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Sorption Characteristics of Radionuclides on Clays in Yucca Mountain Alluvium

Presented to:
2006 IHLRWM

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April 30-May 4, 2006, Los Vegas, Nevada

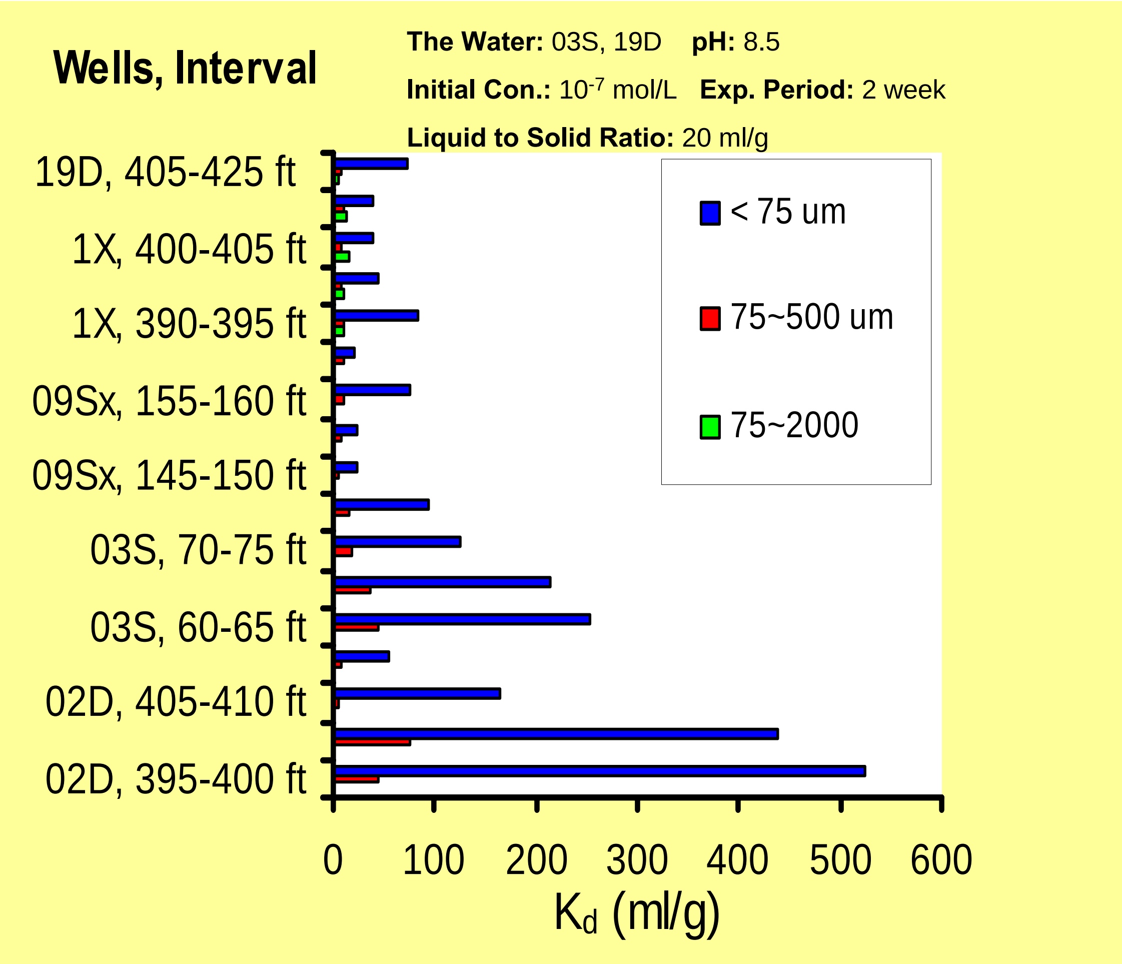
This presentation has been funded in whole or in part by the U.S. Department of Energy

Goal

- Evaluate the capability of the Yucca Mountain tuffs and alluvium as natural barriers to radionuclides by determining the apparent distribution coefficient K_d (ml/g) under conditions relevant to the field.
- Explore chemical reaction mechanisms between geomedia and these radionuclides.
- Provide the data and models necessary to allow the Department of Energy (DOE) to take additional credit for the retardation of sorbing radionuclides in UZ and SZ in Yucca Mountain repository performance assessments.

Small Particles Have Larger K_d Values

Distribution coefficient of $^{237}Np(V)$ as a function of depth interval and particle size fraction in alluvium from various wells



Questions

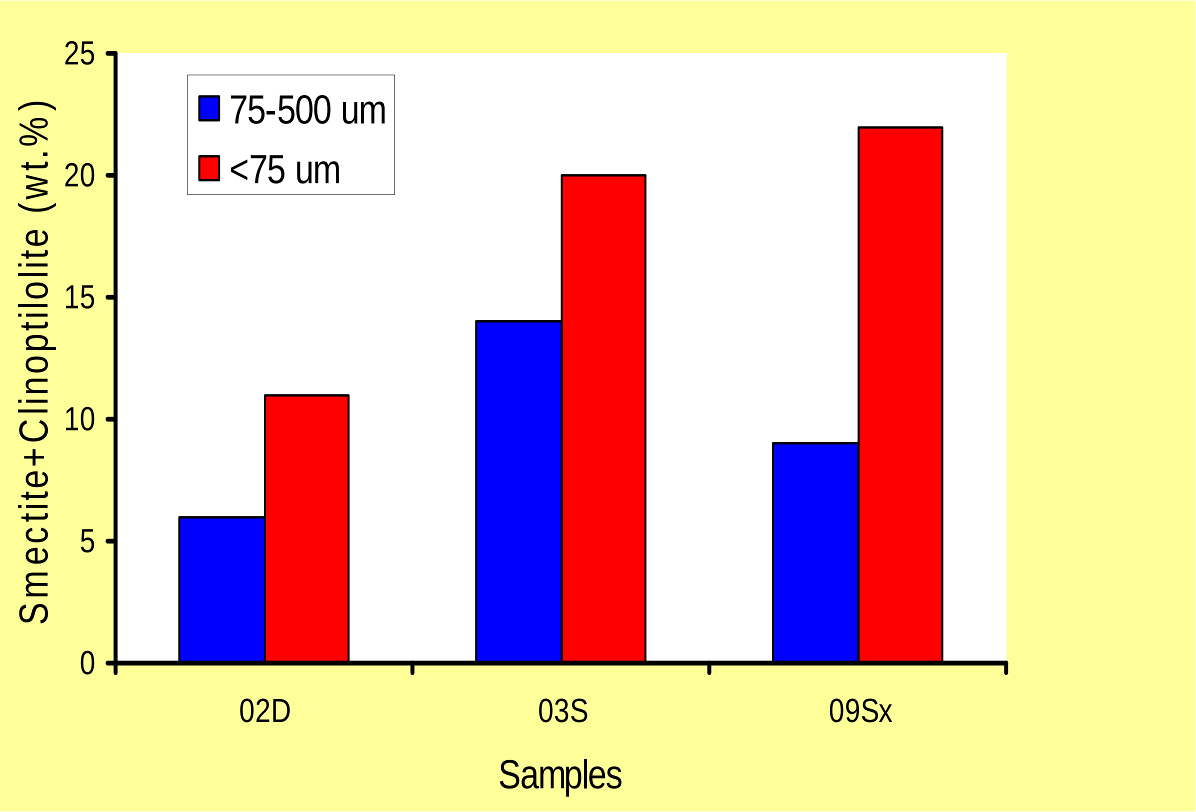
1. Do smaller particles differ mineralogically from larger ones?

2. Is the larger K_d value merely due to larger surface area of smaller particle?

1. M.Ding, et al., 2003 IHLRWM proceedings, Las Vagas NV.

2. YMP DTN: LA0401MD831341.001

Smaller particle has larger combined smectite + clinoptilolite content



YMP DTN: LA0401MD831322.003

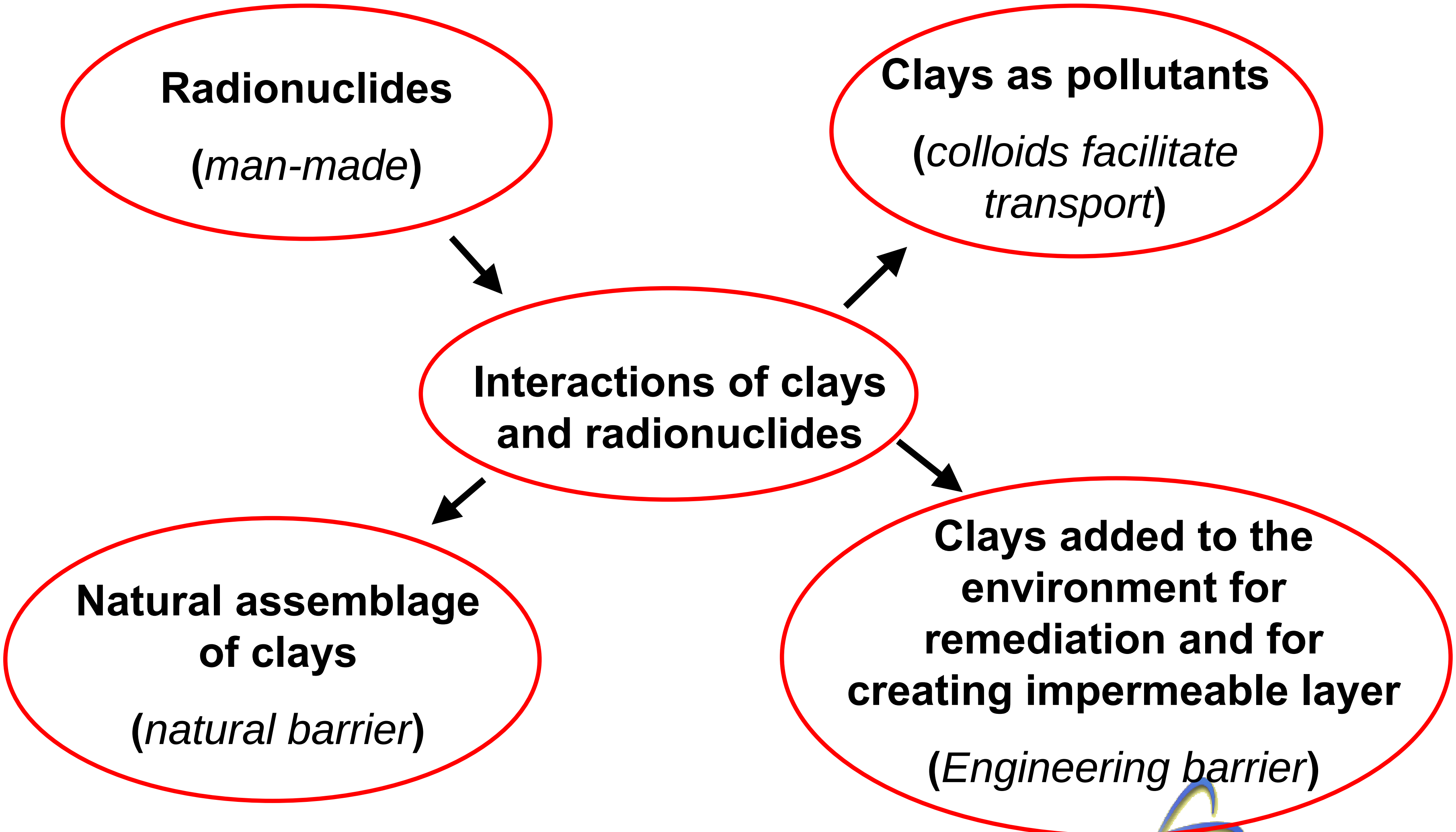
Questions Cont.

3. Which mineral is dominating?

Specific Objective

- **Characterize the adsorption of U and Np onto clay minerals in the alluvium south of Yucca Mountain**
- **Provide Yucca Mountain with a sound technical bases for a more realistic predictions of adsorbing radionuclides transport rates in the SZ and UZ.**

Why Clays: The role of clays in radionuclides transport in environment



Approach

Step 1

Separation of clays from the parenting geological material, e.g., Yucca Mountain alluvium → *Settling –velocity method*

Step 2

Characterization of the clays → *PMS, QXRD, BET*

Step 3

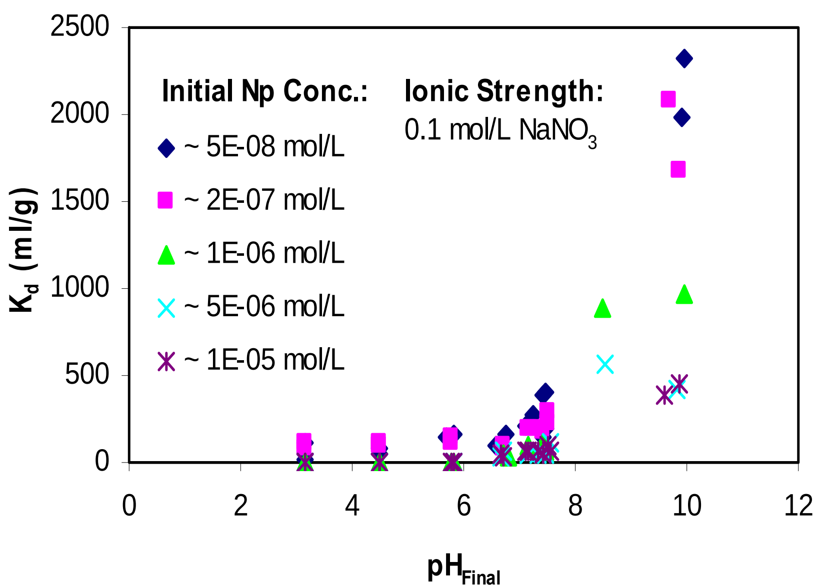
Sorption of ^{233}Uranium(VI) and ^{237}Neptunium(V) on the clays → ***$K_{d,}$ as function of pH, Actinides Conc.***

Step 4

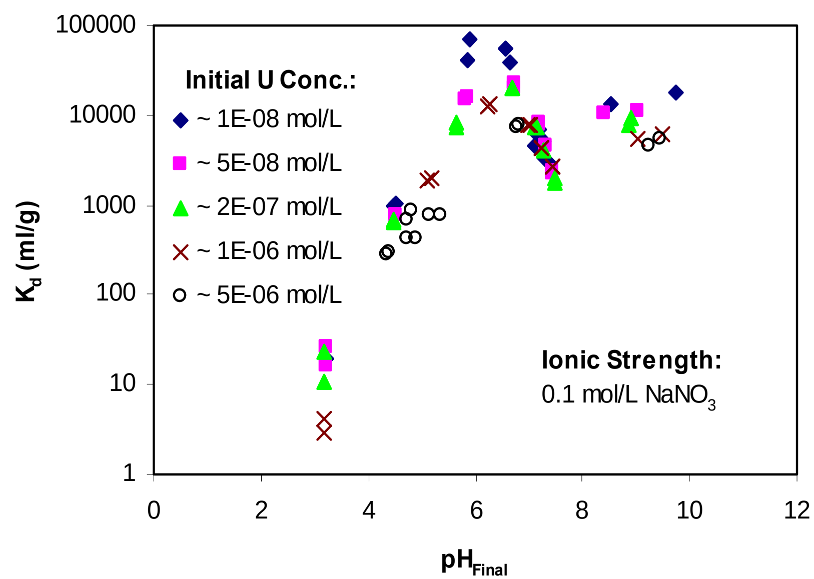
Characterization of Interaction between actinides and clays → ***Sorption Isotherm*** / ***X-ray Adsorption Spectrscopy on sorbed Np***

Sorption of U and Np on clays depends strongly on solution pH

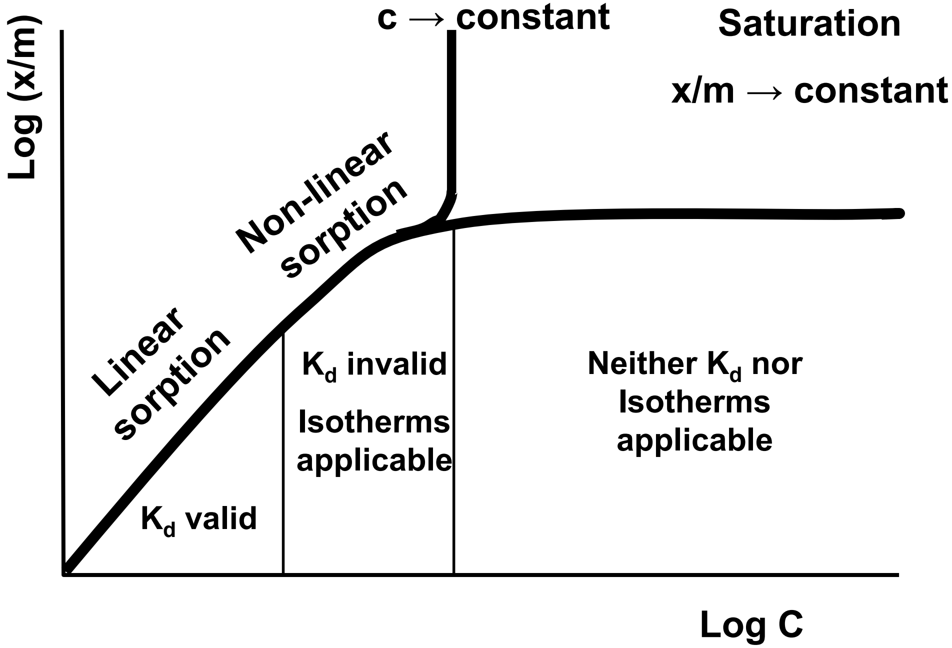
Np(V) Adsorption Increases Non-Linearly with Increasing pH



U(VI) Adsorption Shows a Maximum Around pH 6



Sorption Isotherm



(I. G. Mckinley and W.R. Alexander, J. of Contaminant Hydrology, 13 1993, 249-259.)

Freundlich isotherm equation

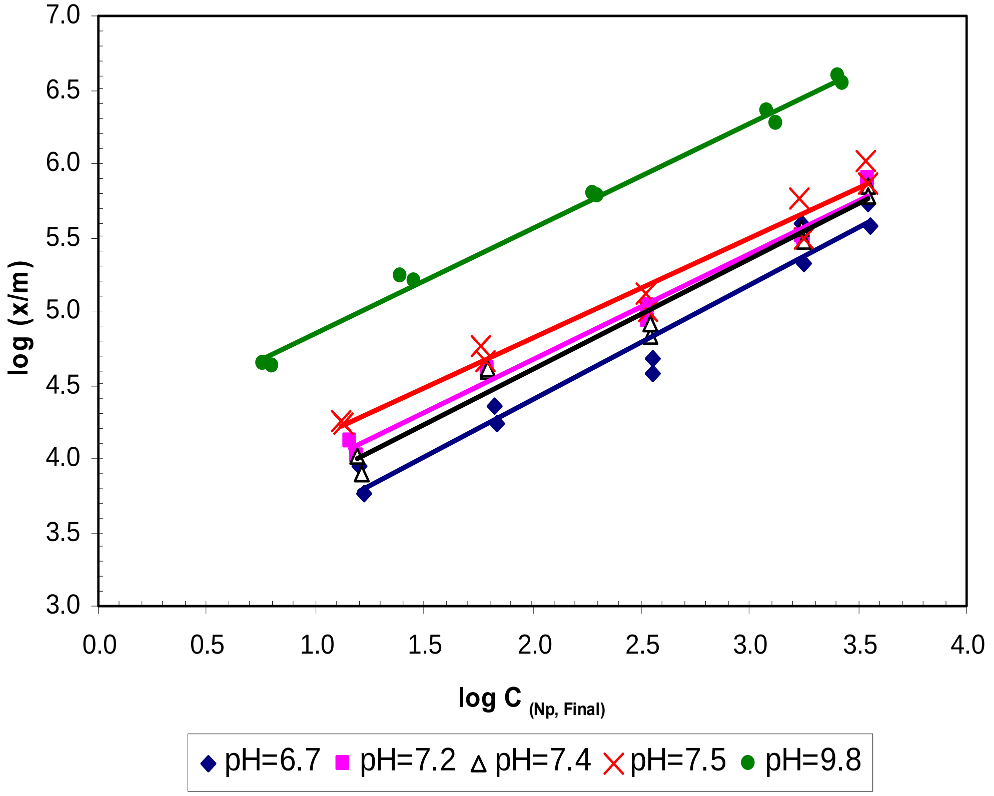
$$\frac{x}{m} = KC^n$$

$$\log (x/m) = \log K + n \log C$$

x/m is the mass of solute sorbed per unit mass of sorbent

C is the final concentration of species in solution

Sorption isotherms of Np on clays exhibit Freundlich behavior

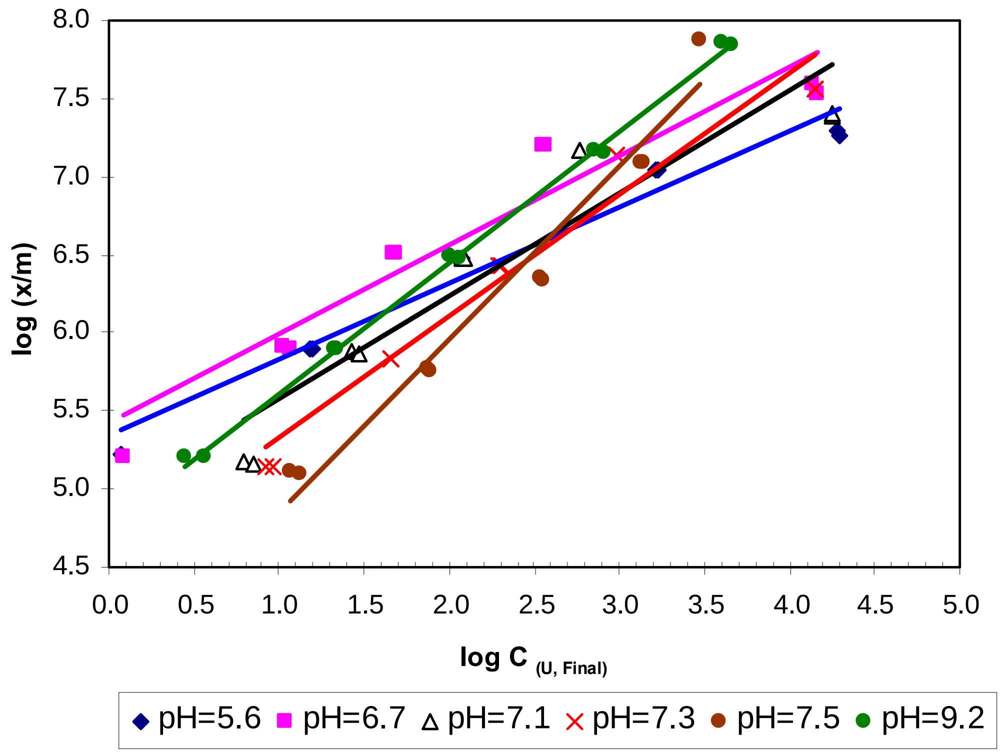


Initial Np concentration: $5*10^{-8}$ to $5*10^{-5}$ mol·L^{-1}.

Ionic strength: 0.1 mol·L^{-1} $NaNO_3$.

liquid to solid ratio (L/S) ~ 1000 ml·g^{-1}.

Sorption isotherms of U on clays also exhibit Freundlich behavior



Initial Np concentration: $1*10^{-8}$ to $1*10^{-6}$ mol·L^{-1}.

Ionic strength: 0.1 mol·L^{-1} $NaNO_3$.

liquid to solid ratio (L/S) ~ 1000 ml·g^{-1}.

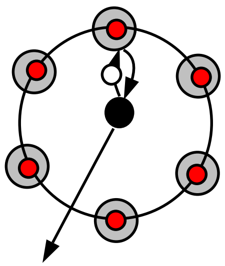
Isotherm constants and characteristics of Np and U sorption on alluvium clay fraction

	pH	Log K	n	r^2
Np	6.7	2.85	0.78	0.96
	7.2	3.24	0.72	0.98
	7.4	3.11	0.75	0.97
	7.5	3.45	0.68	0.97
	9.8	4.14	0.71	0.99
U	5.6	5.34	0.49	0.97
	6.7	5.42	0.57	0.92
	7.1	4.93	0.66	0.88
	7.3	4.57	0.77	0.96
	7.5	3.73	1.11	0.96
	9.2	4.78	0.84	1.00

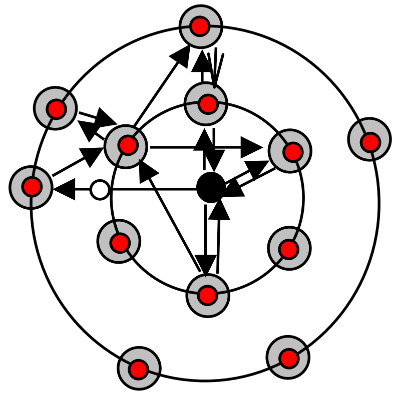
X-ray absorption spectroscopy (XANES and EXAFS)

Absorbing atom

Photoelectron



EXAFS



XANES

Characteristics

- Local atomic coordination
- Chemical oxidation state
- Works at low concentration
- Minimal sample requirement
- Applicable to solid and liquid

XANES: X-ray Adsorption Near-Edge Spectroscopy

EXAFS: Extended X-ray Absorption Fine-Structure

G.A. Waychunas, Chaper 4, in J.F.Banfield & A. Navrotsky, editors, Nanoparticles and the Environment, *Reviews in Mineralogy & Geochemistry*, Vol.44, 105-166, 2001.

Experimental Protocol

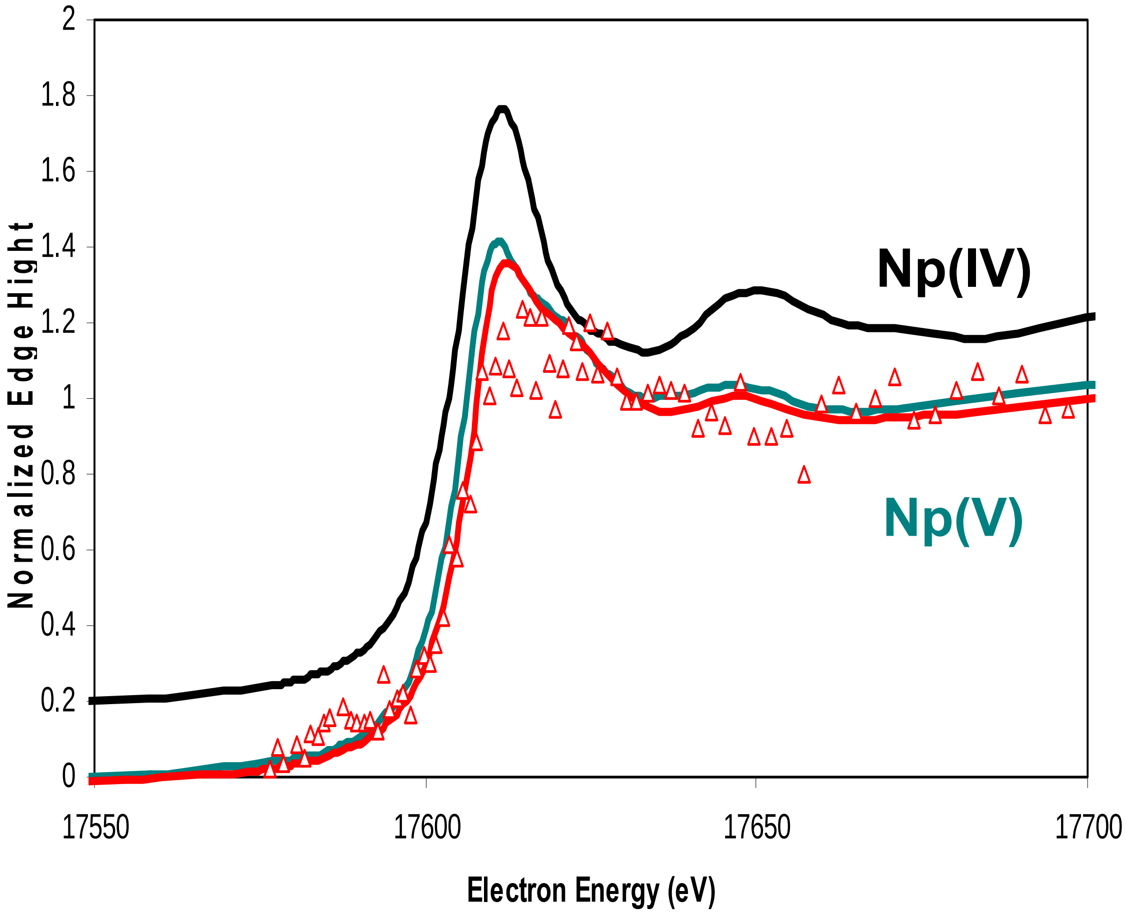
Sorption Experiment

- Clay Used: 200 mg
- Tracer Solution Volume: 200 ml
- Initial Conc. of Tracer: $2*10^{-6}$ mol/L
- Conc. of Tracer in Solution after Sorption (mol/L): $1.2*10^{-6}$(pH=8.5); $1.7*10^{-7}$(pH=10.2)
- The amount of adsorbate per mass unit of adsorbent (mg/Kg): 190 (pH=8.5); 434 (pH=10.2)

X-ray Absorption Spectroscope

- Harmonic content of beam was reduced using a cutoff mirror set at approximately 24 keV
- X-rays monochromatized using a l N2 monochromator with Si(220) crystals
- Data were obtained in fluorescence using a locally built 4-element germanium detector
- XANES spectra obtained on beamline 11-2 of SSRL

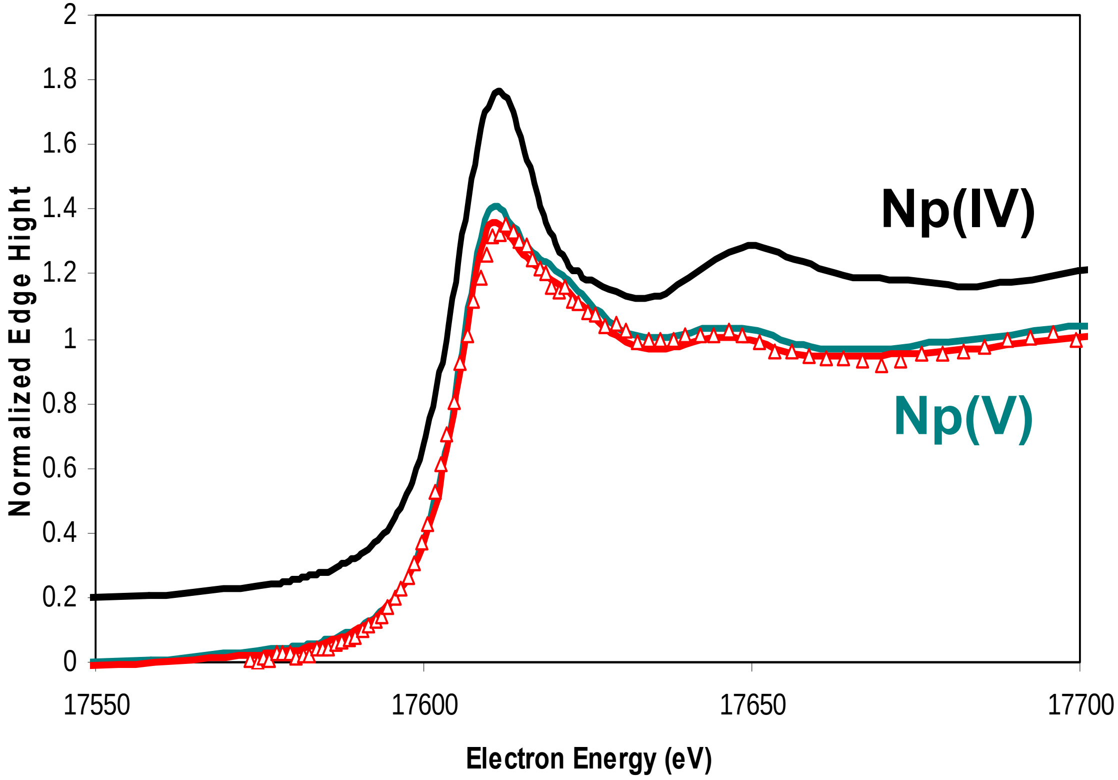
XANES spectra of Np sorbed on clays at pH 8.5



Fitting results:

- **93(34)% Np(V), 0(35)% Np(IV)**
- **Almost all Np present in the sample is Np(V)**

XANES spectra of Np sorbed on clays at pH 10.2



Fitting results:

- **97(10)% Np(V), 0(20)% Np(IV)**
- **All Np present in the sample is Np(V)**

Summary

- Distribution coefficients (K_d values, ml/g) of U and Np on clays in Yucca Mountain alluvium are much higher than those of the bulk alluvium.
- The sorption of U and Np on clays in the alluvium depends strongly on solution pH.
- Sorption of U and Np on clays in Yucca Mountain alluvium can be described by a Freundlich isotherm between pH 5 and 10.
- Np “sorbed” on clays are in oxidation state of Np(V).
- XAS is a powerful technique to study the essential chemistry of elements including actinides in solids and solutions.

Acknowledgements

- This work was supported and managed by the Office of Civilian Radioactive Waste Management, Science & Technology and International Program.
- Dr. Robert Roback provided thoughtful comments and suggestions.
- D. Ware, M. Haga and H. Kinkead are thanked for their help in conducting the experiments.