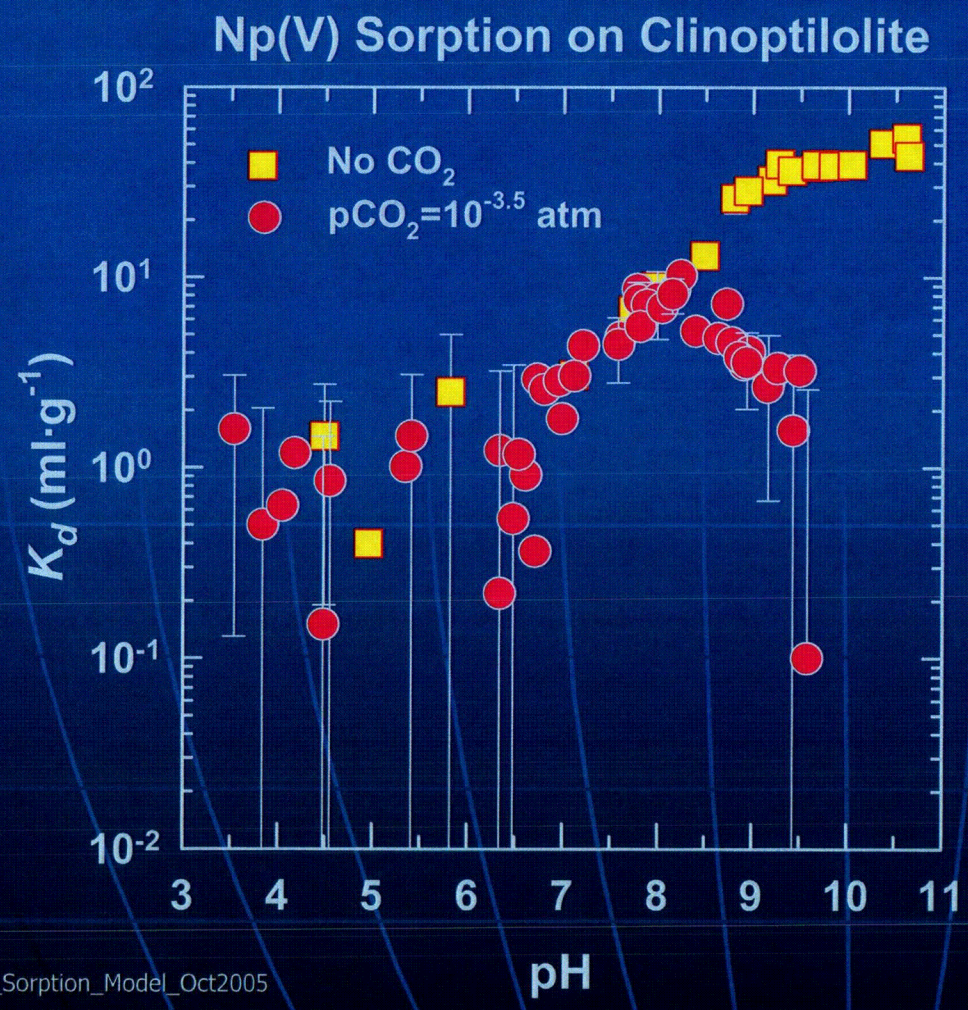

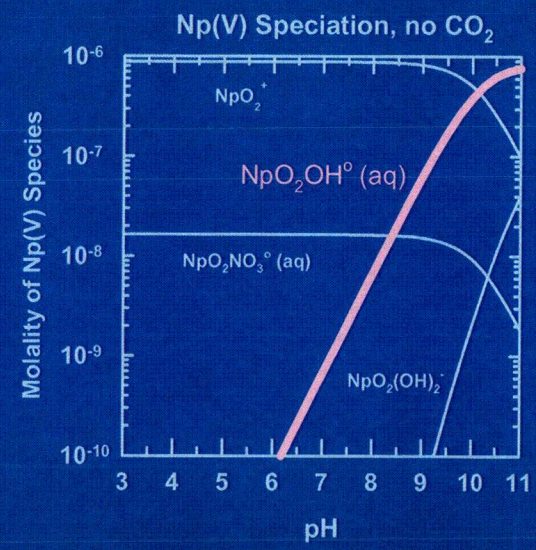

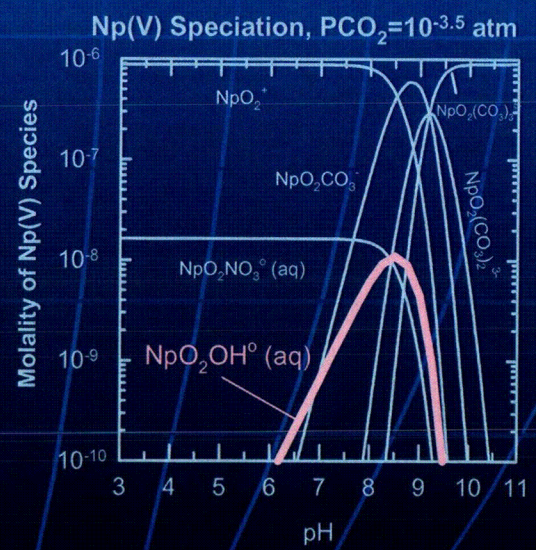

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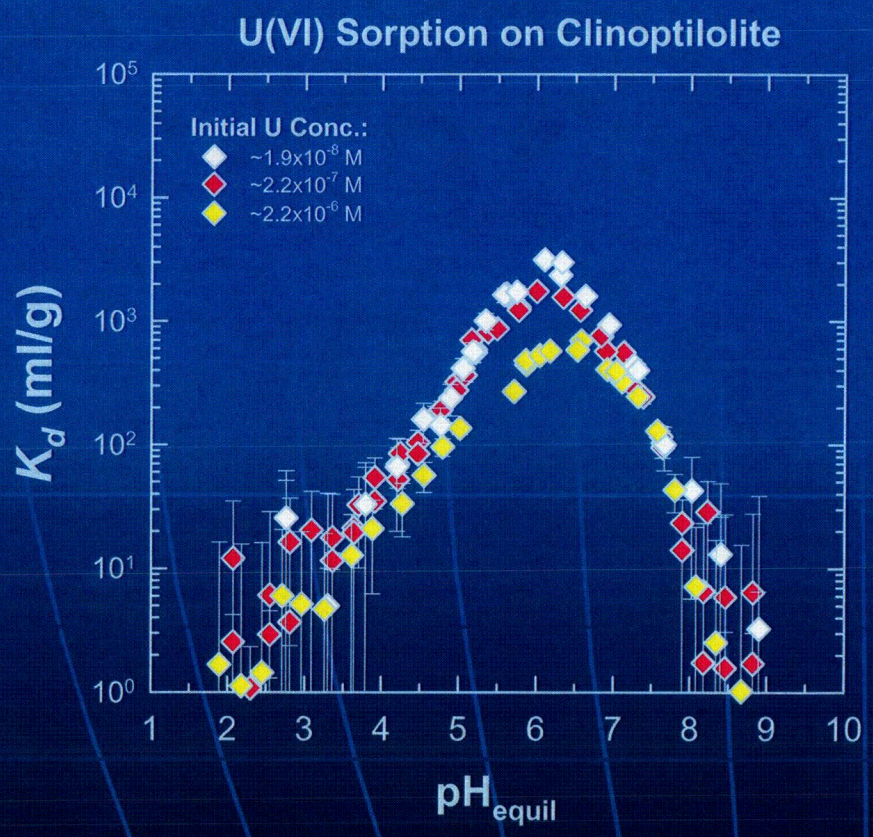
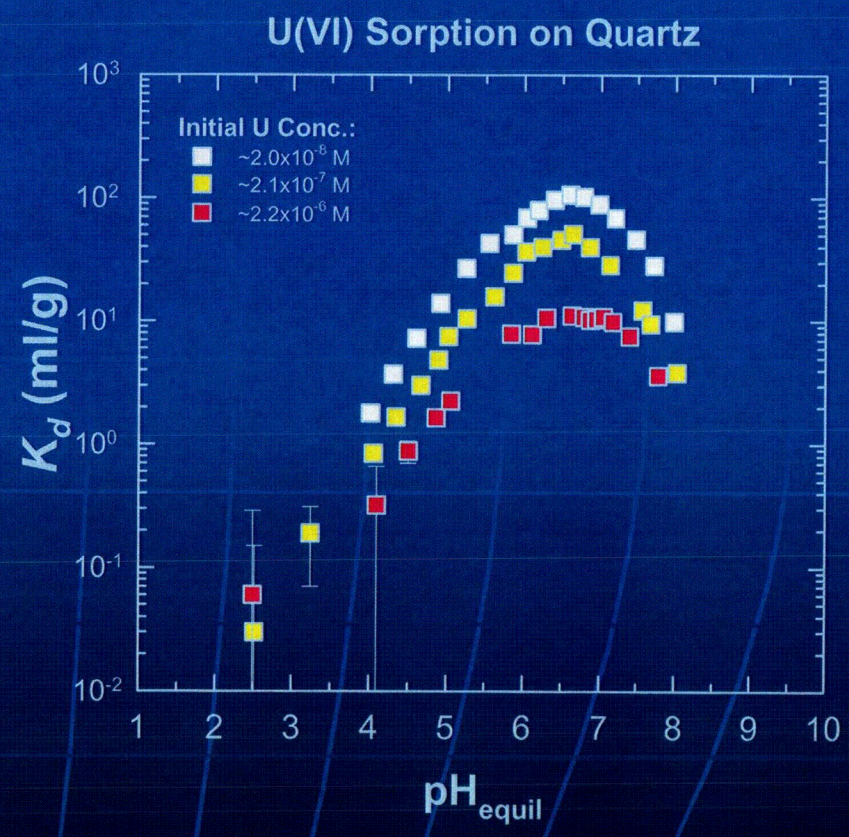
Effect of Sorbate Concentration





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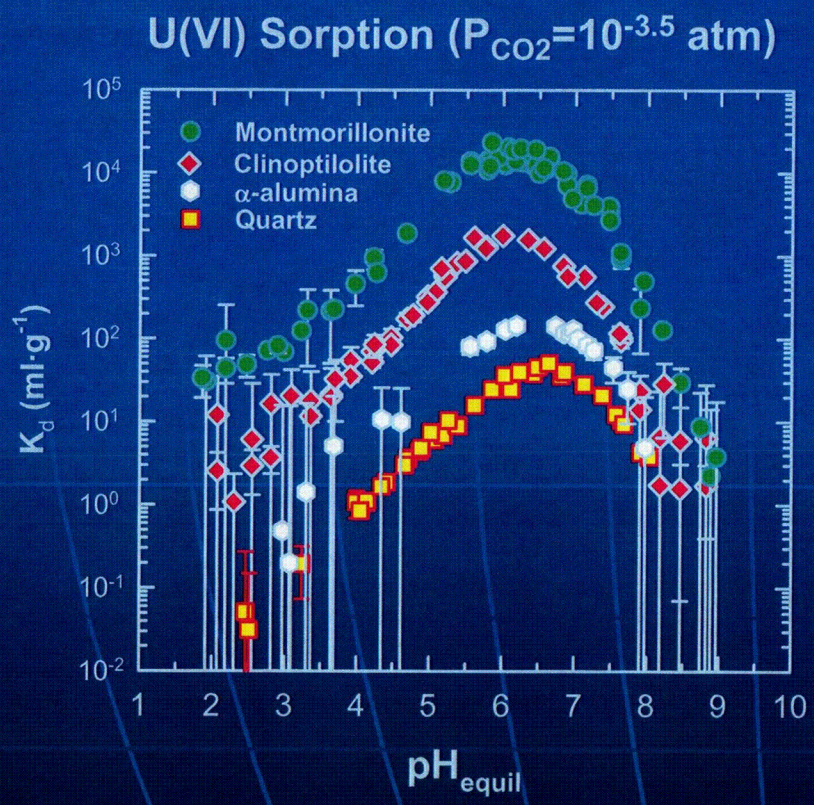
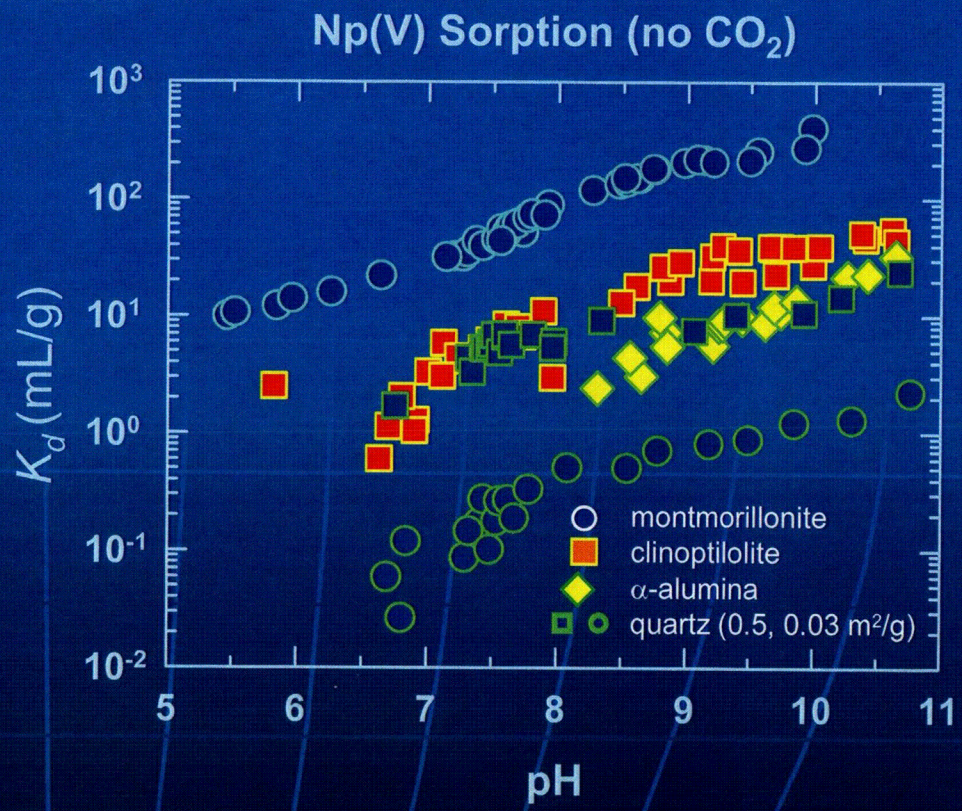
Effect of Surface Area: K_d (mL/g)

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





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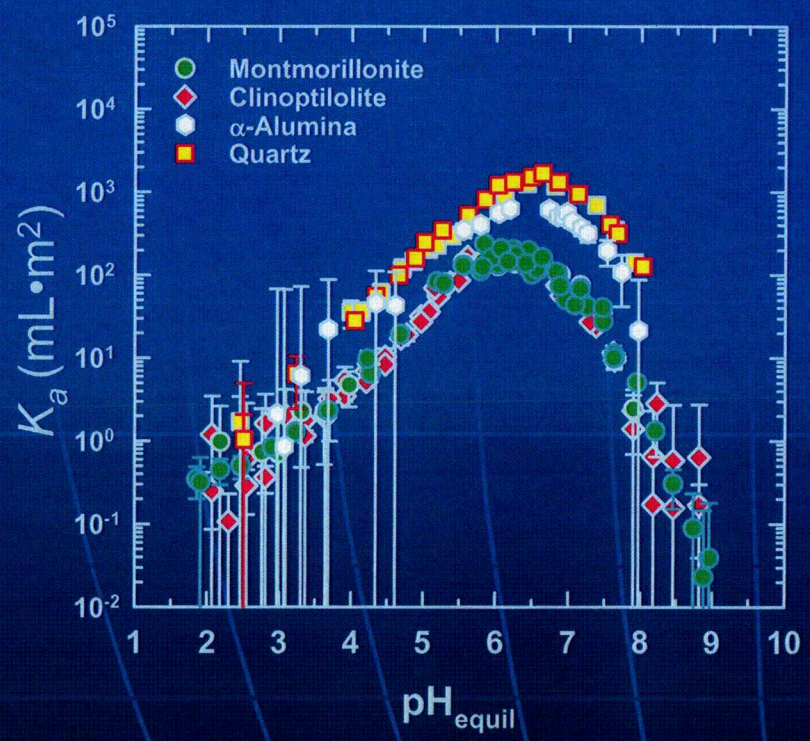
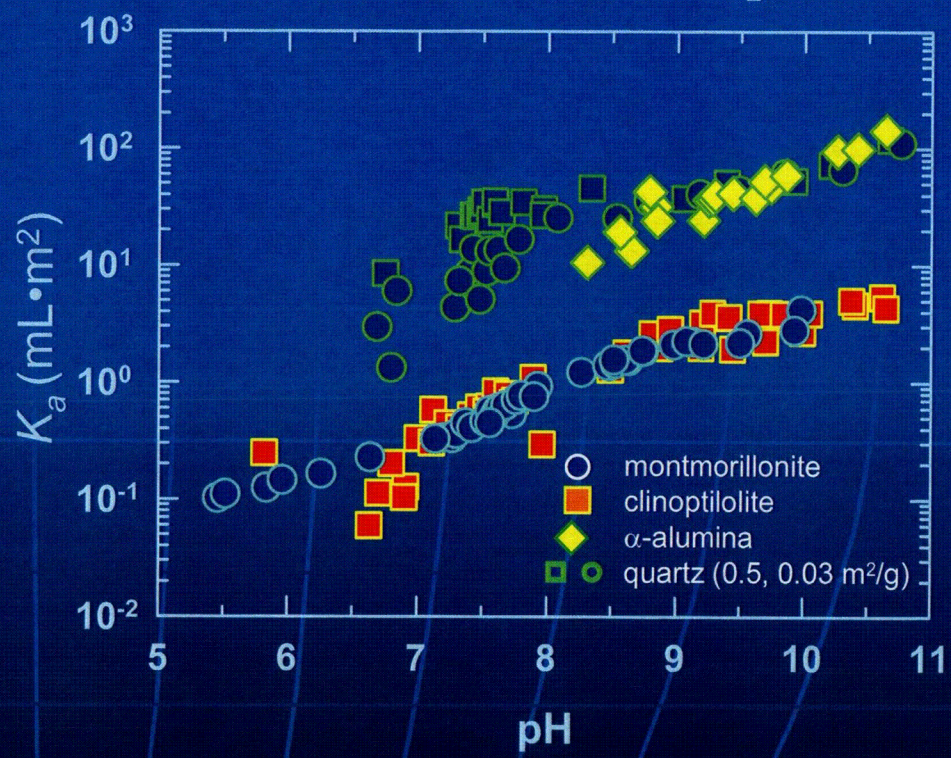
Effect of Surface Area (cont'd.)

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

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



Np(V) Sorption (no CO_2)



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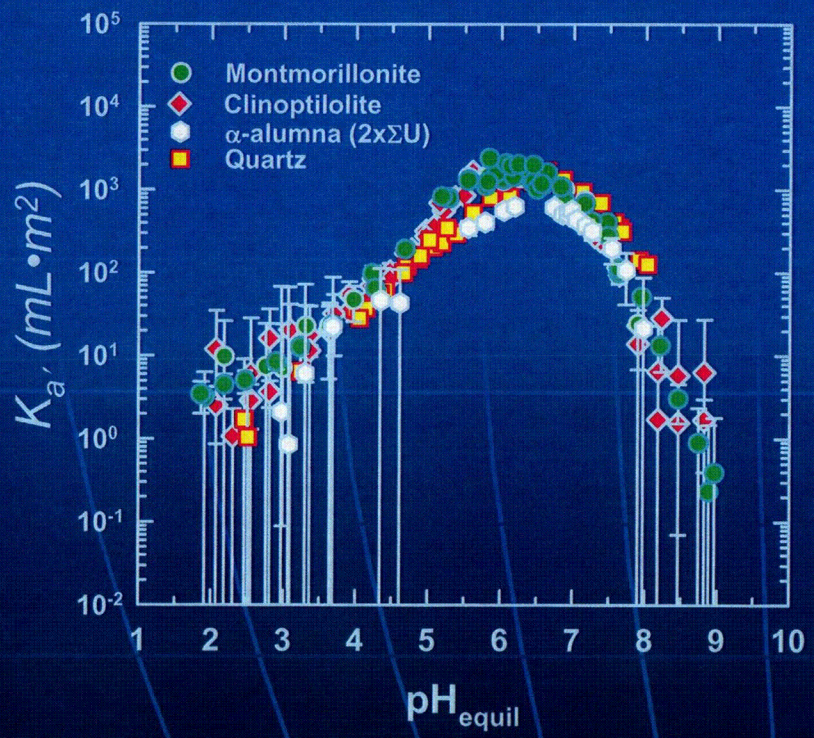
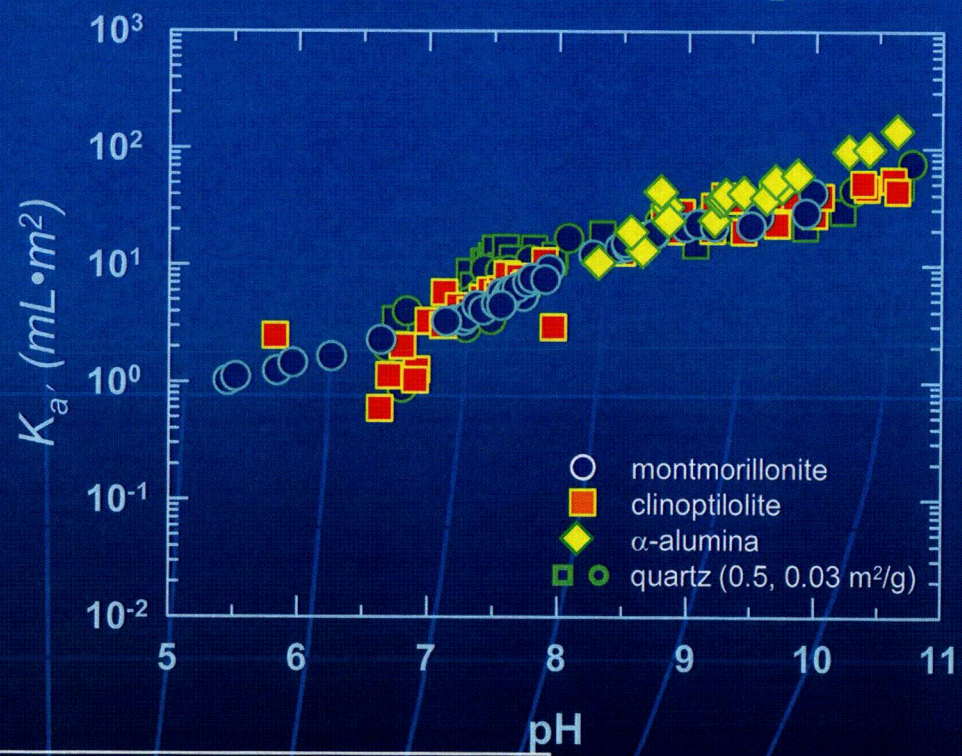
Effect of Surface Area (cont'd.)

$K_{a'}$ (mL/m^2) = K_d/SA_{eff}
(For clinop & mont, $SA_{eff} = 0.1 \times SA$)





∴ $K_{a'}$ 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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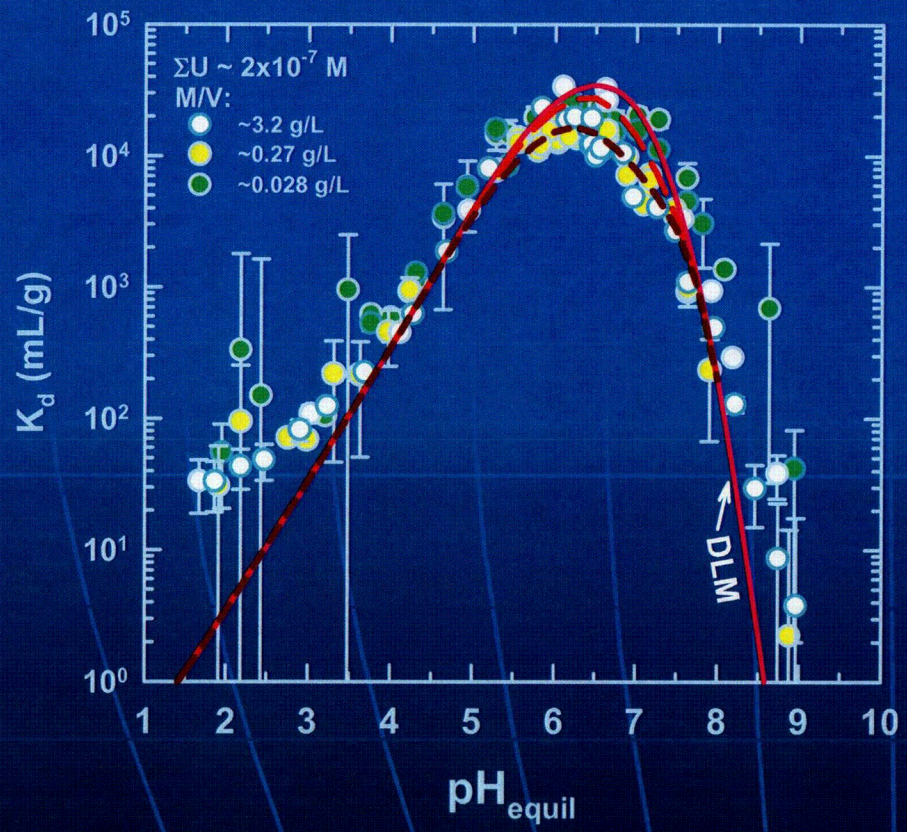
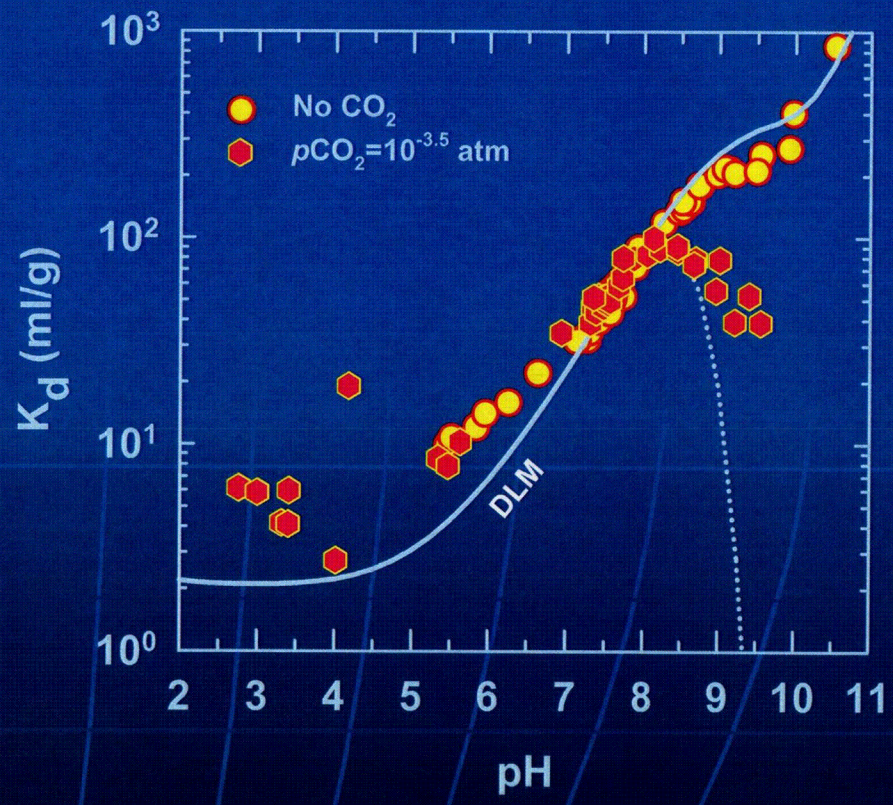
Surface Complexation Modeling: Calculated vs. Experimental Data

U(VI)-montmorillonite



Np(V)-montmorillonite



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

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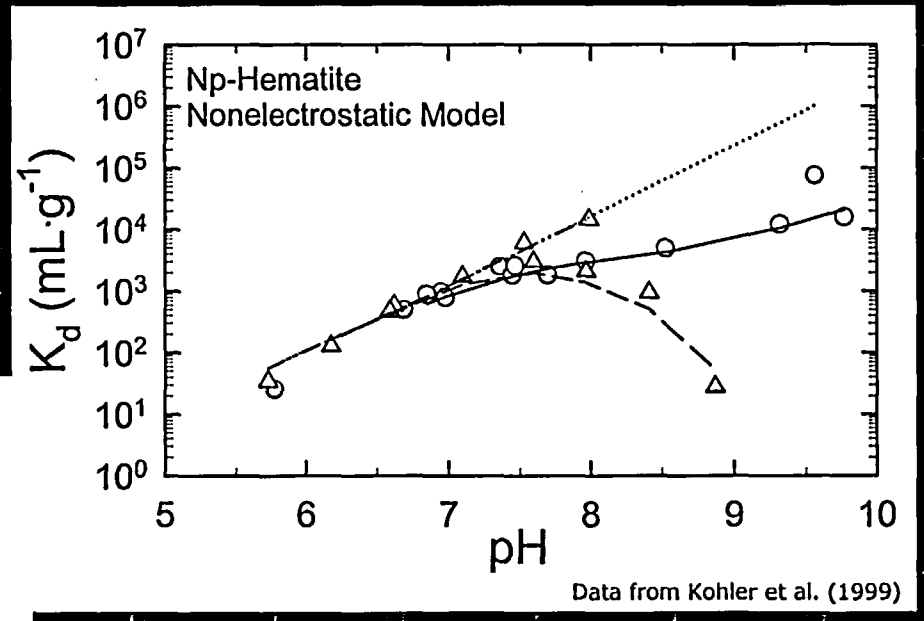
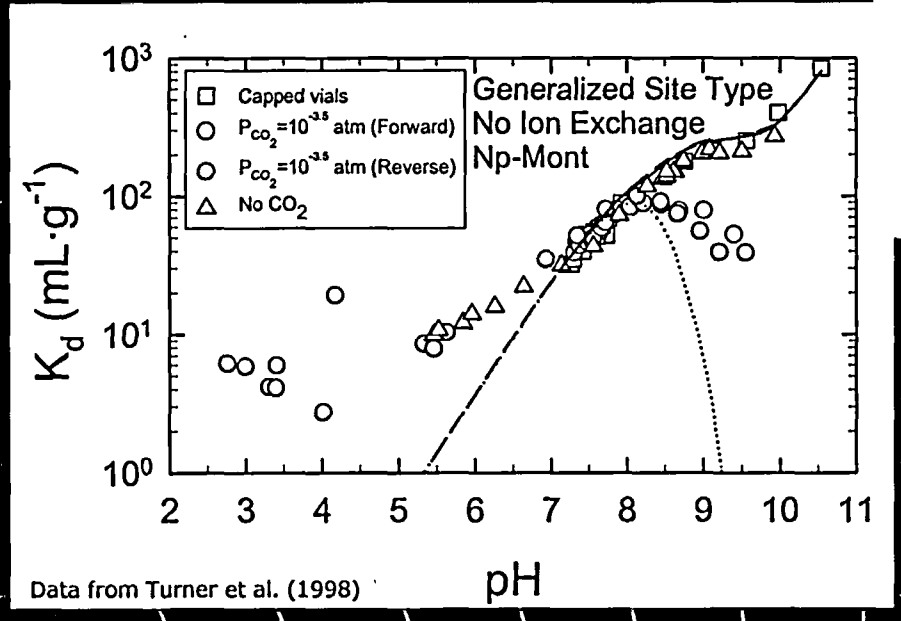
Potential Future Modeling Efforts

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





- 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

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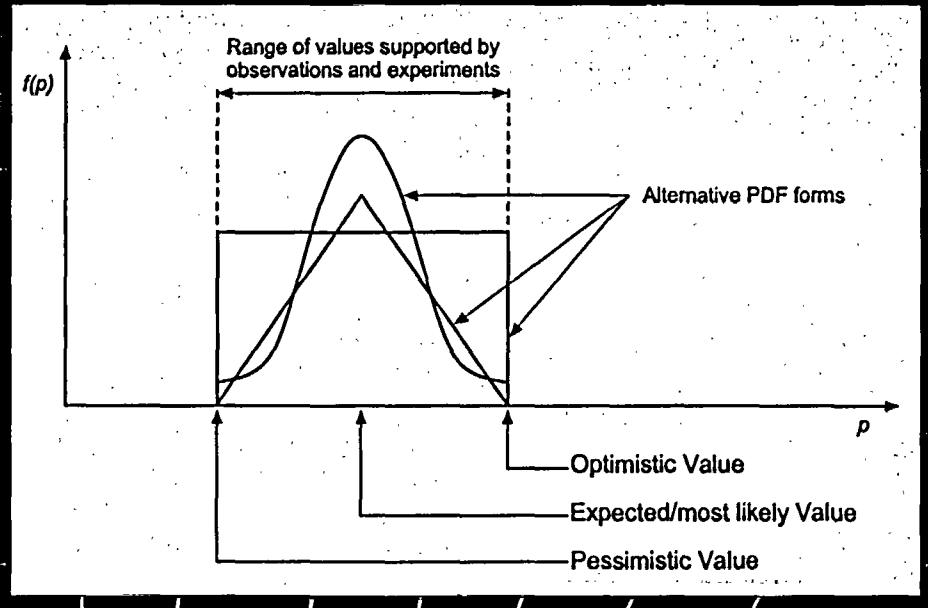
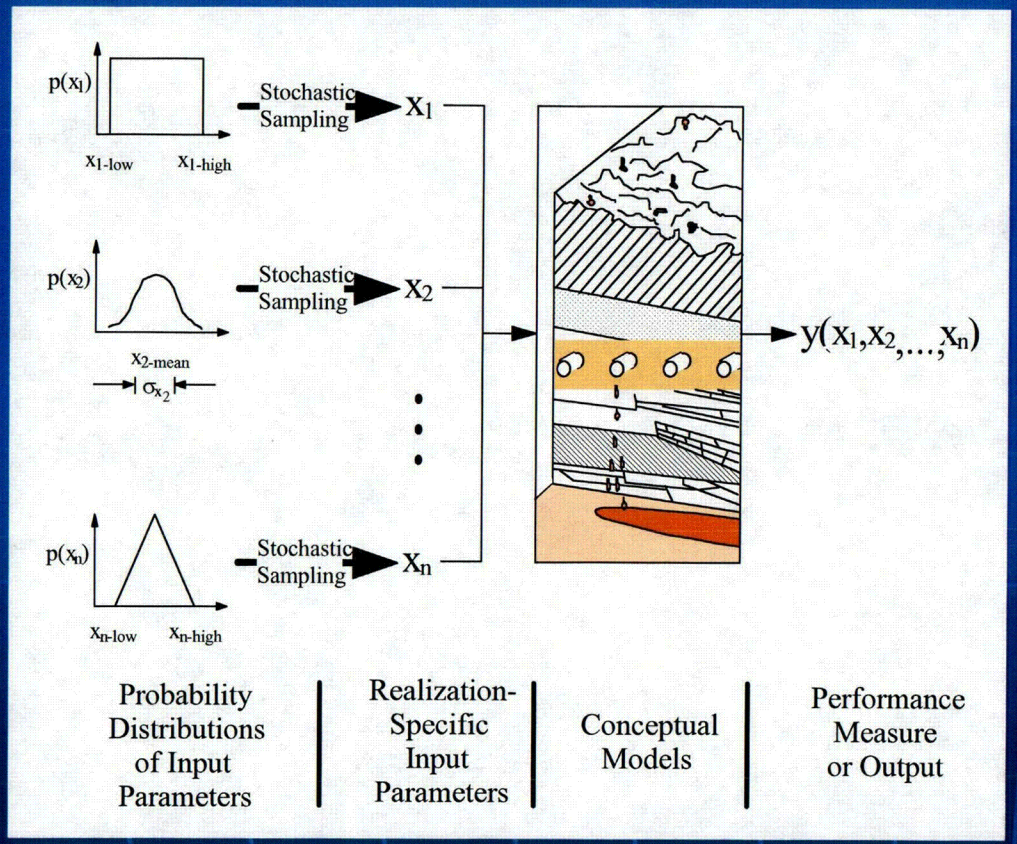
Abstraction of Radionuclide Sorption in TPA

- 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



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



NRC TPA Code

- Transport Modeled with K_d Approach $\mathbf{R_f = 1 + \frac{\rho_b}{\theta} K_d}$
  - 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

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

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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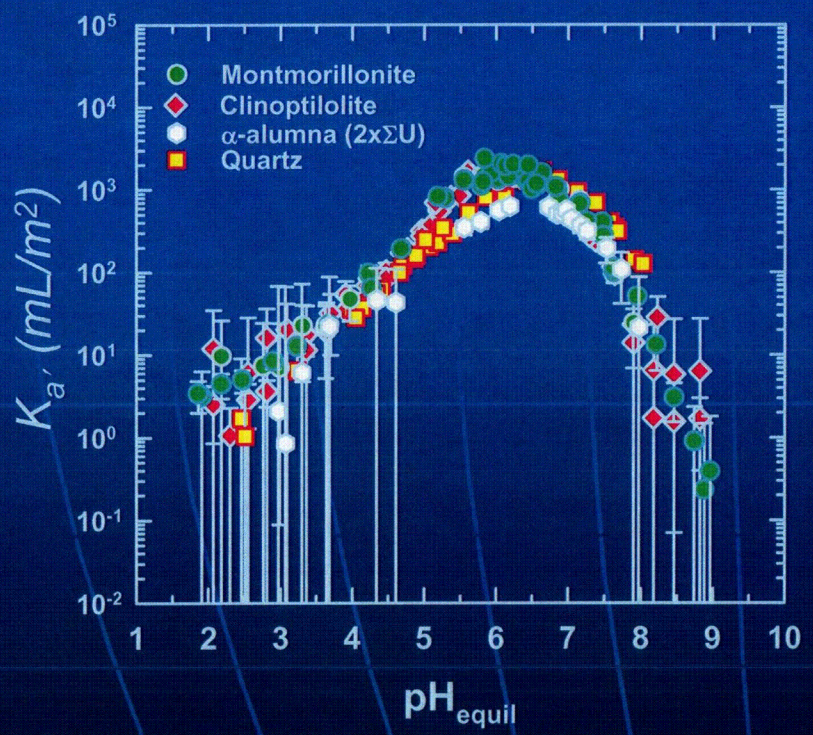
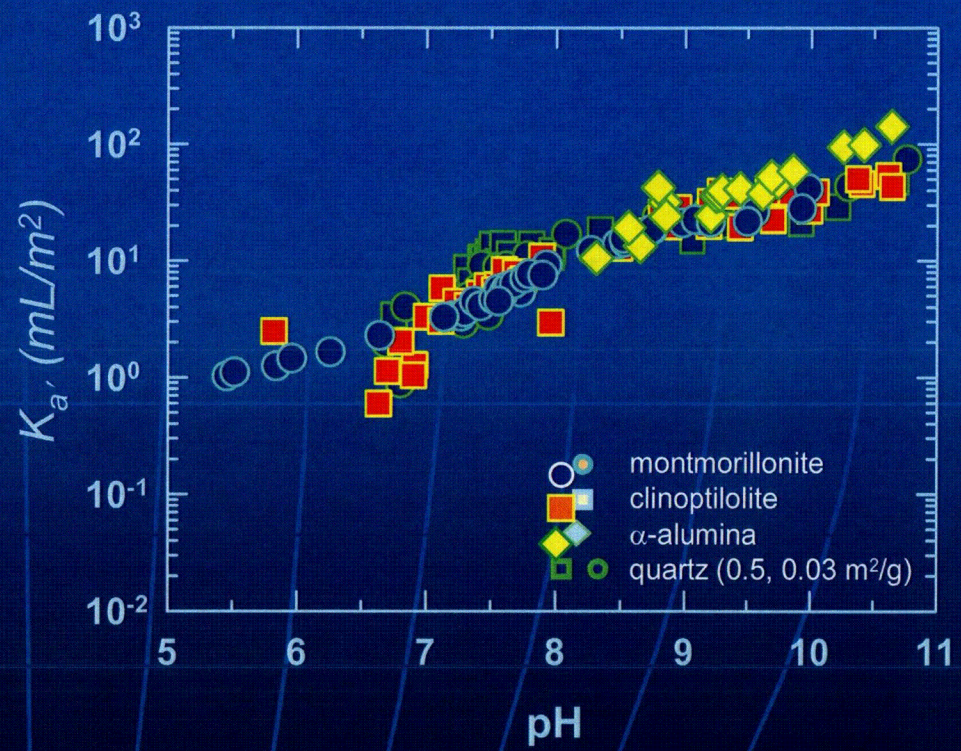
Effect of Surface Area

$K_{a'}$ (mL/m^2) = K_d/SA_{eff}
(For clinop & mont, $SA_{eff} = 0.1 \times SA$)

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)
- Np(V), U(VI)—Montmorillonite (CNWRA Data)
- Am(III), Pu(V), Th(IV)—α-Alumina (Literature Data)

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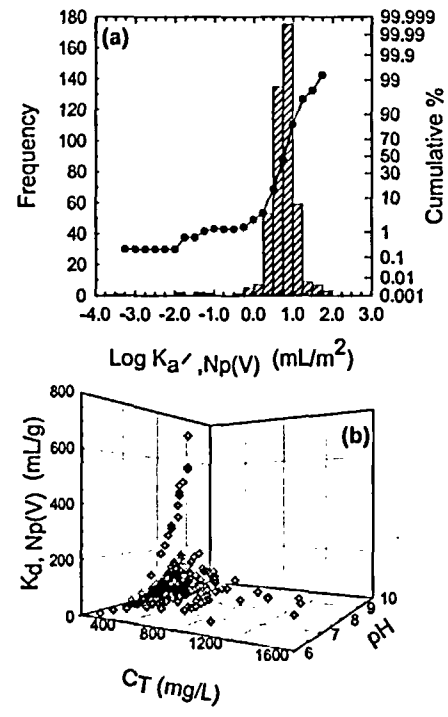
Process Model Abstraction for TPA: Refining K_d Parameter Distributions

- 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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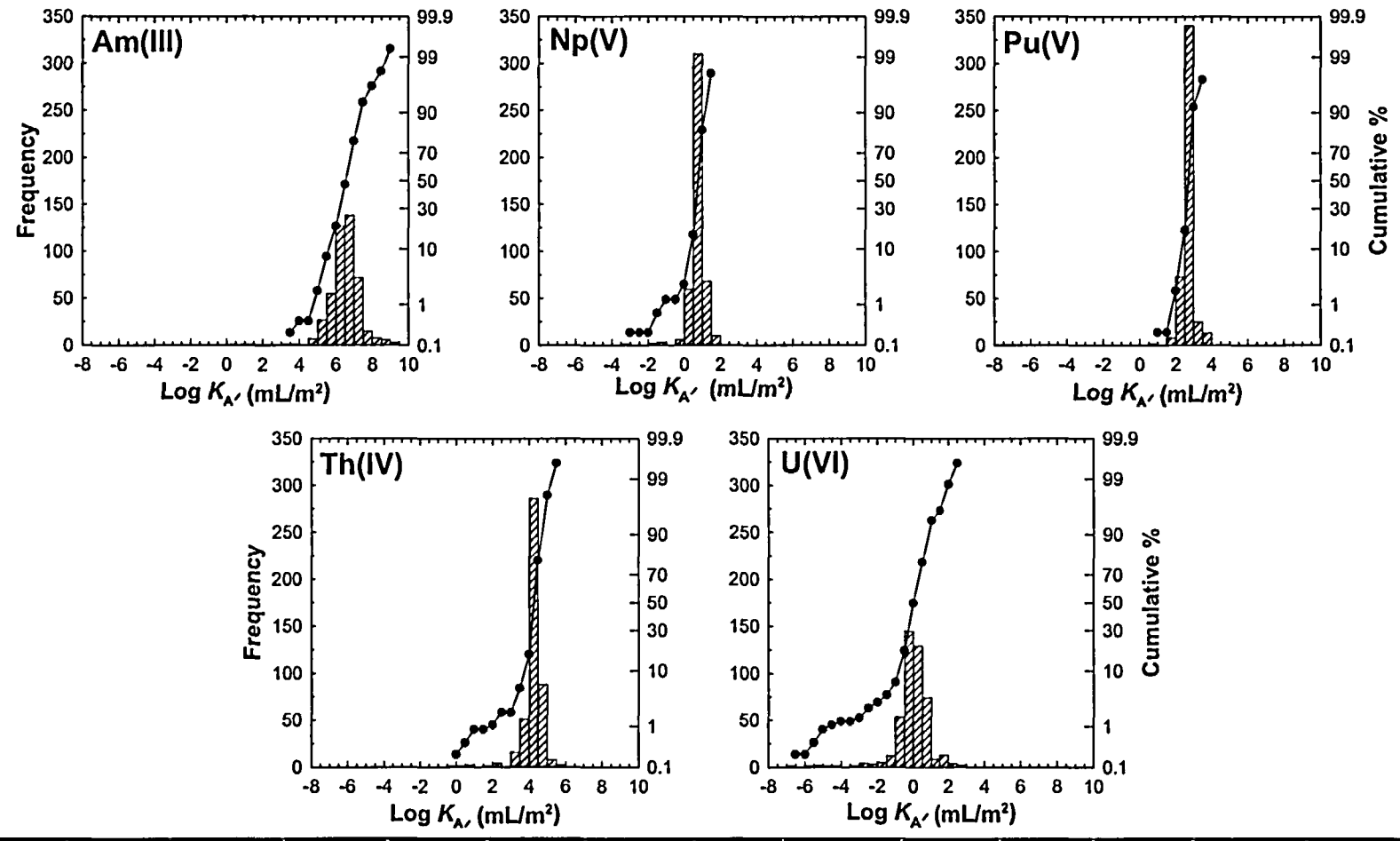
Process Model Abstraction for TPA: Actinide Sorption



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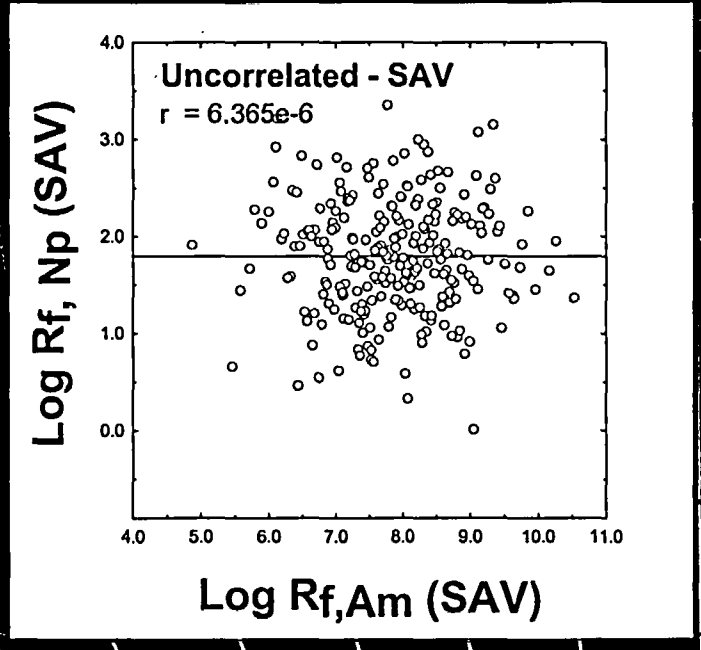
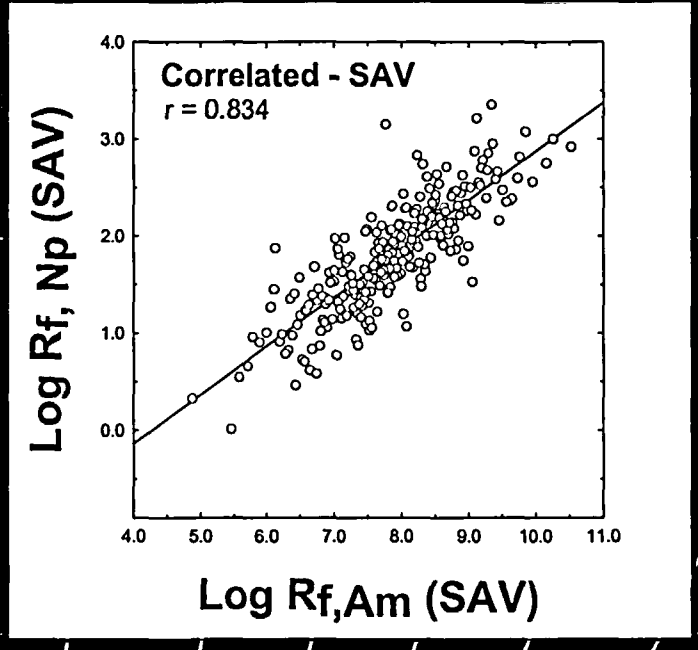
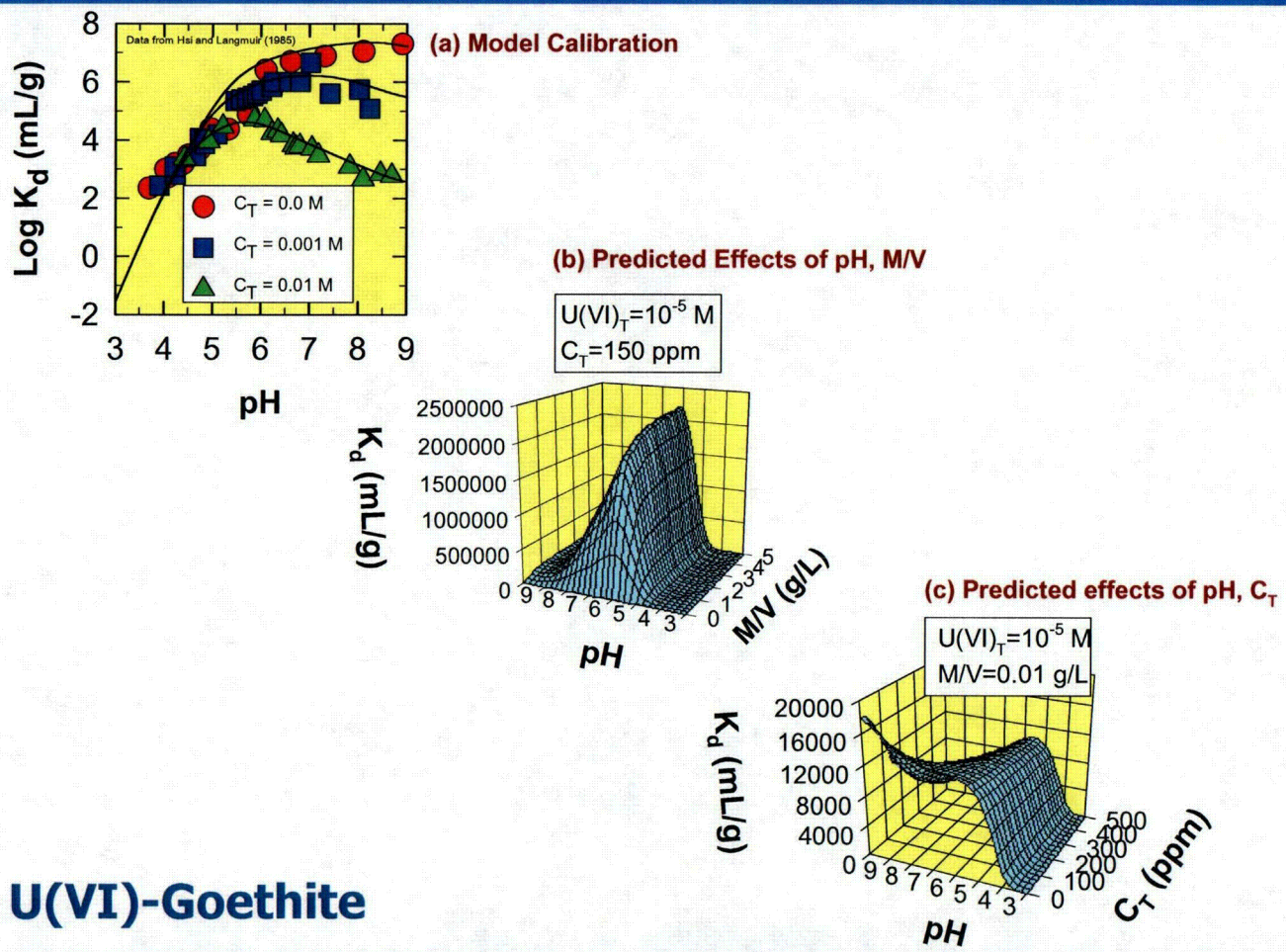
Process Model Abstraction for TPA: Actinide Sorption

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





Further Refinements: Developing Response Surfaces



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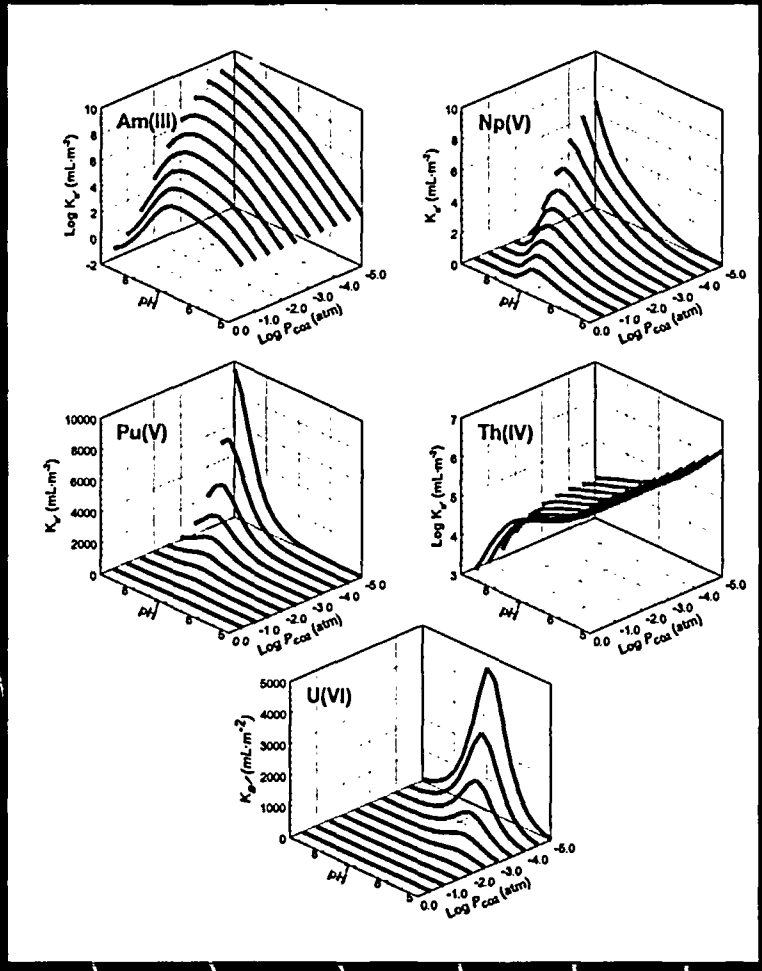
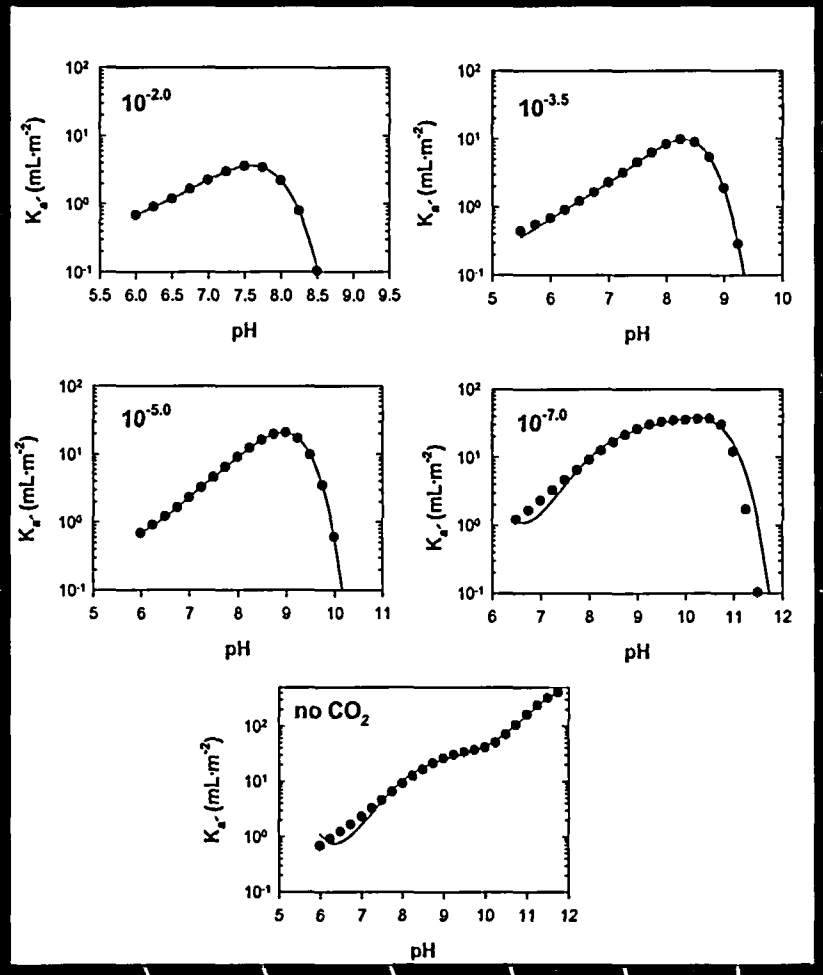
Further Refinements: Response Surfaces



- 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

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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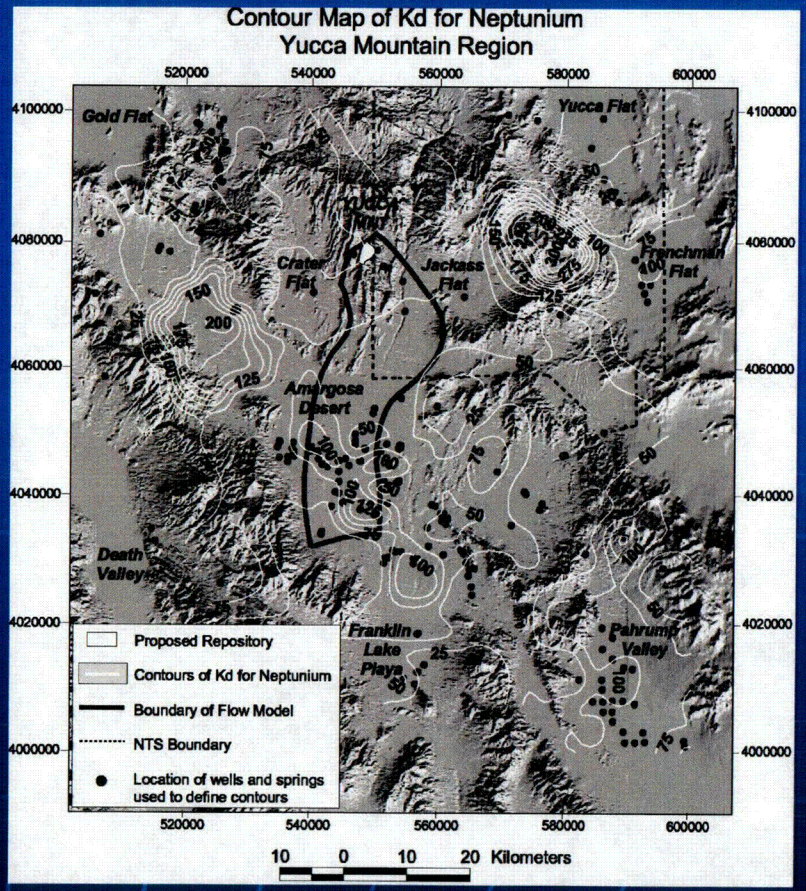
Process Model Abstraction for TPA: Effects of Geochemical Variability

- 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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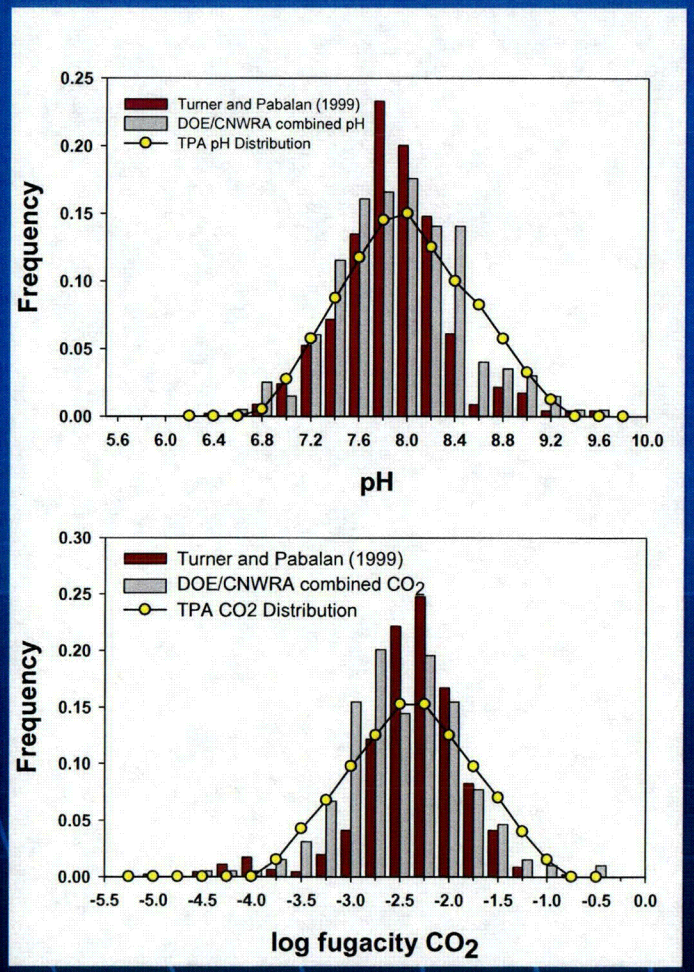
Refining Site-Specific Groundwater Chemistry Data



- 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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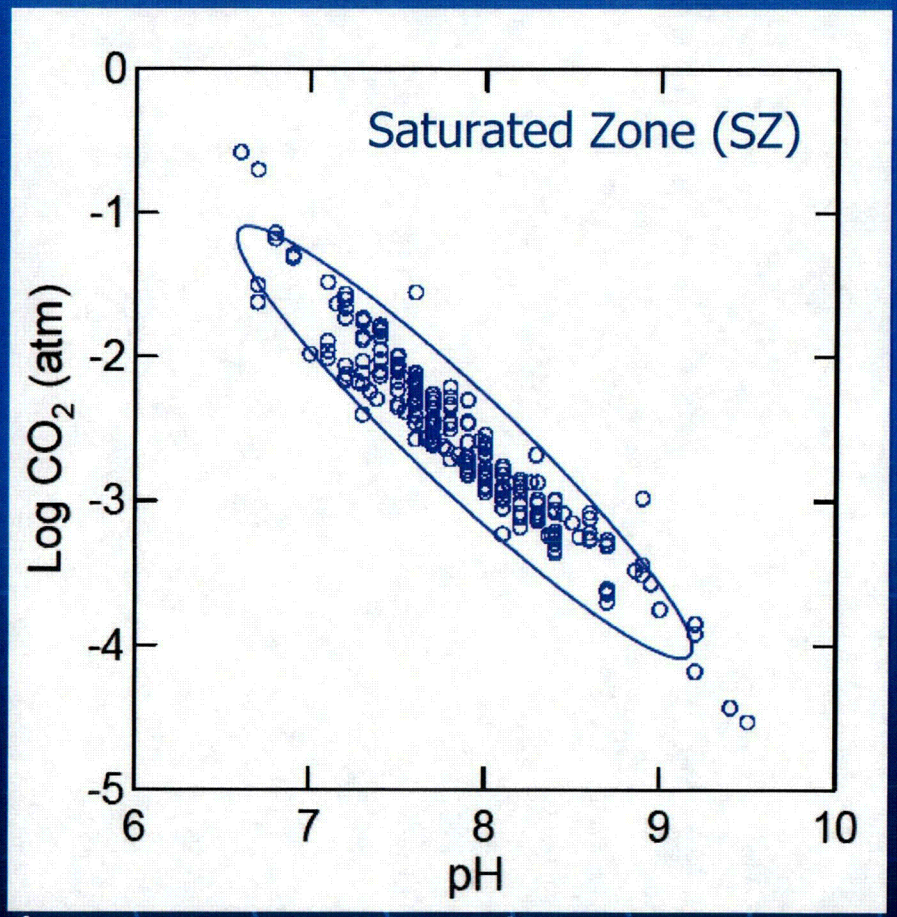
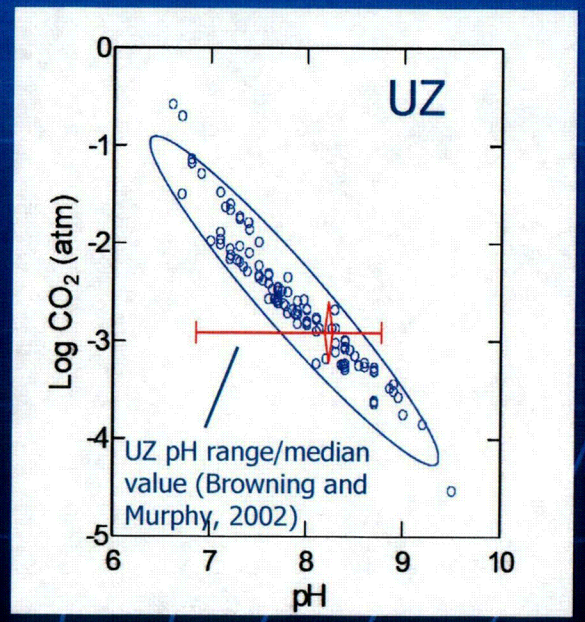
Correlating Key Geochemical Parameters



(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