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 OECD Nuclear Energy Agency
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APR 18 1994

Dear Dr. Rügger:

In response to your letter of March 11, 1994, requesting extended bibliographic references on measured sorption data, I have enclosed two tables listing this information. One of the tables contains sorption data generated from experiments done at the Center for Nuclear Waste Regulatory Analyses (CNWRA), the prime contractor of the U.S. Nuclear Regulatory Commission. The other table includes information from important sorption studies published in the open literature. The information in these tables was compiled by Dr. David Turner from the CNWRA. Sorption data from the U.S. Department of Energy High-Level Waste Program are not included in this transmittal as it is assumed their Performance Assessment Advisory Group representative(s) will supply that information under separate cover.

Along with the tables, I have provided publications and reports from the CNWRA which may be difficult to obtain from libraries. If you would like the tables in electronic format (ASCII), please call John Bradbury at (301) 504-2535.

The NRC continues to endorse the effort of the Nuclear Energy Agency to maintain a limited sorption database. As additional sorption information is collected in the various countries, it becomes increasingly advantageous to have a single source of readily available experimental sorption data against which researchers can make comparisons.

Sincerely,

MS

Margaret Federline, Chief
 Performance Assessment & Hydrology Branch
 Division of Waste Management
 Office of Nuclear Material Safety
 and Safeguards

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Reference	Radionuclide	Concentration	T(C)	Solid	Solid Concentration	pH Range	Background Electrolyte	Ligand(s)	Container	Kinetic Experiments	Filtration/Phase Separation	Models
Pabalan et al. (1993)	U(VI)	2E-5 M 2E-6 M	25	Na-Clinoptilolite	2 g/l	2.5 to 9.0	n.r.	Atmospheric CO ₂ (10 ^{-3.5} atm)	Polypropelene	Yes (0-400 hr)	n.r.	
Pabalan and Turner (1993a)	U(VI)	2E-5 M 2E-6 M	25	Na-Clinoptilolite	2 g/l	2.5 to 9.0	n.r.	Atmospheric CO ₂ (10 ^{-3.5} atm)	Polypropelene	n.r.	n.r.	
Pabalan and Turner (1993b)	U(VI)	2E-5 M 2E-6 M	25	Na-Clinoptilolite	2 g/l	2.5 to 9.0	n.r.	Atmospheric CO ₂ (10 ^{-3.5} atm)	Polypropelene	Yes (0-400 hr)	n.r.	
Pabalan and Turner (1993c)	U(VI)	50 ppb	25	Na-Montmorillonite	2 g/l	2.5 to 9.0	0.1 m NaNO ₃	Atmospheric CO ₂ (10 ^{-3.5} atm)	Polypropelene	n.r.	0.2 μm DynaGard filters	
Pabalan and Turner (1993c)	U(VI)	5 ppb	25	α-Al ₂ O ₃ (2.09 m ² /g)	2 g/l	2.5 to 9.0	0.1 m NaNO ₃	Atmospheric CO ₂ (10 ^{-3.5} atm)	Polypropelene	n.r.	0.2 μm DynaGard filters	
Pabalan and Turner (1994)	U(VI)	5, 50, 500 ppb	25	Na-Clinoptilolite	2 g/l	2.0 to 9.0	0.1 m NaNO ₃ 1.0 m NaNO ₃	Atmospheric CO ₂ (10 ^{-3.5} atm)	Teflon	n.r.	Centrifuge 20 m @ 13000 rpm	DLM
Pabalan and Turner (1994)	U(VI)	95 ppb	25	α-Al ₂ O ₃ (2.09, 0.229, 0.0686 m ² /g)	2.5 g/l	2.0 to 9.0	0.1 m NaNO ₃	Atmospheric CO ₂ (10 ^{-3.5} atm)	Teflon	n.r.	Centrifuge 20 m @ 13000 rpm	DLM
Pabalan and Bertetti (1994)	Sr ²⁺	0.005, 0.05, 0.5 N	25	Na-Clinoptilolite	0.03 to 1.6 g 10 to 250 ml	n.r.	NaCl/SrCl ₂	Atmospheric CO ₂ (10 ^{-3.5} atm)	n.r.	n.r.	n.r.	IE-Margules
Prikryl et al. (1994)	U(VI)	95 ppb	25	α-Al ₂ O ₃ (2.09, 0.229, 0.0686 m ² /g)	2.5 g/l	2.0 to 9.0	0.1 m NaNO ₃	Atmospheric CO ₂ (10 ^{-3.5} atm)	Teflon	Yes (0-475 hr)	Centrifuge 20 m @ 13000 rpm	DLM

a) DLM = Double Layer Model; CCM = Constant Capacitance Model; TLM = Triple Layer Model; IE = Ion-Exchange Model
n.r. Not Reported

REFERENCES:

Pabalan, R.T., J.D. Prikryl, P.M. Muller, and T.B. Dietrich. 1993. Experimental study of Uranium(6+) Sorption on the zeolite mineral clinoptilolite. *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management - XVI*. C.G. Interrante and R.T.Pabalan, eds. Pittsburgh, PA: Materials Research Society: 294: 777-782.

Pabalan, R.T. and D.R. Turner. May 1993a. Sorption modeling for high-level waste performance assessment. *NRC High-Level Radioactive Waste Research at CNWRA January through June 1992*. W.C. Patrick, ed. NUREG/CR-5817, CNWRA 92-01S, Vol. 3, No. 1: San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-24.

Pabalan, R.T. and D.R. Turner. July 1993b. Sorption modeling for high-level waste performance assessment. *NRC High-Level Radioactive Waste Research at CNWRA July through December 1992*. B. Sagar, ed. NUREG/CR-5817, CNWRA 92-02S, Vol. 3, No. 2: San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-18.

Pabalan, R.T. and D.R. Turner. August 1993c. Sorption modeling for high-level waste performance assessment. *NRC High-Level Radioactive Waste Research at CNWRA January through June 1993*. B. Sagar, ed. CNWRA 93-01S: San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-24.

Pabalan, R.T. and D.R. Turner. February 1994. Sorption modeling for high-level waste performance assessment. *NRC High-Level Radioactive Waste Research at CNWRA July through December 1993*. B. Sagar, ed. CNWRA 93-02S: San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-24.

Pabalan, R.T. and F.P. Bertetti. 1994. Thermodynamics of ion-exchange between Na⁺/Sr²⁺ solutions and the zeolite mineral clinoptilolite. *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management - XVII*. R. Van Koneyenberg, ed. Pittsburgh, PA: Materials Research Society: (In Submission).

Prikryl, J.D., R.T. Pabalan, D.R. Turner, and B.W. Leslie. 1994. Uranium sorption on α-Alumina: Effects of pH and Surface-Area/Solution-Volume Ratio. Proceedings of the Fourth International Conference on the Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere: Migration '93. *Radiochimica Acta*: (In Submission).

4/18/94

OTHER RADIONUCLIDE SORPTION EXPERIMENTS (UNITED STATES)

Reference	Radio-nuclide	Concentration	T(C)	Solid	Solid Conc.	pH Range	Background Electrolyte	Ligand(s)	Container	Kinetic Experiments	Filtration/Phase Separation	Models
Hsi (1981)	U(VI)	10^{-5} to 10^{-8} M	25	Synthetic Hematite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes (0-72 hr)	Centrifuge 15 m @ 3000 rpm	TLM
Hsi (1981)	U(VI)	10^{-5} to 10^{-8} M	25	Natural Hematite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes (0-72 hr)	Centrifuge 15 m @ 3000 rpm	TLM
Hsi (1981)	U(VI)	10^{-5} to 10^{-8} M	25	Goethite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes (0-72 hr)	Centrifuge 15 m @ 3000 rpm	TLM
Hsi (1981)	U(VI)	10^{-5} to 10^{-8} M	25	Ferrihydrite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes (0-72 hr)	Centrifuge 15 m @ 3000 rpm	TLM
Riese (1982)	Th,Ra	10^{-5} m Th 10^{-11} m Ra	25	α -SiO ₂	5 g/l	2.0 to 6.0	0.01 m Na ₂ SO ₄ 0.01 m NaCl 0.01 m NaNO ₃	CO ₂ free (?)	Plastic	n.r.	Centrifuge 90 m @ 12000 rpm	TLM; TAM; PEM
Riese (1982)	Th,Ra	10^{-5} m Th 10^{-11} m Ra	25	Kaolinite	2.5 g/l	2.0 to 6.0	0.01 m Na ₂ SO ₄ 0.01 m NaCl 0.01 m NaNO ₃	CO ₂ free (?)	Plastic	n.r.	Centrifuge 90 m @ 12000 rpm	TLM; TAM; PEM
Tripathi (1984)	U(VI)	10^{-5} , $10^{-5.4}$, $10^{-5.8}$, 10^{-6} , $10^{-6.4}$, $10^{-6.7}$, $10^{-7.1}$ M	25	Goethite	0.10 g/l 0.41 g/l 0.96 g/l 2.10 g/l	5.0 to 9.0	0.1 M NaNO ₃ 0.5 M NaNO ₃ 0.7 M NaNO ₃	CO ₂ free; Atmospheric CO ₂ ($10^{-3.2}$ atm); 50ppb-5ppm F; 40-100ppb PO ₄ ³⁻	Nalgene	Yes (0-8 hr)	Centrifuge; 0.2 μ m Nucleopore filter	TLM
Hsi and Langmuir (1985)	U(VI)	10^{-5} M	25	Synthetic Hematite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes	Centrifuge 15 m @ 3000 rpm	TLM
Hsi and Langmuir (1985)	U(VI)	10^{-5} M	25	Natural Hematite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes	Centrifuge 15 m @ 3000 rpm	TLM
Hsi and Langmuir (1985)	U(VI)	10^{-5} M	25	Goethite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes	Centrifuge 15 m @ 3000 rpm	TLM
Hsi and Langmuir (1985)	U(VI)	10^{-5} M	25	Ferrihydrite	1 g/l	4.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10^{-2} to 10^{-3} M	Polycarbonate	Yes	Centrifuge 15 m @ 3000 rpm	TLM
Sanchez et al. (1985)	Pu(IV) Pu(V)	10^{-10} , 10^{-11} M 10^{-10} , 10^{-11} M	20	Goethite	0.55 g/l	2.0 to 9.0	0.1 M NaNO ₃	CO ₂ free; C _T = 10, 30, 100, 200, 400, 1000 meq/l @ pH = 8.6	Borosilicate Glass	n.r.	Filter not specified	TLM
LaFlamme and Murray (1987)	Th	10^{-13} M	20	Goethite	5.22E-3 g/l	1.8 to 10.5	0.01 M NaNO ₃ 0.1 M NaNO ₃ 1.0 M NaNO ₃ 2.0 M NaNO ₃	CO ₂ free; C _T = 15 to 1788 meq/l @ pH = 9.0	Glass	n.r.	0.45 μ m Millipore filter	TLM
Hunter et al. (1988)	Th	4.5E-6 M 9.0E-6 M 9.0E-6 M	20	Goethite	0.54 g/l 0.54 g/l 8.60 g/l	2.0 to 8.0	0.422 m NaCl; 0.422 NaCl + 0.054 m MgCl ₂ ; 0.422 NaCl + 0.010 m CaCl ₂ ; 0.422 NaCl + 0.028 m Na ₂ SO ₄ ; Seawater	CO ₂ (?)	Pyrex	Yes	Centrifuge 15 m @ 4500 g	TLM

Reference	Radio-nuclide	Concentration	T(C)	Solid	Solid Conc.	pH Range	Background Electrolyte	Ligand(s)	Container	Kinetic Experiments	Filtration/Phase Separation	Models ₁
Hunter et al. (1988)	Th	4.5E-6 M 9.0E-6 M	20	δ -MnO ₂	8.3E-3 g/l	2.0 to 8.0	0.422 m NaCl; 0.422 NaCl + 0.054 m MgCl ₂ ; 0.422 NaCl + 0.010 m CaCl ₂ ; 0.422 NaCl + 0.028 m Na ₂ SO ₄ ; Seawater	CO ₂ (?); EDTA; CDTA	Pyrex	Yes	Centrifuge 15 m @ 4500 g	TLM
Girvin et al. (1991)	Np(V)	4.5E-11 M 4.7E-12 M 4.5E-13 M	25	Ferrihydrite	0.88 g/l 0.33 g/l .089 g/l	5.0 to 9.5	0.1 M NaNO ₃ (0.01 and 1.0 M results not reported)	Atmospheric CO ₂ (10 ^{-3.5} atm), capped with 5 ml headspace	Polyethylene	Yes (1 to 96 hr)	0.18 μ m filter	TLM
Kohler et al. (1992)	Np(V)	1.2E-7 M	n.r.	Hematite	1 g/l	4.0 to 11.0	0.005 M NaClO ₄ 0.01 M NaClO ₄ 0.05 M NaClO ₄ 0.1 M NaClO ₄	3.3E-7 M Na-EDTA 3.3E-7 M Ca-EDTA	n.r.	n.r.	n.r.	
Kohler et al. (1992)	Np(V)	1.2E-7 M	n.r.	Kaolinite	5 g/l	4.0 to 11.0	0.1 M NaClO ₄	10 ⁻³ M EDTA 10 ⁻⁴ M EDTA 10 ⁻⁶ M EDTA	n.r.	n.r.	n.r.	

a) DLM = Double Layer Model; CCM = Constant Capacitance Model; TLM = Triple Layer Model; IE = Ion-Exchange Model; TAM = Thermodynamic Adsorption Model; PEM = Power Exchange Model
n.r. Not Reported

Girvin, D.C., L.L. Ames, A.P. Schwab, and J.E. McGarrah. 1991. Neptunium adsorption on synthetic amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science* 141:67-78.

Hsi, C-K.D. 1981. *Sorption of Uranium(VI) by Iron Oxides*. Ph.D. Dissertation. Golden, Colorado: Colorado School of Mines.

Hsi, C-K.D. and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta* 49:1931-1941.

Hunter, K.A., D.J. Hawke, and L.K. Choo. 1988. Equilibrium adsorption of thorium by metal oxides in marine electrolytes. *Geochimica et Cosmochimica Acta* 52:627-636.

Kohler, M., E. Wieland, and J.O. Leckie. 1992. Metal-ligand-surface interactions during sorption of uranyl and neptunyl on oxides and silicates. *Proceedings of the 7th International Symposium on Water-Rock Interaction - WRI-7. Volume 1: Low Temperature Environments*. Y.K. Kharaka and A.S. Maest, eds. Rotterdam: A.A. Balkema.

LaFlamme, B.D., and J.W. Murray. 1987. Solid/Solution Interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochimica et Cosmochimica Acta* 51:243-250.

Riese, A.C., *Adsorption of Radium and Thorium onto Quartz and Kaolinite: A Comparison of Solution/Surface Equilibria Models*. Ph.D. Dissertation. Colorado School of Mines: Golden, CO.

Sanchez, A.L., J.W. Murray, and T.H. Sibley. 1985. The adsorption of plutonium IV and V on goethite. *Geochimica et Cosmochimica Acta* 49:2297-2307.

Tripathi, V.S. 1984. *Uranium(VI) Transport Modeling: Geochemical Data and Submodels*. Ph.D. Dissertation. Stanford, California: Stanford University.

3. Sorption and assimilation of Uranium by *Trichoderma Viride* (Fig. N° 2-3)

Growth of *Trichoderma viride* is obtained in a fermentor containing glucose and U or Cs in a mineral solution. At the end of the experiment, the culture medium is filtered and the amount of U is measured in the biomass.

4. Study of radionuclides complexation phenomena by cellulolytic microorganisms (Fig. N° 2-4)

Two operating compartments are obtained by a separative membrane of 0.45 μm of porosity. Compartment A contains the matrix with U or Cs. Compartment B contains the mineral solution with the microorganism (Fig. N° 2-4).

Produced organic acids diffuse through the membrane and lead to the desorption of U initially incorporated in the matrix.

In figure 4 is shown the amount of U released from clay by the various organic acids, which are produced, as a function of the pH, by the fungus.

The difference of the amount of U desorbed with biological organic acid to compared to the amount of U desorbed with mineral acid is explained by the complexing properties of the organic acids.

CONCLUSION

The aim of this work is to study the various processes, that permit evaluations to be made for the interactions between microorganisms and radionuclides under simulated repository conditions and to characterize the general effect of microbial activity on the leaching of radionuclides embedded in barriers. Initial results indicate a large production of organic acids in anaerobic conditions that simulate deep storage conditions. These acids have evidenced properties of complexation.

Index terms: migration, deep repository, radionuclide transport/retardation, microbial effect, cellulose biodegradation.

REFERENCES

1. J.M. West, D.G. Haigh, P.J. Hooker and E.J. Rowe, *Experientia* 47 (6), 549-552 (1977).
2. L.D. Birch and R. Bachofen, *Soil Biochemistry* 6, 483-527 (1989).

ACKNOWLEDGEMENT

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EXPERIMENTAL STUDY OF URANIUM(6+) SORPTION ON THE ZEOLITE MINERAL CLINOPTILOLITE

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ABSTRACT

Experiments on the sorption of uranium(6+) on clinoptilolite from solutions in equilibrium with atmospheric $\text{CO}_2(\text{g})$ were conducted to understand the fundamental controls on uranium sorption on zeolite minerals, including the effects of pH, aqueous uranium speciation, and uranium concentration in solution. The results indicate that uranium(6+) species are strongly sorbed on the zeolite mineral clinoptilolite at near-neutral pH. The amount of uranium sorbed is strongly dependent on pH and, to some extent, on the total concentration of uranium. Uranium sorption on clinoptilolite is important in the pH range where $\text{UO}_2(\text{OH})_2^{\circ}(\text{aq})$ is the predominant uranium aqueous species, whereas sorption is inhibited at pH's where carbonate- and hydroxy-carbonate-complexes are the primary uranyl species. Surface adsorption appears to be the main sorption mechanism, although at $\text{pH} < 4$ the results suggest ion exchange may occur between the UO_2^{2+} ions in solution and the cations in the intracrystalline cation exchange sites of clinoptilolite.

The effectiveness of zeolite-rich horizons underneath Yucca Mountain, Nevada, as barriers to actinide transport through sorption processes will depend strongly on groundwater chemistry. Reliable predictions of radionuclide transport through these horizons will need to properly account for changes in solution chemistry.

INTRODUCTION

The occurrence of thick, laterally-continuous horizons of zeolite-rich (predominantly clinoptilolite) tuffs underneath the proposed high-level nuclear waste repository at Yucca Mountain, Nevada, could provide important geologic barriers to radionuclide migration from the repository horizon to the accessible environment. The favorable selectivity of natural zeolites, such as clinoptilolite, for alkali and alkaline earth radionuclides (e.g., ^{137}Cs and ^{90}Sr) through an intracrystalline ion exchange mechanism is well-known [1,2]. This property has made these minerals suitable for use in reducing the concentration of those radionuclides in aqueous solutions of various origins [3,4,5]. However, the ability of these zeolites to sorb actinides, which have a more complex aqueous chemistry than Cs and Sr, is not well-known. Although experimental studies indicated good correlation of Cs and Sr sorption ratios with the clinoptilolite content of zeolitized tuffs [6,7], there were no trends observed in the amount of sorbed uranium, neptunium, and plutonium with increased zeolitization of silicic tuffs [6]. On the other hand, uranium-bearing clinoptilolite occurs as an ore mineral in the uranium deposit of Tono, Japan [8,9]. This indicates that under certain geochemical conditions clinoptilolite can be an important sorber of an actinide element.

To evaluate the potential importance of zeolite-rich horizons as barriers to actinide transport, experiments on the sorption of uranium(6+) on clinoptilolite were conducted. The study was designed to understand fundamental controls on uranium sorption on zeolites, including the effects of pH, aqueous uranium speciation, and solution concentration of uranium. The results of the initial experiments are discussed below.

EXPERIMENTAL

Materials and Pretreatment

Purified clinoptilolite powder (75-150 μm) was prepared from clinoptilolite-rich tuff from Death Valley Junction, California, in a manner similar to that described previously [10]. However, prior to removing mineral impurities by density separation using mixtures of tetrabromoethane and dimethyl-formamide, the material was treated with 1 N sodium acetate buffer (pH adjusted to 5) to dissolve carbonate minerals. Subsequent to density separation, iron oxide minerals and coatings were dissolved using a sodium dithionite-citrate-bicarbonate mixture [11]. This last step was necessary because iron oxides and oxyhydroxides are strong sorbers of uranium [12,13].

Near homolitic Na-clinoptilolite was generated by treating 40 g of the purified material with 400 ml of 3 M NaCl solution at 90°C in a shaker water bath for two weeks. The NaCl solution was replaced every two days. The samples thus treated were washed several times with deionized water at 90°C to eliminate excess NaCl, dried in an oven at about 65°C, and then equilibrated with water vapor over saturated sodium chloride solution in a desiccator until constant weight was attained (~10 days). No secondary mineral phases were observed to have formed during pretreatment as determined by scanning electron microscopy and x-ray diffraction.

The compositions of Na-clinoptilolite samples were analyzed by plasma emission spectrometry subsequent to lithium metaborate fusion and dissolution in an HCl/HNO₃ matrix. The water content was determined by weighing the samples before and after heating at 900°C for two hours. A chemical formula (based on 24 oxygens per unit cell) corresponding to $(\text{Na}_{1.807}\text{K}_{0.122}\text{Ca}_{0.091}\text{Mg}_{0.034})\text{Al}_{1.948}\text{Fe}_{0.044}(\text{Si}_{10.044}\text{Th}_{0.004})\text{O}_{24}\cdot 7.43\text{H}_2\text{O}$ was calculated from the average of the analytical data for Na-clinoptilolite.

Uranium Sorption Experiments

Sorption Kinetics

To determine the time required to reach sorption equilibrium, kinetics experiments were first conducted. These consisted of duplicate sets of two mixtures of 0.95 g of Na-clinoptilolite and 950 ml of 2.1×10^{-6} M U solution in polypropylene bottles. The uranium solutions were prepared from ACS grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ reagent. Before clinoptilolite was added, the pH of one set of solutions was adjusted from its initial value of 5.26 to ~4.5 by addition of HNO₃. The pH of the second set was not adjusted. The bottles were kept open to the atmosphere and constantly agitated using a gyratory shaker. At certain time intervals, 10-ml aqueous samples were taken using volumetric pipets and transferred into 15-ml polypropylene bottles. A 500 μl aliquot of a 1.05 M tartaric-acid/triethanolamine solution was added to each sample for later uranium analysis. The pH of each solution was also measured at each sampling time.

The uranium concentrations of the aqueous samples were measured with an EG&G Princeton Applied Research Model 384B polarographic analyzer and Model 303A static mercury drop electrode. The analyses were done in a matrix of tartaric-acid/triethanolamine (0.05 M final concentration) using a differential pulse stripping method. Uranium solutions used to generate calibration curves for the polarographic analysis were prepared from commercial 1000 ppm $\text{UO}_2(\text{NO}_3)_2$ standards. The pH of the solutions was measured with a Ross combination pH electrode and an Orion 920A pH/mVISE/°C meter.

Equilibrium Sorption

The sorption experiments were conducted by reacting 0.20 g of Na-clinoptilolite with 100 ml of uranium solutions in polypropylene bottles. The solutions had initial uranium concentrations of 2.0×10^{-5} or 2.0×10^{-6} M. Prior to addition of the solid phase, the initial pH of each solution was adjusted to a value in the range 2.5 to 9.0 at approximately 0.5 pH intervals by addition of HNO₃ or NaHCO₃. The amount of reagent needed to achieve the desired initial pH of the uranium solution was estimated using the EQ3NR geochemical code (version 3245.R124) with database Data0.com.R12 [14]. The solutions, which were kept open to atmospheric CO₂(g) throughout the experiment, were agitated using gyratory shakers.

The clinoptilolite powder was added after all solutions have attained a constant pH. For uranium solutions with added NaHCO₃, it took at least ten days to equilibrate with atmospheric CO₂(g) and reach a constant pH. Control experiments consisting of uranium solutions without added clinoptilolite were used to determine potential losses of uranium to the container walls. After a reaction time sufficient to reach sorption equilibrium as determined from the kinetics studies, 10-ml aqueous samples were taken from each mixture. The equilibrium pH of each solution was also measured.

Subsequently, a second set of experiments was conducted to determine the reproducibility and/or reversibility of the sorption reactions. These were initiated by lowering the pH of the solutions by 1 to 2 units by adding HNO₃ solution. The mixtures were then allowed to reequilibrate for about the same period of time as the previous experiment and new samples and pH measurements were taken. The solution analyses were conducted similarly to the kinetics studies.

RESULTS AND DISCUSSION

The results of the kinetics experiments are given in Fig. 1, which shows the amount of uranium sorbed on clinoptilolite and the solution pH as functions of time. The data indicate that it takes about 300 hrs to reach a constant pH and %U sorbed. The equilibrium sorption mixtures were therefore allowed to equilibrate for at least 14 days. Additional data from other experiments indicate that the increase in pH with time is mainly due to ion exchange between H⁺ in solution and Na⁺ initially in the intracrystalline sites of clinoptilolite.

The results of the equilibrium sorption experiments are summarized in Figs. 2A and 2B, for mixtures with initial ΣU of 2.0×10^{-5} and 2.0×10^{-6} M, respectively. The control experiments indicated that uranium loss from solution to the container wall was negligible; thus, the %U sorbed was calculated from the initial and final solution

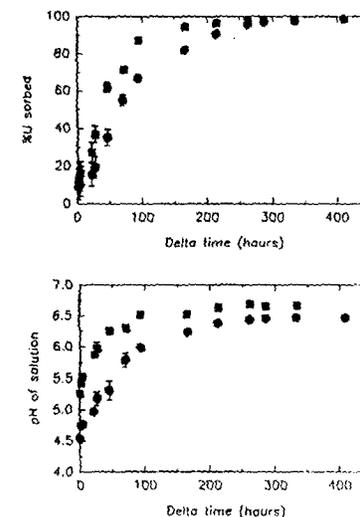


Figure 1. Results of kinetics experiments. Initial uranium concentration is 2.1×10^{-6} M. Circles and squares represent data for mixtures with initial pH of 4.54 and 5.26, respectively. Error bars in %U sorbed were calculated based on $\pm 5\%$ uncertainty in uranium analyses. Error bars in pH are based on measurements on duplicate sets of solutions.

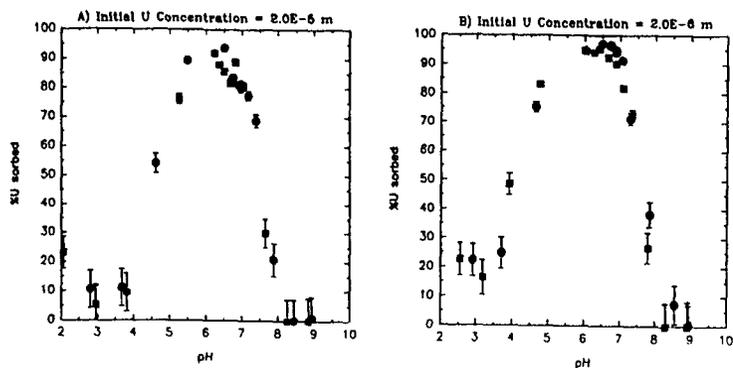


Figure 2. Uranium sorption on clinoptilolite versus equilibrium pH for solutions with initial uranium concentrations of: A) 2.0×10^{-6} and B) 2.0×10^{-6} m. The circles and squares represent data from the first and second set of equilibrium sorption experiments, respectively. Error bars were calculated based on $\pm 5\%$ uncertainty in uranium analyses.

concentrations of uranium. The results indicate that uranium sorption on clinoptilolite is strongly dependent on pH. The amount of uranium lost from solution increases sharply with increasing pH at pH values above about 3.5 ('adsorption edge'). At near neutral pH (~6.5), almost complete removal (>90%) of uranium from solution occurs. However, at pH>6.5, the amount of uranium sorbed on the solid phase sharply decreases with increasing pH ('desorption edge').

The circles and squares in Fig. 2 represent, respectively, data from the first and second sets of equilibrium sorption experiments. The good agreement between the two data sets indicates that uranium sorption on clinoptilolite is reproducible. The squares at pH less than about 6.5 represent reversals along the adsorption edge and demonstrate that the uranium sorption reactions are reversible. In addition, a comparison of data in Figs. 2A and 2B indicates that the adsorption edge shifts to lower pH with a decrease in total uranium concentration. This is consistent with the trends in uranium sorption observed by Tripathi [12] and by Payne et al. [15] in their studies using goethite and ferrihydrite, respectively. There is also a slight, but discernible, shift of the desorption edge to higher pH at lower total uranium concentration, which is similar to that observed by Tripathi [12]. Payne et al. [15] also observed this trend in their data on ferrihydrite, but the pH shift in their adsorption and desorption edges with changes in uranium concentration are almost equal in magnitude.

Aqueous uranium speciation for solutions analogous to those in the sorption experiments is illustrated in Fig. 3. The figure shows the relative stabilities of the aqueous uranyl species as a function of pH for solutions in equilibrium with atmospheric $\text{CO}_2(\text{g})$. The uranium speciation was calculated using the EQ3NR geochemical code and the uranium thermodynamic database recommended by the Nuclear Energy Agency (NEA) [16]. A comparison of Figs. 2 and 3 indicates that the decrease in the amount of uranium sorbed at alkaline pH can be related to the increasing importance of carbonate- and hydroxy-carbonate-complexes of uranium at higher pH. This is consistent with published sorption data on other geologic material such as clays [17] and iron oxides/oxyhydroxides [13,15]. In addition, it appears that uranium sorption on clinoptilolite becomes important in the pH range where $\text{UO}_2(\text{OH})_2^{\circ}(\text{aq})$ is the predominant aqueous uranium species. It is possible that $\text{UO}_2(\text{OH})_2^{\circ}$ could be an important species sorbed

on the surface of clinoptilolite, although spectroscopic (e.g., EXAFS) data is required to determine if this is correct.

The results shown in Fig. 2 indicate that at pH less than 3.5, the amount of uranium lost from solution appears to increase with decreasing pH. In this pH range most of the aqueous uranium is present as the UO_2^{2+} species as shown in Fig. 3. The $\text{O}=\text{U}=\text{O}$ group is linear in both crystalline compounds and in solution, with the $\text{U}=\text{O}$ distance ranging from about 1.6-2.0 Å [18]. On the other hand, the intracrystalline channels in clinoptilolite have dimensions of 4.0×5.5 , 4.1×4.7 , and 4.4×7.2 Å [19]. This suggests that an ion exchange reaction is possible between UO_2^{2+} in solution and Na^+ initially in the zeolite intracrystalline cation exchange sites. The experimental data of Andreeva et al. [20] on uranium sorption on clinoptilolite at pH of 2 to 4 also suggest that the sorption reaction has an intracrystalline ion exchange character. Additional experiments are underway to further investigate this sorption mechanism.

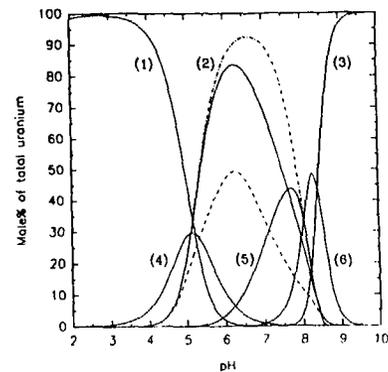


Figure 3. Aqueous uranyl speciation at 25°C as a function of pH for a 2.0×10^{-6} m $\text{UO}_2(\text{NO}_3)_2$ solution (solid curves) and $\log p\text{CO}_2 = -3.5$ atm. Dashed and dotted-dashed lines represent mole% of $\text{UO}_2(\text{OH})_2^{\circ}(\text{aq})$ species for $\Sigma \text{U} = 2.0 \times 10^{-6}$ and 2.0×10^{-7} m, respectively. Minor species with maximum mole% less than 5 are not shown. 1) UO_2^{2+} , 2) $\text{UO}_2(\text{OH})_2^{\circ}$, 3) $\text{UO}_2(\text{CO}_3)_2^{2-}$, 4) $\text{UO}_2(\text{OH})^+$, 5) $(\text{UO}_2)_2\text{CO}_3(\text{OH})^-$, and 6) $\text{UO}_2(\text{CO}_3)_2^{2-}$.

CONCLUSIONS

Sorption experiments involving uranium solutions in equilibrium with atmospheric $\text{CO}_2(\text{g})$ indicate that uranium(6+) species are strongly sorbed on the zeolite mineral clinoptilolite at pH's near neutral. The amount of uranium sorbed is strongly dependent on pH and, to some extent, on the total concentration of uranium. Uranium sorption on clinoptilolite is important in the pH range where $\text{UO}_2(\text{OH})_2^{\circ}(\text{aq})$ is the predominant uranium aqueous species, whereas sorption is inhibited at pH's where carbonate- and hydroxy-carbonate-complexes are the primary uranyl aqueous species. Surface adsorption appears to be the main sorption mechanism, although at pH<4 the results suggest that ion exchange may occur between the UO_2^{2+} ions in solution and the cations in the intracrystalline cation exchange sites of clinoptilolite.

The effectiveness of zeolite-rich horizons beneath Yucca Mountain as barriers to actinide transport through sorption processes will depend strongly on groundwater chemistry. Reliable predictions of radionuclide transport will need to account for changes in solution chemistry. Because the sorption reactions are reversible, uranium sorbed on clinoptilolite may later be desorbed due to changes in groundwater chemistry (e.g., increase in pH). However, a comparison with sorption data on other minerals (e.g., clays, iron oxides/oxyhydroxides) indicates that the dependence of uranium sorption on various parameters is similar for different geologic materials, which may help in modeling sorption processes involving mineral mixtures (i.e., rocks). Experiments to understand the effects of other factors such as solid/liquid ratio, ionic strength, and partial pressure of $\text{CO}_2(\text{g})$ on uranium sorption on clinoptilolite are currently underway.

ACKNOWLEDGEMENTS

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REFERENCES

1. L.L. Ames, Jr., *Amer. Mineral.* **45**, 689 (1960); **49**, 127 (1964); **49**, 1099 (1964).
2. N.F. Chelischev, B.G. Berenshtein, T.A. Berenshtein, H.K. Grebanova and H.C. Martynova, *Dokl. Akad. Nauk SSSR* **210**, 1110 (1973).
3. F.A. Mumpton, in Natural Zeolites: Occurrence, Properties, Use, edited by L.B. Sand and F.A. Mumpton (Pergamon, New York, 1978), pp. 3-27.
4. M. Howden and J. Pilot, in Ion Exch. Technol., edited by D. Naden and M. Sreat (Horwood, Chichester, U.K., 1984) pp. 66-73.
5. M. Vavrova, O. Musatovova, and S. Bartha, *Isotopenpraxis* **27**, 325 (1991).
6. W.R. Daniels, K. Wolfsberg, R.S. Rundberg, A.E. Ogard, J.F. Kerrisk, C.J. Duffy, T.W. Newton, S.D. Knight, F.O. Lawrence, V.L. Rundberg, M. Sykes, G. Thompson, B. Travis, E. Treher, R. Vidale, G. Walter, R. Aguilar, M. Cisneros, S. Maestas, A. Mitchell, P. Oliver, P. Oliver, N. Raybold, and P. Wanek, Summary Report on the Geochemistry of Yucca Mountain and Environs, LA-9328-MS, Los Alamos Nat. Lab., Los Alamos, NM (1982).
7. R.E. Meyer, W.D. Arnold, F.I. Case, G.D. O'Kelley, and J.F. Land, in Scientific Basis for Nuclear Waste Management XIV, edited by T.A. Abrajano, Jr. and L.H. Johnson (Mater. Res. Soc. Proc. **212**, Pittsburgh, PA, 1991) pp. 569-576.
8. N. Katayama, K. Kubo, and S. Hirono, in Symposium on the Formation of Uranium Ore Deposits, (International Atomic Energy Agency, Vienna, 1974), no. IAEA-SM-183/11.
9. K.S. Doi, S. Hirono, and Y. Sakamaki, *Econ. Geol.* **70**, 628 (1975).
10. R.T. Pabalan, in Scientific Basis for Nuclear Waste Management XIV, edited by T.A. Abrajano, Jr. and L.H. Johnson (Mater. Res. Soc. Proc. **212**, Pittsburgh, PA, 1991) pp. 559-567.
11. O.P. Mehra and M.L. Jackson in Clays and Clay Minerals, 7th Conf. (Pergamon, New York, 1960) pp. 317-327.
12. V.S. Tripathi, PhD thesis, Stanford University, 1984.
13. C.-K. D. Hsi and D. Langmuir, *Geochim. Cosmochim. Acta* **49**, 1931 (1985).
14. T.J. Wolery, K.J. Jackson, W.L. Bourcier, C.J. Bruton, B.E. Viani, K.G. Knauss, and J.M. Delany, in Chemical Modeling in Aqueous Systems II, edited by D.C. Melchior and R.L. Bassett (Amer. Chem. Soc., Washington D.C., 1990), pp. 104-116.
15. T.E. Payne, K. Sekine, J.A. Davis, and T.D. Waite, in Alligator Rivers Analogue Project Annual Report 1990-1991, edited by P. Duerden (Aust. Nucl. Sci. Tech. Org., Menai, NSW, 1992) pp. 57-85.
16. I. Grenthe, J. Fuger, R. Konings, R. Lemire, A. Muller, C. Nguyen-Trung, H. Wanner, Chemical Thermodynamics of Uranium (North-Holland, Amsterdam, 1992).
17. M.D. Siegel, J.O. Leckie, S.W. Park, S.L. Phillips, and T. Sowards, Sandia National Laboratories Report No. SAND89-2387, 1990.
18. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (John Wiley, New York, 1980), p. 1016.
19. W.M. Meier and D.H. Olson, D. H. Atlas of Zeolite Structure Types. (Polycrystal Book Service, Pittsburgh, 1978).
20. N.R. Andreeva and N.B. Chernyavskaya, *Radiokhimiya* **24**, 9 (1982).

RADIONUCLIDE SORPTION MODELING
USING THE MINTEQA2 SPECIATION CODE

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ABSTRACT

The MINTEQA2 database has been updated and expanded to include radionuclide data from the most recent release of the EQ3/6 database. Comparison of U(VI)-speciation predicted using the old and new MINTEQA2 databases indicates several significant differences, including the introduction of neutral and anionic species at neutral to alkaline pH. In contrast, comparison of results calculated by EQ3 and MINTEQA2, both using Nuclear Energy Agency (NEA) uranium data, reveals only small differences that are likely due to differences in calculated activity coefficients.

With the new database, MINTEQA2 was used to model U(VI)-goethite sorption data from the literature with the Triple-Layer Model (TLM). Values were independently fixed for all but one of the model parameters. The parameter optimization code FITEQL was then used to determine binding constants for mononuclear uranium complexes ($\text{UO}_2(\text{OH})_2^{2+}$). The surface complex $\text{MOH}_2\text{-UO}_2(\text{OH})_2$ produced a very good fit of the sorption data, which was not significantly improved by the use of two or more surface complexes.

INTRODUCTION

A key measure of performance for a geologic high-level waste (HLW) repository is the degree of attenuation of radionuclide transport provided by sorption on the geologic media along flow paths to the accessible environment. Performance assessment calculations commonly model sorption processes using empirical isotherms such as the K_d approach. However, because these methods do not explicitly consider the chemistry of the system of interest, the adequacy of empirical isotherms has been questioned [1-5]. In contrast, mechanistic approaches to sorption modeling such as surface complexation have been developed to provide flexible, robust models that are able to accommodate changes in system chemistry. These models require a detailed understanding of the chemical system, which in turn requires a thermodynamic database appropriate to the system of interest. The complexity of mechanistic models tends to make them more computationally intensive, limiting their practical application in performance assessment. For this reason, mechanistic models must be evaluated and streamlined where possible.

The equilibrium speciation code MINTEQA2 (Version 3.0) [6] includes empirical, electrostatic, and ion exchange sorption models. By comparing different models, appropriate simplifications for incorporating mechanistic approaches into performance assessment codes may be identified. Important radionuclides in HLW include U, Pu, Np, Am, Tc, Cs, Sr, Zr, Th, Ra, and Sn [7]. With thermodynamic data imported from WATEQ3 [8], MINTEQA2 has a broad database for elements common in natural systems. However, of the radionuclides listed above, only strontium and uranium [9] are currently available in the MINTEQA2 database, and recent studies [10] suggest revisions are needed to previously published uranium data. Until the database is updated and expanded to contain other radionuclides, MINTEQA2 cannot be used to investigate radionuclide sorption processes.

The present study develops a radionuclide database suitable for use in the MINTEQA2 equilibrium speciation code. Radioelement speciation calculated using this database has several important implications for guiding sorption modeling. An example is given of the

8 SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

by Roberto T. Pabalan and David R. Turner

Investigators: Roberto T. Pabalan, David R. Turner, James D. Prikryl, Paula Muller, Tim Griffin and Todd Dietrich (CNWRA)

8.1 TECHNICAL OBJECTIVES

A fundamental concern in evaluating the suitability of Yucca Mountain, Nevada, as a repository for high-level nuclear wastes (HLW) is the possibility of radionuclide migration from the repository to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is sorption of radionuclides on minerals encountered along the flow paths. Sorption is specifically referred to as a favorable geochemical condition in 10 CFR 60.122(b) that will tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed as a potentially adverse condition [10 CFR 60.122(c)(8)] that could reduce the effectiveness of the natural barrier system.

To support the Nuclear Regulatory Commission's (NRC) HLW program, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is conducting research activities under the Sorption Modeling for HLW Performance Assessment Research Project. The objectives are to:

- Obtain a mechanistic understanding of the important processes governing radionuclide sorption and the physical and chemical parameters that affect these processes in the Yucca Mountain environment.
- Investigate the applicability of coupled hydrogeochemical models which use simple representations of sorption phenomena in performance assessment of the proposed repository.
- Develop practical but scientifically defensible approaches to modeling sorption at Yucca Mountain, and the databases required to support such models.

The goal of the research project is to develop sufficient understanding of radionuclide transport issues so that timely prelicensing guidance can be provided to the Department of Energy (DOE) and a sound basis is available for evaluating the DOE license application. The results will also be used in addressing NRC's needs in evaluating the use of K_d 's in modeling sorption. The project comprises Task 1—Literature Review and Development of Approach; Task 2—Coupled Hydrogeochemical Modeling: Application of Simplified Models to NRC Regulatory Needs; and Task 3—Sorption Experiments. Task 1 was completed by the end of 1991 with the development of workplans for Tasks 2 and 3 and the submission of the following reports: (i) "Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review", and (ii) "Effects of Variable Hydrologic Saturation on Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review". The results of activities undertaken in Tasks 2 and 3 are discussed below.

8.2 TASK 2—HYDROGEOCHEMICAL MODELING

The adequacy of the K_d approach commonly used to model sorption processes in performance assessment has been increasingly questioned (Reardon, 1981; Kent et al., 1988; Turner, 1991). To develop a more mechanistic approach, several different surface complexation models have been developed to consider explicitly the effects of aqueous chemistry on sorption on charged mineral surfaces (Westall and Hohl, 1980; Davis and Kent, 1990). Although desirable from the point-of-view of accurately predicting radionuclide sorption, the incorporation of surface complexation approaches in computer simulations of radionuclide migration may lead to excessive computational requirements relative to simple empirical models (Yeh and Tripathi, 1989). Therefore, evaluation of different mechanistic models and their possible simplification is necessary prior to incorporation into performance assessment codes.

Investigation of different sorption models can be accomplished using computer methods. Methods that use empirical constants such as K_d do not explicitly consider the speciation of a particular element. Therefore, modeling sorption only requires input values for the necessary empirical constants. Application of mechanistic models, however requires an understanding of the chemical system of interest. Since aqueous speciation is a nonlinear function of key chemical variables such as pH, $p(\text{CO}_2)$, and total concentration, it is apparent that a thermodynamic database is needed to adequately model sorption processes using mechanistic surface complexation models.

Kerrisk (1985) used U. S. Environmental Protection Agency (EPA) release limits specified in 40 CFR Part 191 and the anticipated makeup of HLW to identify important radionuclides. These include U, Am, Pu, Np, Tc, Cs, Zr, Th, Ra, and Sn. Simulating migration of these radionuclides depends on the simultaneous consideration of a number of chemical processes (sorption, precipitation/ dissolution), and the thermodynamic data used in modeling studies is critical to the predicted results (Carnahan, 1988).

The present study involves the development of a radionuclide database suitable for use in the MINTEQA2 equilibrium speciation code (Allison et al., 1990). MINTEQA2 was selected because it offers seven different sorption models. With appropriate data, these models can be compared and contrasted. This evaluation in turn can be used to identify critical parameters and appropriate simplifications of mechanistic models for incorporation into performance assessment codes.

8.2.1 MINTEQA2, Version 3.0

Based on the mathematical approach of the MINEQL code (Westall et al., 1976), MINTEQA2 (Version 3.0, Allison et al., 1990) is a versatile code for modeling sorption, offering seven different options, including empirical, electrostatic, and ion exchange models. In addition, precipitation/dissolution reactions can be considered based on an assumption of equilibrium. Equilibrium speciation is calculated using mass balance/mass action constraints. Extrapolation beyond 25° C is generally accomplished using the van't Hoff equation, assuming constant enthalpies of reaction (ΔH_r). Construction of input files is simplified by the interactive preprocessor code PRODEFA2.

As released, MINTEQA2 incorporates the thermodynamic database of WATEQ3 (Ball et al., 1981). One major advantage to this union has been the extensive use and scrutiny of the WATEQ3 data in a variety of environments and its exhaustive documentation of data sources (Ball and Nordstrom, 1991). As a result, the MINTEQA2 databases THERMO.DBS (aqueous species), TYPE6.DBS (solids), and REDOX.DBS provide extensive coverage of elements common in natural systems. Of the key

radionuclides listed above, however, only uranium (Langmuir, 1978) is currently available (Allison et al., 1990). Recent studies (Grenthe et al., 1992) suggest significant modifications are necessary to the uranium data. Until the MINTEQA2 databases are updated to include new uranium data and expanded to include other important radionuclide species, the code cannot be used to investigate sorption of radionuclides.

Many efforts have been made to develop comprehensive, critically evaluated tabulations of thermodynamic data for important radionuclides (e.g., Tripathi, 1984; Phillips et al., 1988; Wolery et al., 1990; Cross and Ewart, 1991; Grenthe et al., 1992). In most cases, however, the data are not available in the proper format for use in MINTEQA2. Formatting requirements for the modification of MINTEQA2 databases are described in the MINTEQA2 User's Manual (Allison et al., 1990). Although it is beyond the intended scope of the Sorption Research Project to extensively evaluate thermodynamic data, it is possible to take advantage of these efforts to expand the existing MINTEQA2 databases to include key radionuclides.

The EQ3/6 code uses the same geochemical principles as MINTEQA2 to calculate equilibrium aqueous speciation. Unlike MINTEQA2, EQ3/6 in its current form is unable to model sorption processes, except for recent modifications to consider ion exchange (Viani and Bruton, 1992). In a comparison of earlier versions of the two codes, Morrey et al. (1986) concluded that given the same data, the codes produced similar speciation results. The latest release of the EQ3/6 database (Data0.com.r12, 26Feb92) includes an extensive tabulation of data for radionuclides listed above. Because the EQ3/6 code will be used by the DOE in site characterization at Yucca Mountain, its database was chosen as an initial source for expanding the MINTEQA2 database. Like MINTEQA2, the EQ3/6 database includes 25° C log K values (log equilibrium constants) referenced to a zero ionic strength reference state. Although not used by the code, the EQ3/6 database also tabulates enthalpies of formation (ΔH_f° in kcal or kJ/mole) for aqueous species, solids, gases, and redox reactions. Original data sources are shown in Table 8.1.

Procedures described by Allison et al. (1990) were followed for formatting data from EQ3/6 for use in MINTEQA2. Many of the reactions written in EQ3/6 must be recast in terms of component species used by MINTEQA2. This involved the selection of auxiliary reactions such as the dissociation of water, the formation of HCO_3^- from CO_3^{2-} , and the oxidation of water. Where possible, these data were selected from the MINTEQA2 database to provide consistency with other reactions. Upon inspection, however, the differences between EQ3/6 and MINTEQA2 data were very small for these common, more well characterized auxiliary reactions. A spreadsheet program was used to calculate enthalpies of reaction (ΔH_r°) from the ΔH_f° values reported in the EQ3/6 data.

8.2.2 Database Comparison

Uranium is the only radionuclide included in the original databases distributed with MINTEQA2. With the exception of some solids, the uranium data in the Data0.com.r12 release of the EQ3/6 data that have been incorporated into the MINTEQA2 database developed here are from draft [Nuclear Energy Agency (NEA)^{1, 2}] versions of the recently released NEA uranium database (Grenthe

¹NEA. 1990. *NEA-TDB:Chemical Thermodynamics of Uranium*. Draft Report. OECD Data Bank. Saclay, France:NEA.

²NEA. 1989. *NEA-TDB:Chemical Thermodynamics of Uranium*. Draft Report. OECD Data Bank. Saclay France:NEA.

Table 8-1 Sources for EQ3 radioelement data adapted to MINTEQA2

Element	Data Source(s) †
Am	a,b,c,d
Co	e,f,g,h,i,j,k,l
Cs	<u>e</u> ,m ¹
Eu	e, <u>n</u> ,o
Np	a, <u>p</u>
Pu	q,r,s,t
Ra	e, <u>i</u>
Ru	<u>u</u> ,v
Sn	e,i,l, <u>w</u>
Tc	<u>x</u> ,y
Th	a, <u>f</u> ,g,i,m,z,aa
U	i, ¹ bb,cc, ² dd,ee,ff,gg
Zr	<u>f</u> ,j

† Underlined references are predominant data source for element of interest.

¹ NEA. 1990. *NEA-TDB:Chemical Thermodynamics of Uranium*. Draft Report. OECD Data Bank. Saclay, France:NEA.

² NEA. 1989. *NEA-TDB:Chemical Thermodynamics of Uranium*. Draft Report. OECD Data Bank. Saclay, France:NEA.

[a] Fuger and Oetting (1976); [b] Kerrisk (1984); [c] Kerrisk and Silva (1986); [d] Oetting et al. (1976); [e] Johnson et al. (1991); [f] Naumov et al. (1974); [g] Baes and Mesmer (1976); [h] Smith and Martell (1976); [i] Wagman et al. (1982); [j] Robie et al. (1979); [k] Garrels and Christ (1965); [l] Kubaschewski and Alcock (1979); [m] Cox et al. (1989); [n] Rard (1987b); [o] Rard (1985b); [p] Lemire (1984); [q] Lemire and Tremaine (1980); [r] Schwab and Felmy (1982); [s] Nash and Cleveland (1984); [t] Morss (1986); [u] Rard (1985a); [v] Rard (1987a); [w] Jackson and Helgeson (1985); [x] Rard (1983); [y] Rard (1984); [z] Langmuir and Herman (1980); [aa] Mills (1974); [bb] Langmuir (1978); [cc] Hemingway (1982); [dd] Rickard and Nriagu (1978); [ee] O'Hare et al. (1988); [ff] Tripathi (1984); [gg] Owens and Mayer (1964).

et al., 1992). Figures 8-1 through 8-4 illustrate the differences in U(VI) speciation in a 0.1 M NaNO₃ solution that result from using the old and new MINTEQA2 databases. One prominent difference is the larger number of U-species available in the new database (Figures 8-1 and 8-2). At pH < 5, UO₂²⁺ decreases due to the presence of the new species UO₂NO₃⁺. The relative importance of (UO₂)₃(OH)₅⁺ for pH > 6 is greatly reduced using the NEA data, and the newly entered species UO₂(OH)₂^o and

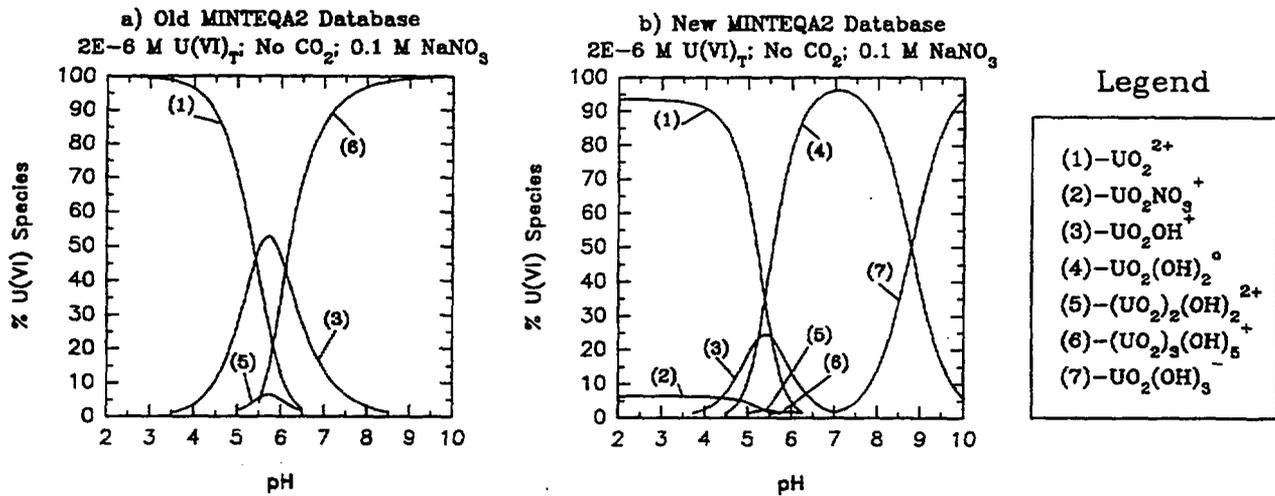


Figure 8-1. $\text{U(VI)}_T = 2 \times 10^{-6} \text{ M}$, No CO_2 , $I = 0.1 \text{ M NaNO}_3$, $T = 25^\circ \text{ C}$; (a) U(VI)-speciation predicted by THERMO.DBS database as distributed with MINTEQA2. Uranium data from Langmuir (1978). (b) U(VI)-speciation as predicted by the expanded MINTEQA2 database. Uranium data from EQ3/6 database. MINTEQA2 does not report species present at less than one percent U(VI)_T .

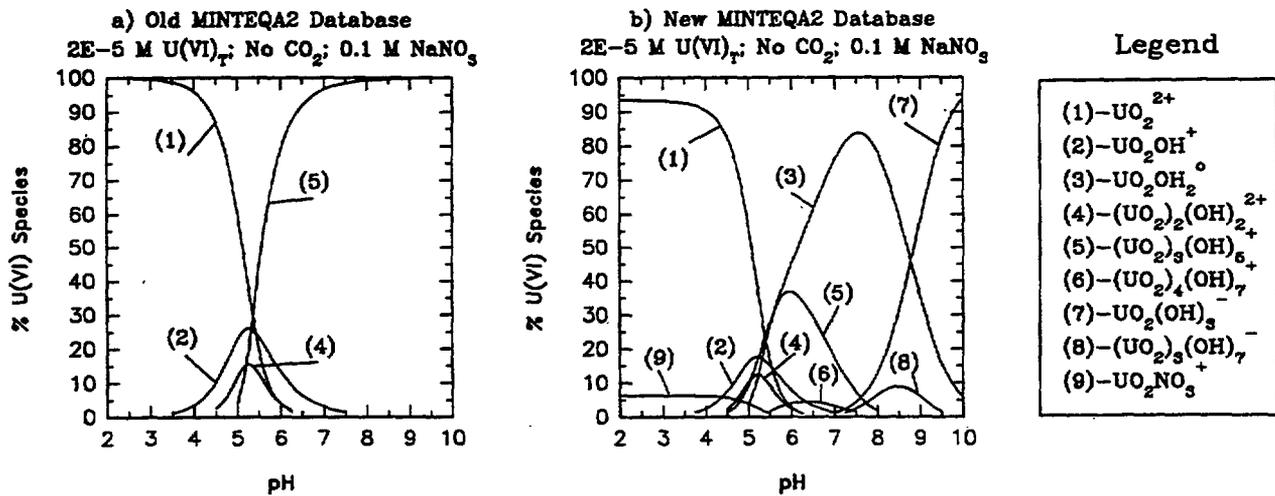


Figure 8-2. $\text{U(VI)}_T = 2 \times 10^{-5} \text{ M}$, No CO_2 , $I = 0.1 \text{ M NaNO}_3$, $T = 25^\circ \text{ C}$; (a) U(VI)-speciation predicted by THERMO.DBS database as distributed with MINTEQA2. Uranium data from Langmuir (1978). (b) U(VI)-speciation as predicted by the expanded MINTEQA2 database. Uranium data from EQ3/6 database. MINTEQA2 does not report species present at less than one percent U(VI)_T .

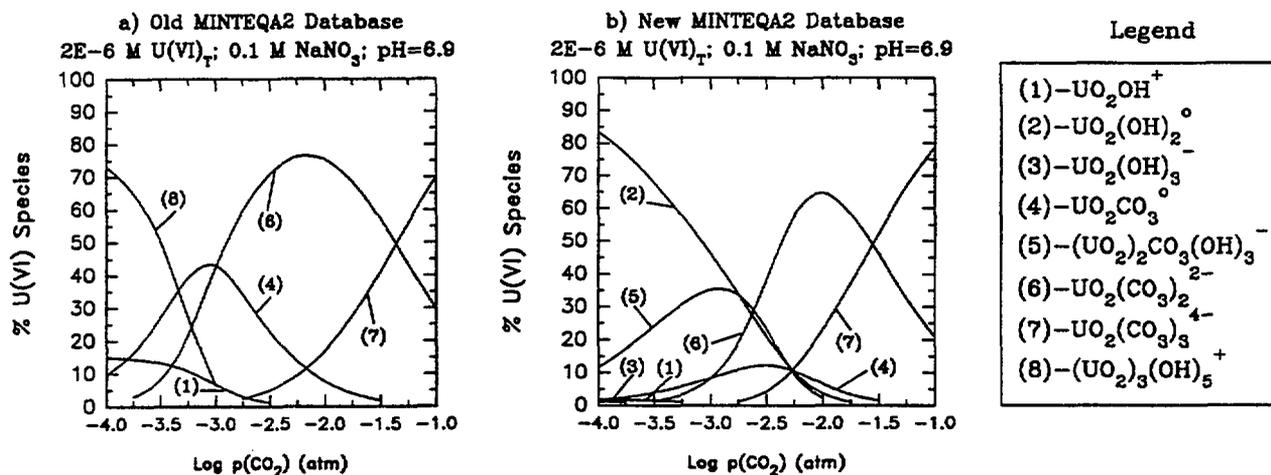


Figure 8-3. $\text{U(VI)}_T = 2 \times 10^{-6} \text{ M}$, variable CO_2 , $I = 0.1 \text{ M NaNO}_3$, $\text{pH} = 6.9$, $T = 25^\circ \text{C}$; (a) U(VI) -speciation predicted by THERMO.DBS database as distributed with MINTEQA2. Uranium data from Langmuir (1978). (b) U(VI) -speciation as predicted by the expanded MINTEQA2 database. Uranium data from EQ3/6 database. MINTEQA2 does not report species present at less than one percent U(VI)_T .

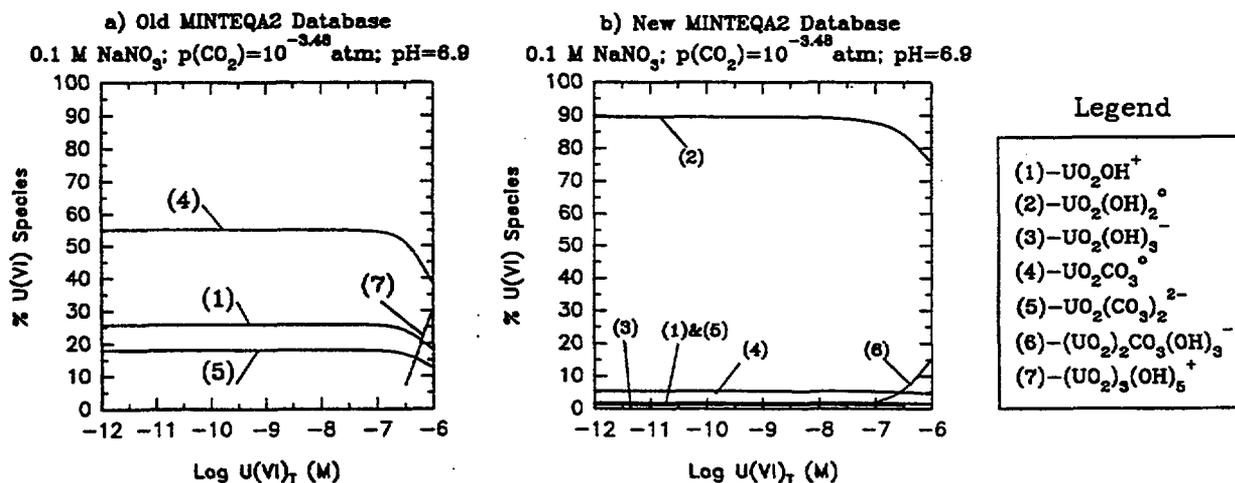


Figure 8-4. Variable U(VI)_T , $p(\text{CO}_2) = 10^{-3.48} \text{ atm}$, $I = 0.1 \text{ M NaNO}_3$, $\text{pH} = 6.9$, $T = 25^\circ \text{C}$; (a) U(VI) -speciation predicted by THERMO.DBS database as distributed with MINTEQA2. Uranium data from Langmuir (1978). (b) U(VI) -speciation as predicted by the expanded MINTEQA2 database. Uranium data from EQ3/6 database. MINTEQA2 does not report species present at less than one percent U(VI)_T .

$\text{UO}_2(\text{OH})_3^-$ are predicted to dominate. For low $p(\text{CO}_2)$ at $\text{pH} = 6.9$, similar to values measured for J-13 water at Yucca Mountain, $(\text{UO}_2)_3(\text{OH})_5^+$ is eliminated and replaced by $\text{UO}_2(\text{OH})_2^\circ$ (Figure 8-3). Also, the importance of $\text{UO}_2\text{CO}_3^\circ$ is greatly reduced and the new species $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ is significant at $p(\text{CO}_2)$ near atmospheric values ($10^{-3.48}$ atm).

Varying total uranium concentration in the presence of atmospheric CO_2 with $\text{pH} = 6.9$, (Figure 8-4) demonstrates the changes in speciation with the new database. At low $\text{U}(\text{VI})_{\text{T}}$, UO_2OH^+ , $\text{UO}_2\text{CO}_3^\circ$, and $\text{UO}_2(\text{CO}_3)_2^{2-}$ are the only species predicted to be present in significant quantities ($>1\%$) using the original MINTEQA2 database. Using the new database, these species are reduced to less than 10 percent of $\text{U}(\text{VI})_{\text{T}}$, and the dominant species is calculated to be $\text{UO}_2(\text{OH})_2^\circ$. A difference of particular interest with respect to modeling sorption is the introduction in the NEA data of anionic $\text{U}(\text{VI})$ -species at alkaline pH . This may greatly influence the modeling of sorption of uranium on charged surfaces.

Adapting the EQ3/6 database to MINTEQA2 also allows comparison of speciation predicted by the two codes. Figures 8-5 and 8-6 show $\text{U}(\text{VI})$ -speciation predicted by both EQ3 (the equilibrium speciation part of the EQ3/6 code) and MINTEQA2 as a function of pH . The match is very good in the absence of CO_2 ; with CO_2 present, the differences are slightly more pronounced. Because the thermodynamic data are identical, the variations are due to a combination of several factors related to differences in code design and model formulation.

EQ3 and MINTEQA2 differ in how activity coefficients are corrected for ionic strength effects. EQ3 uses the "b-dot" extension of the Debye-Hückel relation, while MINTEQA2 defaults to the Davies equation (Allison et al., 1990). Also, the activity coefficient (γ_i) of neutral species is expressed in MINTEQA2 by the relationship $\log \gamma_i = 0.1 I$, while EQ3 assumes $\gamma_i = 1$ for uncharged species. Another difference is in the way the codes fix pH . EQ3 balances charge, adding enough acid or base species to adjust the pH to the desired values. As a result, the ionic strength (and therefore activity coefficients) will vary as a function of pH , particularly at extreme values where more acid or base is needed. This leads to an addition of species (such as NO_3^- and CO_3^{2-}) which can complex with $\text{U}(\text{VI})$, changing the speciation. In contrast, MINTEQA2 does not have a charge balance option and externally fixes pH without considering the addition of acid or base species. As a result of this approach, the background electrolytes remain fixed, and ionic strength is largely independent of pH , varying from 0.1 M NaNO_3 only at the extreme values where H^+ and OH^- become significant.

For the speciation shown in Figure 8-6, the chief differences are at $\text{pH} < 3$ where UO_2NO_3^+ is predicted to be greater by EQ3. This is due to a higher ionic strength and a slightly greater amount of NO_3^- in solution due to charge balancing. In the range $5.5 < \text{pH} < 8.5$, the difference is due to the activity coefficient of the neutral species $\text{UO}_2(\text{OH})_2^\circ$ and $\text{UO}_2\text{CO}_3^\circ$. In MINTEQA2, $\gamma_i = 10^{0.01} = 1.023$, while EQ3 assumes that $\gamma_i = 1.0$ for these species. As can be seen from Figure 8-6, the difference between the two codes is greatest for these species, reaching a maximum when $\text{UO}_2(\text{OH})_2^\circ$ becomes the predominant species. The disparity between the two codes is also pronounced for the charged uranyl carbonate species. This is due to the increased amounts of carbonate and bicarbonate in solution from the charge balance option of EQ3.

8.2.3 Sorption Modeling with MINTEQA2

Surface complexation models consider the specific interaction between aqueous species and surface functional groups at the mineral/water interface. The surface complexes formed in this manner can then be modeled using mass action/mass balance relations. In all surface complexation models, the

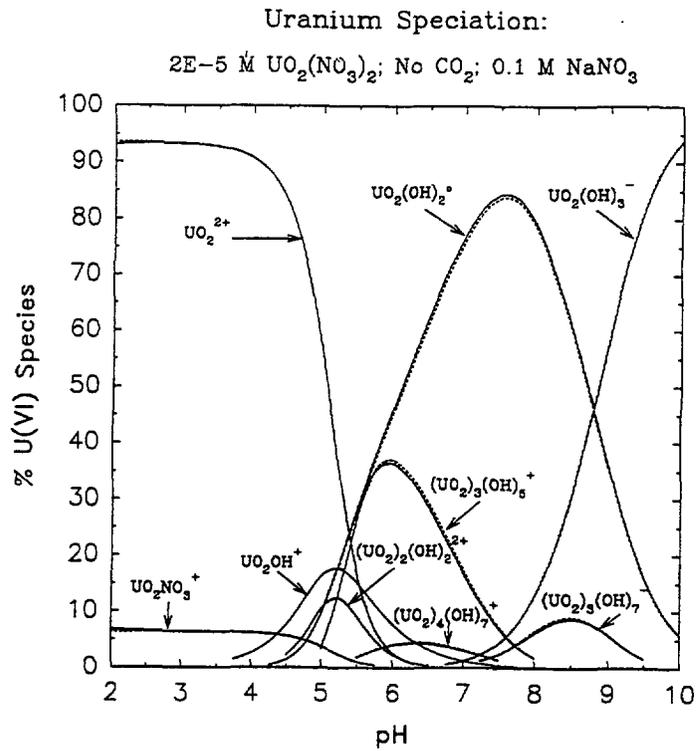


Figure 8-5. $\text{U(VI)}_T = 2 \times 10^{-5} \text{ M}$, No CO_2 , $I = 0.1 \text{ M } \text{NaNO}_3$, $T = 25^\circ \text{ C}$. U(VI) speciation predicted by EQ3 (solid lines) and MINTEQA2 (dashed lines).

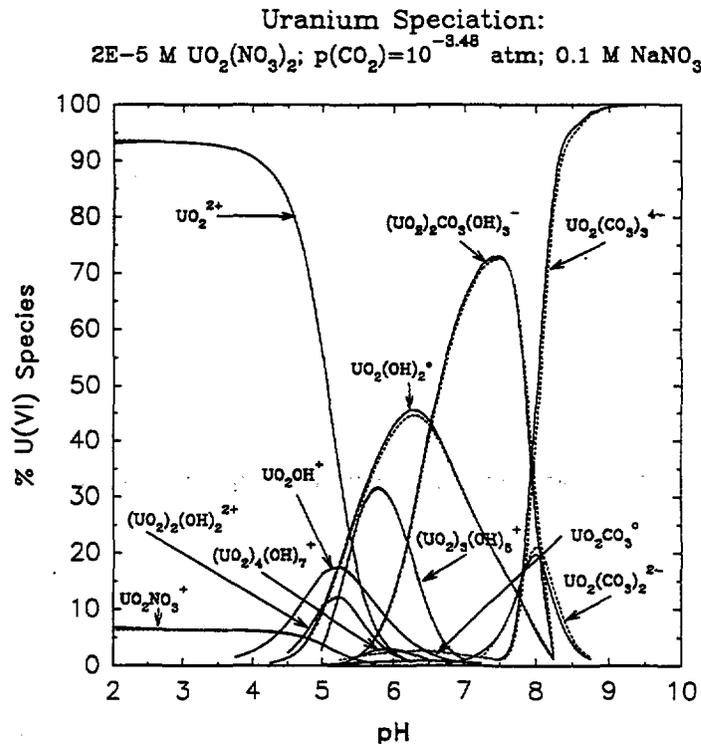


Figure 8-6. $\text{U(VI)}_T = 2 \times 10^{-5} \text{ M}$, $p(\text{CO}_2) = 10^{-3.48} \text{ atm}$, $I = 0.1 \text{ M } \text{NaNO}_3$, $T = 25^\circ \text{ C}$. U(VI) speciation predicted by EQ3 (solid lines) and MINTEQA2 (dashed lines).

particle surface with specific charge σ_s (coulombs), is separated from the bulk solution by a diffuse layer of nonspecific bound counterions. The models differ in how the mineral/water interface is divided between the charged surface and the bulk solution. Only a brief discussion is presented here. Commonly used surface complexation models are discussed in more detail elsewhere (Allison et al., 1990; Pabalan and Turner, 1992).

In writing mass action expressions for sorption reactions, activity corrections are necessary for the electrostatic effects of surface charge. For the general sorption reaction



MOH° represents a neutral surface site, and Cat^{z+} is a sorbing cation. The corresponding mass action expression K_{Cat} is

$$K_{\text{Cat}} = \frac{[\text{MO-Cat}^{(z-1)}] [\text{H}^+] e^{-\Psi_1 F/RT}}{[\text{MOH}^\circ] [\text{Cat}^{z+}] (e^{-\Psi_1 F/RT})^z} \quad (8-2)$$

where $e^{-\Psi_1 F/RT}$ is the Boltzmann factor, Ψ_1 is electrostatic potential (volts), z is the charge of the ion, F is the Faraday constant (J/volt equiv), R is the ideal gas constant (J/K·mole), and T is absolute temperature (K). A similar construction is used for describing anion adsorption (K_{An}).

Complexation models treat the formation of charged surface sites (MOH_2^+ , MO^-) from neutral MOH° sites to be the result of equilibrium protonation/deprotonation reactions of the form



Reaction (8-3) shows the pH dependence of surface charge formation. Intrinsic surface acidity constants (K_+ , K_-) are corrected for electrostatic effects in a manner analogous to Eq. (8-2).

Mass balance for the total concentration of available surface sites (T_{MOH}) is

$$T_{\text{MOH}} = (N_s) \times (\text{SA}) \times (C_s) \quad (8-4)$$

where N_s is site density (sites/m²), SA (m²/g) is specific surface area, and C_s is the solid mass (g/l). Eq. (8-4) is combined with charge-potential relationships specific to a given model and activity and mass-action relationships analogous to Eq. (8-2) to describe concentration distributions of surface and aqueous species as a function of solution chemistry and surface charge.

One of the more commonly used models (Tripathi, 1984; Sanchez et al., 1985; Hsi and Langmuir, 1985; LaFlamme and Murray, 1987; Payne and Waite, 1991), is the triple-layer surface complexation model (TLM), which divides the mineral/water interface into three layers. In this model, protonation/deprotonation at surface sites (K_+ and K_-) is restricted to the innermost o-plane, while the specifically adsorbed ions such as the background electrolyte (e.g., K_{Na^+} and $K_{\text{NO}_3^-}$ for a NaNO_3 solution) and the element of interest are typically assigned to the β -plane. The outermost layer, the d-plane, is made up of a diffuse region of counterions extending into the bulk solution.

Surface charges in the TLM are designated σ_o and σ_β for the o- and β -layers, respectively. At the boundary between the intermediate β -layer and the diffuse outer d-layer, the diffuse layer charge (σ_d) is defined such that $\sigma_o + \sigma_\beta + \sigma_d = 0$. Charge/potential relations are

$$\sigma_o = (\psi_o + \psi_\beta)C_1 \quad (8-5)$$

$$\sigma_o + \sigma_\beta = (\psi_\beta + \psi_d)C_2 = -\sigma_d \quad (8-6)$$

$$\sigma_d = -(\sqrt{8\epsilon\epsilon_o IRT}) \left[\sinh \frac{(z\psi_d F)}{2RT} \right] \quad (8-7)$$

where C_1 , and C_2 (Farads/m²) are capacitances associated with the areas between the o- and β -planes and β - and d-planes, respectively. I is the ionic strength of the medium, and z , Ψ_d , F , R , and T are as defined previously.

8.2.4 Parameter Estimation with FITEQL

Earlier studies have generally determined the required parameters for the TLM by fitting sorption data or potentiometric titration data. One approach uses graphical methods to extract sorption parameters (e.g., Kent et al., 1988). An alternative approach is numerical nonlinear optimization. Westall (1982) developed the iterative nonlinear least squares optimization program FITEQL, Version 2.0 to determine constants for several electrostatic models, including the Diffuse-Layer (DLM), Constant Capacitance (CCM), Triple-Layer (TLM), and Stern surface complexation models. The code requires experimental data for the chemical system, and Log K values and reactions for the chemical equilibrium model. Sorption-pH or potentiometric titration data are also entered. In calculating equilibrium constants, FITEQL seeks to minimize the difference between experimental values and those calculated based on mass action constraints for those components where both the free and total concentrations are known. The parameters required by FITEQL to extract sorption constants depends on the model under consideration, and is discussed in more detail elsewhere (Westall, 1982; Dzombak and Morel, 1990).

As a result of its construction, the TLM offers seven types of adjustable parameters: Protonation/Deprotonation (K_+ , K); Sorbing Background Electrolytes and Radionuclides (K_{Ca} and K_{An} such as K_{Na+} , $K_{NO_3^-}$, and $K_{UO_2^{2+}}$); Site Density (N_s), and Capacitances for the inner and outer layers (C_1 and C_2 , respectively). Earlier studies have relied largely on adjusting several of these parameters at the same time to fit observed sorption data (Davis et al., 1978; Davis and Leckie, 1978; Sanchez et al., 1985; LaFlamme and Murray, 1987). Because of the large number of parameters, it is possible, however, that the resultant fits are nonunique (Davis and Kent, 1990). In order to minimize this possibility, it is desirable to fix externally as many parameters as possible, and reducing the number of parameters fit to the data (Davis and Kent, 1990; Dzombak and Morel, 1990; Bradbury and Baeyens³).

One objective of this study has been to use the new database to evaluate radionuclide sorption data using different complexation models. The case presented here is a reinterpretation of the data of

³M.H. Bradbury, and B. Baeyens. 1991. A mechanistic approach to the generation of sorption databases. Draft Report. Nuclear Energy Agency (NEA) Sorption Workshop '91. Interlaken, Switzerland.

Tripathi (1984) for U(VI)-sorption on goethite using the NEA uranium data. The parameter values used in this study (Table 8-2) are derived from two basic sources. Hayes et al. (1989, 1991) used FITEQL to perform a sensitivity analysis of model input parameters for DLM, CCM, and TLM surface complexation models of goethite (α -FeOOH), α -Al₂O₃, and TiO₂. Based on this analysis, Hayes et al. (1991) recommended TLM constant values for N_s, C₁, C₂, and sorption constants (K_{Na+}, K_{NO3-}) for a NaNO₃ background electrolyte. Although not able to specifically fix values for K₊ and K₋, Hayes et al. (1991) recommended a value $\Delta pK_a = -[(\log K_+) + (\log K_-)] \geq 4.0$. Smith and Jenne (1991) examined the sorption literature to compile a list of parameters used in TLM models of contaminant sorption. Surface acidity constants defined a narrow range, with Log K₊ = 5.0±0.5 and Log K₋ = -10.9±0.5. These mean values meet the criteria of Hayes et al. (1991) with $\Delta pK_a = 5.9$.

With these parameters (Table 8-2), FITEQL was used to fit the controlled atmosphere (No CO₂) U(VI)-goethite sorption data of Tripathi (1984) with the TLM. After loading the parameters listed in Table 8-2 and the necessary data for the chemical equilibrium model, a series of monodentate sorption reactions involving mononuclear uranyl hydroxides [UO₂(OH)_n²⁻ⁿ] were fit to the data. All uranium sorption reactions were modeled as outer-sphere (β -plane) complexes. EXAFS data for U(VI)-sorption on iron oxide supports the use of mononuclear rather than polynuclear species (Payne et al., 1992).

The resulting values for K_{UO₂(OH)_n} are listed in Table 8-3. These values were then used with the TLM sorption option of MINTEQA2 to model the data. The results are shown in Figure 8-7(a). It is apparent that sorption reactions involving either UO₂²⁺ or UO₂OH⁺ were inadequate to model either the sorption edge or the sorption maximum (Γ_{max}). The complex MOH-UO₂(OH)₂⁰ is better able to match the sorption edge, but falls far short of Γ_{max} . This is perhaps surprising as UO₂(OH)₂⁰ is predicted to be the predominant species in the pH range of the sorption edge.

As discussed by Tripathi (1984), the complex MOH₂-UO₂(OH)₃⁰ predicts the sorption edge well, although it does not fit the data near the sorption maximum. The complexation constant (log K_{UO₂(OH)₃}) fit to the data in this study differs by several orders of magnitude from that of Tripathi (1984): -4.3 (this study, Table 8-3) versus -7.0. Most of this difference is due to the use of a different set of adjustable parameters. Incorporation of the different parameters (Tripathi, 1984, Table 3.1) in a FITEQL optimization run changes log K_{UO₂(OH)₃} from -4.3 to -6.2. Comparison of the NEA uranium data to that used by Tripathi (1984) shows only small differences between log K values for those species in common. However, a number of species included in the NEA data (e.g., UO₂(OH)₂⁰, UO₂(OH)₃⁻, UO₂(OH)₄²⁻, and (UO₂)₂(OH)₃⁺) were not considered by Tripathi (1984). These differences are likely to be responsible for the remainder of the disparity. A complexation reaction involving the formation of MOH₂-UO₂(OH)₄⁻ was considered. As shown in Figure 8-7(a), the fit to the data is extremely good.

Tripathi (1984) invoked a combination of sorption reactions involving polynuclear species to fit the data. Figure 8-7(b) shows the results of combining UO₂(OH)₂⁰, UO₂(OH)₃⁻, and UO₂(OH)₄²⁻ as compared to a simple sorption model involving the formation of a MOH₂-UO₂(OH)₄⁻ complex. It is readily apparent that the fit to the data is not significantly improved. Because one aim of Task 2 is to develop simplified sorption models, modeling the data using a single complex is preferred over the use of more complicated sorption schemes. Although UO₂(OH)₄²⁻ is not predicted to form at pH < 12, several studies suggest that hydrolysis of metal cations is enhanced at the oxide/water interface (Davis and Leckie, 1979; Tripathi, 1984; Westall, Personal Communication).

Table 8-2. Triple-layer model parameters used in the present study

Parameter	Value	Source
Log K_+	5.0	a
Log K	-10.9	a
C_1	0.8 F/m ²	b,c
C_2	0.2 F/m ²	b,c
Log K_{Na^+}	-8.33	b,c
Log $K_{NO_3^-}$	8.74	b,c
N_s	10 sites/nm ²	b,c

[a] Smith and Jenne (1991); [b] Hayes et al. (1989);
[c] Hayes et al. (1991)

8.2.5 Summary and Conclusions

The MINTEQA2 code offers seven different sorption models, but the lack of a radionuclide database has prevented extensive application to radioelement sorption. The MINTEQA2 database has been expanded to include thermodynamic data for a number of key radionuclides identified by Kerrisk (1985). The initial source selected for these data is the Data0.com.r12 release of the EQ3/6 database. The only radioelement common to the old and new databases is uranium, and comparison of the predicted speciation indicates a number of significant differences. For dilute uranium solutions, the new data indicate that the neutral species $UO_2(OH)_2^0$ is predominant in the near neutral pH range of most natural waters, instead of the cationic species $(UO_2)_3(OH)_5^+$ predicted by the old database. Perhaps the most significant change with respect to sorption modeling is the introduction of anionic species.

Comparison of U(VI) speciation calculated using EQ3 and MINTEQA2 supports the observation of Morrey et al. (1986) that the codes predict similar speciation given the same data. Differences are very small, and are most likely due to differences in the construction of the two codes related to correction of activity coefficients for ionic strength effects.

The TLM was used to evaluate the new database for sorption modeling. The large number of adjustable parameters makes it important to externally fix as many parameters as possible to minimize the possibility of nonunique fit to the data. The sensitivity analyses of Hayes et al. (1989, 1991) and the compilations of Smith and Jenne (1991) provided values for K_+ , K , N_s , C_2 , C_1 , K_{Na^+} , and $K_{NO_3^-}$, leaving only the complexation coefficient for the radionuclide to be varied to fit the data. The parameter optimization code FITEQL was used to investigate the modeling of U(VI)-sorption data of Tripathi (1984) using $MOH_m-UO_2(OH)_n$ complexes in light of the new NEA uranium data entered in MINTEQA2. The complex $MOH_2-UO_2(OH)_4^-$ produces a very good fit of the data, which is not significantly improved by the use of two or more surface complexes. Although $UO_2(OH)_2^0$ is not predicted to form in dilute U(VI) solutions at pH < 12, it is possible that cation hydrolysis is enhanced at the mineral/water interface.

Table 8-3. Surface complex constant values calculated for the U(VI)-sorption data of Tripathi (1984) with FITEQL and the NEA uranium data

Surface Complex	Complexation Constant [log $K_{UO_2(OH)_n}$]
MO-UO ₂ ⁺	-3.1
MO-UO ₂ OH [°]	-9.1
MOH-UO ₂ (OH) ₂ [°]	-6.5
MOH ₂ -UO ₂ (OH) ₃ [°]	-4.3
MOH ₂ -UO ₂ (OH) ₄ ⁻	-10.0

Because simple sorption models are likely to be more appropriate for performance assessment models, a model using a single surface complex may be preferred over more involved sorption schemes.

The work of several authors (Krupka et al., 1988; Dzombak and Morel, 1990) indicates that simple models are suitable to simulate sorption behavior. Future studies will examine the use of less elaborate sorption models such as the diffuse layer model (DLM) to model radioelement sorption data.

8.3 TASK 3—SORPTION EXPERIMENTS

To develop an understanding of important radionuclide sorption processes and the physical and chemical parameters that affect sorption behavior in the Yucca Mountain environment, experiments are under way to investigate the sorption behavior of uranium on geologic media. Uranium was selected as the initial focus of the experiments for several reasons. First, uranium comprises a large inventory in the high-level wastes which will be emplaced in the proposed repository. Second, uranium has a relatively complicated aqueous chemistry compared to radioelements such as ¹³⁷Cs and ⁹⁰Sr due to complexation reactions as well as hydrolysis leading to formation of polymeric species (Cotton and Wilkinson, 1980). Therefore, its sorption behavior is expected to be more complicated than those for ¹³⁷Cs and ⁹⁰Sr. Although the detailed aqueous chemistry of uranium is different from that of other actinides such as plutonium, americium, and neptunium, the latter radioelements exhibit similarly strong tendencies for hydrolysis and polynuclear ion formation as well as complex formation (Cotton and Wilkinson, 1980; Allard, 1982). Thus uranium is a good analog for understanding the sorption behavior of the other actinides. Third, uranium has a more extensive and better evaluated thermodynamic database for aqueous species compared to the other actinides (e.g., Grenthe et al., 1992). Such a database is a prerequisite for a mechanistic understanding of sorption processes.

The present experiments are investigating uranyl sorption on zeolite minerals, specifically on clinoptilolite. The occurrence of thick, laterally continuous horizons of clinoptilolite-rich tuffs underneath Yucca Mountain could provide important geologic barriers to radionuclide migration from the repository to the accessible environment. To evaluate the effectiveness of these zones as barriers to radionuclide

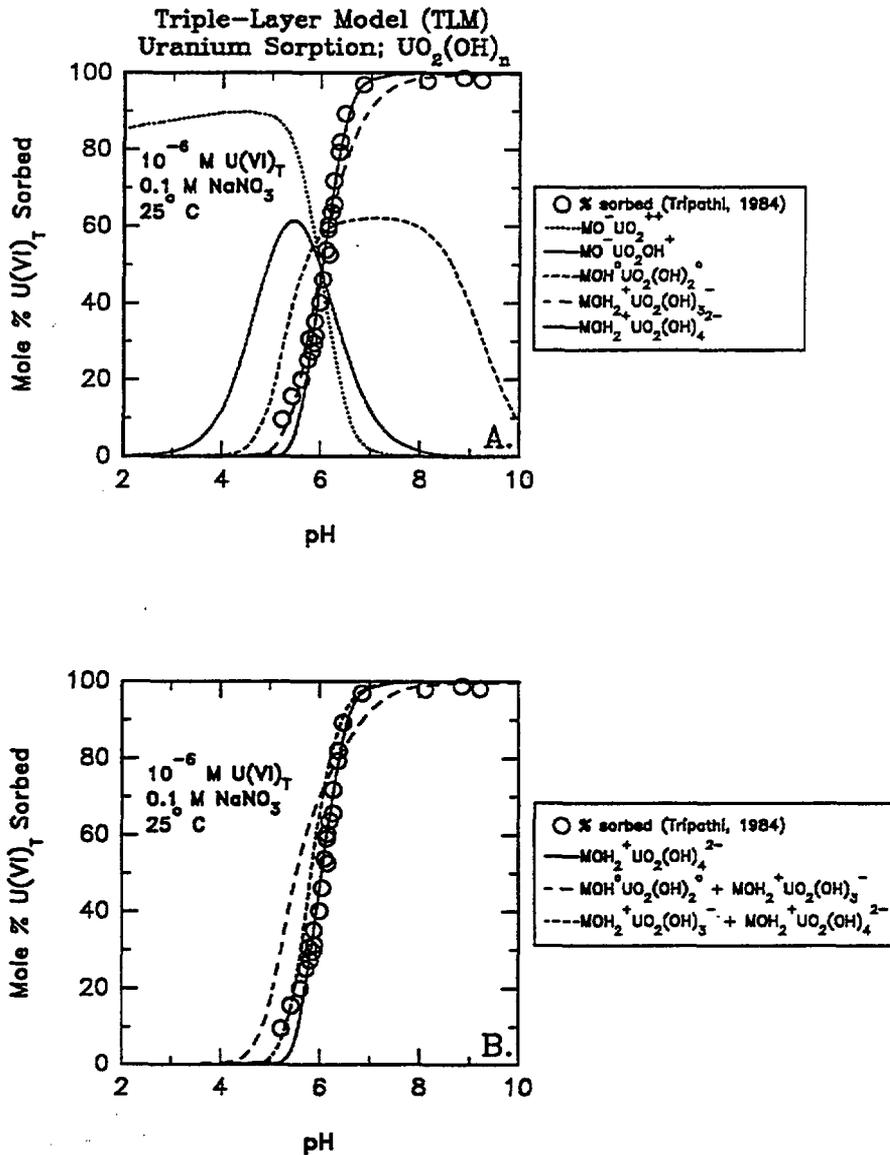


Figure 8-7. $\text{U(VI)}_T = 1 \times 10^{-6}$ M, No CO_2 , $I = 0.1$ M NaNO_3 , $T = 25^\circ \text{C}$, $\text{SA} = 50 \text{ m}^2/\text{g}$, $C_s = 0.41 \text{ g/l}$. Modeling of the U(VI) -goethite sorption data of Tripathi (1984) using the TLM as described in the text with parameter values as listed in Tables 8-2 and 8-3. (a) Models using a single mononuclear complex of the form $\text{UO}_2(\text{OH})_n^{2-n}$. (b) Models using two mononuclear uranyl hydroxide complexes. Data of Tripathi (1984) are shown by open circles.

transport, it is important to understand the fundamental controls on uranium sorption on clinoptilolite. Results of sorption experiments conducted during the first half of 1992 are presented below.

8.3.1 Experimental Procedures

The uranium sorption experiments were conducted using homoionic Na-clinoptilolite powder (100-200 mesh size) previously prepared (Pabalan, 1992) from clinoptilolite-rich tuff specimens from Death Valley Junction, California. The same material was used in conducting the ion exchange experiments and the analcime+clinoptilolite+aqueous-solution kinetics and phase equilibrium studies described in Section 2.1 of this report. In one set of experiments, 14 100-ml aliquots of a 2.0×10^{-5} m uranyl nitrate solution were each reacted at room temperature with 0.20 g of clinoptilolite in 125-ml polypropylene bottles on gyratory shakers. The uranyl solutions were prepared from reagent grade $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Another set of 14 mixtures used solutions of 2.0×10^{-6} m uranyl nitrate.

Prior to addition of the solid phase, the pH of each uranium solution was adjusted to a value in the range 2.5 to 9.0 and at approximately 0.5 pH interval by addition of HNO_3 or NaHCO_3 . The amount of reagent needed to achieve the desired pH was estimated using the EQ3 geochemical code (version 3245R124) and associated database (Data0.com.r12). The solutions, which were kept open to atmospheric $\text{CO}_2(\text{g})$ throughout the experiment, were agitated using gyratory shakers for several days. The pH of each solution was measured periodically with an Orion Ross combination glass electrode until a constant value was attained. Subsequently, clinoptilolite powder was added to each solution to initiate the sorption experiment.

After at least two weeks, two 10-ml samples of each solution were taken; 0.5 ml of a 1.05 M tartaric-acid/triethanolamine solution was immediately added to each sample for later analysis of uranium concentration using an EG&G Princeton Applied Research Model 384B polarographic analyzer. The equilibrium pH of each solution was also measured.

A second series of experiments was conducted to determine the reproducibility and/or reversibility of the sorption reactions. These were initiated by adding dropwise HNO_3 solution to each mixture at the end of the first series of experiments such that the pH decreased by about 0.5 to 1.0 pH unit. The mixtures were then allowed to reequilibrate for at least two weeks. Subsequently, the new equilibrium pH of each solution was measured and samples were taken for polarographic analysis of uranium concentration.

8.3.2 Experimental Results

The results of the uranium sorption experiments are summarized in Figures 8-8(a) and 8-8(b), for mixtures with initial uranium concentrations of 2.0×10^{-5} and 2.0×10^{-6} m, respectively. Each point on the figures is the average of replicate analyses of the two samples from each solution. The results indicate that uranium sorption on clinoptilolite is strongly dependent on pH. The amount of uranium lost from solution increases sharply at pH values above about 3.5 over a narrow pH range ('adsorption edge'). At near neutral pH (~ 6.5) almost complete removal (> 90 percent) of uranium from solution occurs. However, at $\text{pH} > 6.5$ where carbonate complexation of uranium becomes important, the amount of uranium sorbed on the solid phase sharply decreases ('desorption edge').

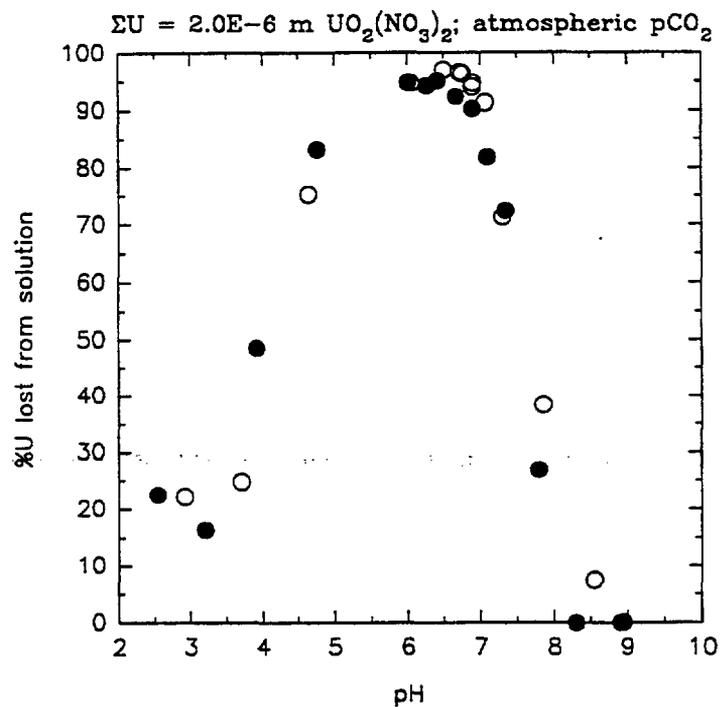
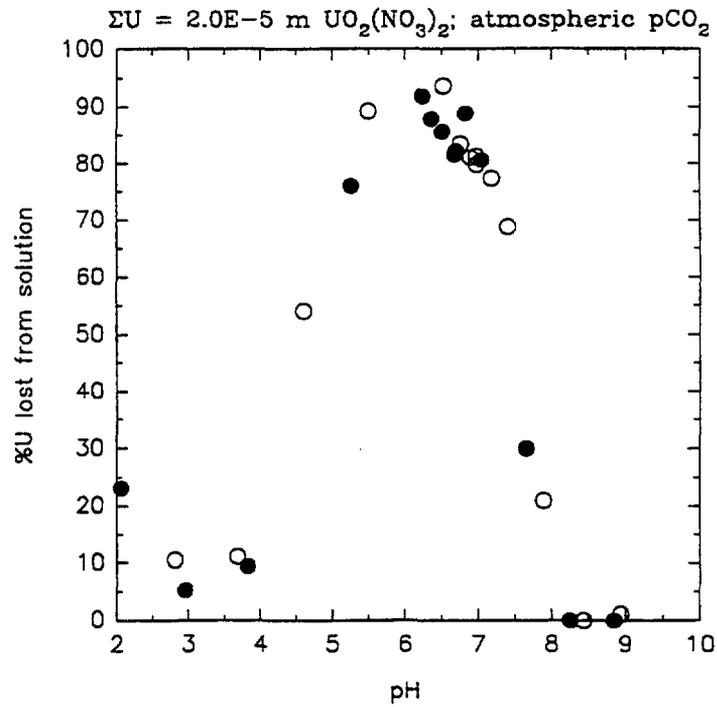


Figure 8-8. Uranium sorption on clinoptilolite versus pH for solutions with initial uranium concentrations of (a) 2.0×10^{-5} and (b) 2.0×10^{-6} m. The open and closed circles represent data from the first and second series of experiments, respectively.

At pH less than 3.5, the amount of uranium lost from solution appears to increase with decreasing pH. In this pH range, most of the aqueous uranium is present as the UO_2^{2+} species. A comparison of the size of the linear molecule UO_2^{2+} with the dimensions of the intracrystalline channels in clinoptilolite suggests that an ion exchange reaction is possible between UO_2^{2+} in solution and Na^+ initially in the zeolite intracrystalline cation exchange sites. Additional experiments are under way to investigate this sorption mechanism.

The open and closed circles in Figure 8-8 represent, respectively, data from the first and second series of sorption experiments. The agreement within experimental uncertainty of the two sets of data demonstrates the reproducibility of uranium sorption on clinoptilolite. In addition, the closed circles at pH less than about 6.5 represent reversals along the adsorption edge and indicate that the uranium sorption reactions are reversible. Furthermore, a comparison of data in Figures 8-8(a) and 8-8(b) indicates that the adsorption edge shifts to lower pH with a decrease in initial total uranium concentration. This is consistent with the trends in uranium sorption observed by Tripathi (1984) and by Payne et al. (1992) in their studies using goethite and ferrihydrite, respectively.

Aqueous uranium speciation as a function of pH was calculated using the EQ3 geochemical code and the NEA uranium thermodynamic database (Grenthe et al., 1992) for solutions corresponding to those used in the sorption experiments. The relative stability of the aqueous uranyl species are plotted as a function of pH in Figures 8-9(a) and 8-9(b) for solutions in equilibrium with atmospheric $\text{CO}_2(\text{g})$ and with total uranium concentrations of 2.0×10^{-5} and 2.0×10^{-6} m, respectively. A comparison of Figures 8-8 and 8-9 indicates that uranium sorption on clinoptilolite becomes important in the pH range where $\text{UO}_2(\text{OH})_2^\circ$ is the predominant aqueous uranium species.

8.3.3 Conclusions

Experiments on uranium sorption on the zeolite mineral clinoptilolite were conducted to evaluate the potential importance of clinoptilolite-rich tuffs underneath Yucca Mountain as barriers to radionuclide migration. The results of sorption experiments conducted during the first half of 1992 demonstrate that sorption of uranium on clinoptilolite is strongly dependent on solution pH. Almost complete removal (>90 percent) of uranium from solution is possible at pH values near neutral, but uranium sorption decreases rapidly at pH away from neutral. A comparison of uranium sorption and aqueous speciation indicates that sorption of uranium on clinoptilolite is important in the pH range where $\text{UO}_2(\text{OH})_2^\circ$ is the predominant aqueous species. The pH range in which the uranium adsorption edge occurs shows a dependence on uranium concentration which is consistent with results obtained by other investigators using different geologic material.

The dependence of uranium sorption on several geochemical parameters implies that a simple distribution coefficient (K_d) to describe radionuclide sorption may be of limited use in predicting uranium migration through geologic media under conditions where the groundwater chemistry exhibits spatial and temporal variability. A better approach may be to use mechanistic type of sorption models such as those described in Section 8.2.

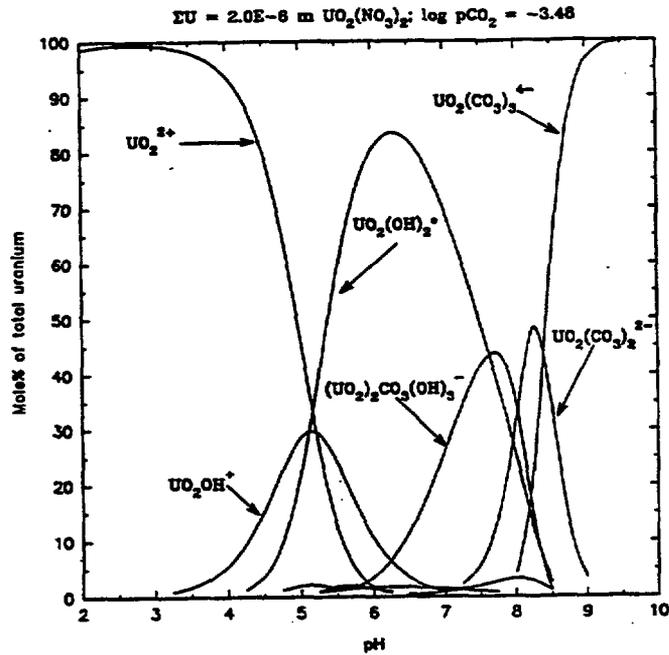
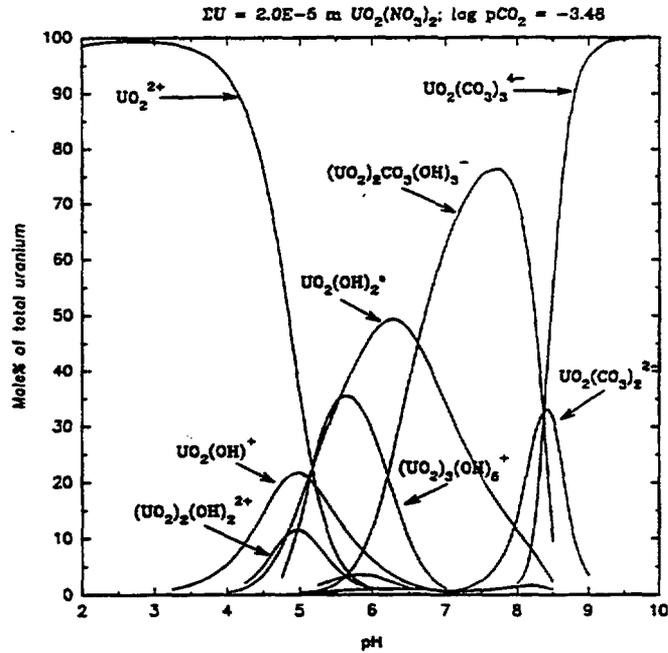


Figure 8-9. Relative stability of uranyl aqueous species as a function of pH for solutions in equilibrium with atmospheric $CO_2(g)$ and concentrations of (a) 2.0×10^{-5} and (b) 2.0×10^{-6} m $UO_2(NO_3)_2$. The calculations were done using the EQ3 geochemical code (version 3245R124). For clarity, uranium species with maximum percentage less than about 5 percent of total uranium are not labeled or included.

8.4 REFERENCES

- Allard, B. 1982. Solubilities of actinides in neutral or basic solutions. N.M. Edelstein, ed. *Actinides in Perspective*. Pergamon Press:553-580.
- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1990. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems:Version 3.0 user's manual*. Environmental Research Laboratory. Office of Research and Development. Athens, GA:EPA.
- Baes, C.F., and R.E. Mesmer. 1976. *The Hydrolysis of Cations*. New York:Wiley-Interscience Publication, John Wiley and Sons.
- Ball, J.W., and D.K. Nordstrom. 1991. *User's Manual for WATEQ4F, With Revised Thermodynamic Data Base and Test Cases for Calculating Speciation of Major, Trace, and Redox Elements in Natural Waters*. USGS-OF-91-183. Menlo Park, CA:U.S. Geological Survey (USGS).
- Ball, J.W., E.A. Jenne, and M.W. Cantrell. 1981. *WATEQ3- A Geochemical Model With Uranium Added*. USGS-OF-81-1183. Menlo Park, CA:USGS.
- Carnahan, C.L. 1988. Some effects of data base variations on numerical simulations of uranium migration. *Radiochimica Acta* 44/45:349-354.
- Cotton, F.A., and G. Wilkinson. 1980. *Advanced Inorganic Chemistry*. New York:John Wiley and Sons.
- Cox, J.D., D.D. Wagman, and V.A. Medvedev, eds. 1989. *CODATA Key Values for Thermodynamics*. New York:Hemisphere Publishing.
- Cross, J.E., and F.T. Ewart. 1991. HATCHES - A thermodynamic database and management system. *Radiochim. Acta* 52/53:421-422.
- Davis, J.A., and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Reviews in Mineralogy:Volume 23. Mineral-Water Interface Geochemistry*. M.F. Hochella, Jr. and A.F. White, eds. Washington, DC:Mineralogical Society of America:177-260.
- Davis, J.A., and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J. Coll. Interface Sci.* 67:90-107.
- Davis, J.A., and J.O. Leckie. 1979. Speciation of adsorbed ions at the oxide water interface. *Chemical Modeling in Aqueous Systems, Speciation, Sorption, Solubility, and Kinetics*. E.A. Jenne, ed. ACS Symposium Series 93. Washington, DC:American Chemical Society:299-317.

- Davis, J.A., R.O. James, and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface 1. Computation of electrical double layer properties in simple electrolytes. *J. Coll. Interface Sci.* 63:480-499.
- Dzombak, D.A., and F.M.M. Morel. 1990. *Surface Complexation Modeling:Hydrous Ferric Oxide*. New York:John Wiley and Sons.
- EPA (40 CFR Part 191). 1991. *Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes*. Title 40, Protection of Environment, Part 191. U.S. Government Printing Office. Washington, DC.
- Fuger, J., and F.L. Oetting. 1976. *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 2. The Actinide Aqueous Ions*. Vienna, Austria:International Atomic Energy Agency (IAEA).
- Garrels, R.M., and C.L. Christ. 1965. *Solutions, Minerals, and Equilibria*. San Francisco, CA:Freeman, Cooper and Company.
- Grenthe, I., J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. 1992. *Chemical Thermodynamics Series, Volume 1:Chemical Thermodynamics of Uranium*. Nuclear Energy Agency (NEA), Organization for Economic Cooperation and Development (OECD). New York:Elsevier.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1989. *Application of Surface Complexation Models for Radionuclide Adsorption:Sensitivity Analysis of Model Input Parameters*. NUREG/CR-5547 PNL-7239. Washington, DC:NRC.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1991. Surface complexation models:An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Coll. Interface Sci.* 142:448-469.
- Hemingway, B.S. 1982. *Thermodynamic Properties of Selected Uranium Compounds and Aqueous Species at 298.15 K and 1 bar and at higher temperatures--Preliminary Models for the Origin of Coffinite Deposits*. U.S. Geological Survey Open-File Report, USGS-OFR-82-619. Reston, VA:USGS.
- Hsi, C.-K.D. and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* 49:1931-1941.
- Jackson, K.J., and J.C. Helgeson. 1985. Chemical and thermodynamic constraints on the hydrothermal transport and deposition of tin. I. Calculation of the solubility of cassiterite at high pressures and temperatures. *Geochim. Cosmochim. Acta* 49:1-22.
- Johnson, J.W., E.H. Oelkers, and H.C. Helgeson. 1991. *SUPCRT92: A Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous*

- Species, and Reactions from 1 to 5000 bars and 0° to 1000°C.* Livermore, California: Lawrence Livermore National Laboratory (LLNL).
- Kent, D.B., V.S. Tripathi, N.B. Ball, J.O. Leckie, and M.D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments.* NUREG/CR-4807, SAND86-7175. Washington, DC:NRC.
- Kerrisk, J.F. 1984. *Americium Thermodynamic Data for the EQ3/6 Data Base.* LA-10040-MS. Los Alamos, NM:Los Alamos National Laboratory (LANL).
- Kerrisk, J.F. 1985. *An Assessment of the Important Radionuclides in Nuclear Waste.* LA-10414-MS. Los Alamos, NM:LANL.
- Kerrisk, J.F., and R.J. Silva. 1986. A Consistent Set of Thermodynamic Constants for Americium(III) Species with Hydroxyl and Carbonate. *Proceedings of the Workshop on Geochemical Modeling.* Fallen Leaf Lake, CA:167-175.
- Krupka, K.M., R.L. Erikson, S.V. Mattigod, J.A. Schramke, and C.E. Cowan. 1988. *Thermochemical Data Used by the FASTCHEM Package.* EPRI-EA-5872, Palo Alto, CA:Electric Power Research Institute (EPRI).
- Kubaschewski, O., and C.B. Alcock. 1979. *Metallurgical Thermochemistry.* 5th Ed. Oxford, UK:Pergamon Press.
- LaFlamme, B.D., and J.W. Murray. 1987. Solid/Solution Interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochim. Cosmochim. Acta* 51:243-250.
- Langmuir, D. 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta* 42:547-569.
- Langmuir, D., and J.S. Herman. 1980. The mobility of thorium in natural waters at low temperatures. *Geochim. Cosmochim. Acta* 44:1753-1766.
- Lemire, R.J. 1984. *An Assessment of the Thermodynamic Behavior of Neptunium in Water and Model Groundwater from 25 to 150° C.* AECL-7817. Pinawa, Manitoba:Atomic Energy of Canada Limited (AECL).
- Lemire, R.J., and P.R. Tremaine. 1980. Uranium and plutonium equilibria in aqueous solutions to 200° C. *J. Chem. Eng. Data.* 25:361-370.
- Mills, K.C. 1974. *Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides.* London, UK:Butterworths.
- Morrey, J.R., C.T. Kincaid, C.J. Hostetler, S.B. Yabusaki, and L.W. Vail. 1986. *Geochemical Models for Solute Migration. Volume 3: Evaluation of Selected Computer Codes.* EPRI-EA-3417. Palo Alto, CA:EPRI.

- Morss, L.R. 1986. Thermodynamic properties. *The Chemistry of the Actinide Elements*, 2nd Ed. T.T. Katz, G. Seaborg, and L.R. Morss, eds. New York:Chapman and Hall:1278-1360.
- Nash, K.L., and J.M. Cleveland. 1984. The thermodynamics of plutonium(IV) complexation by fluoride and its effect on plutonium(IV) speciation in natural waters. *Radiochim. Acta* 36:129-134.
- Naumov, G.B., B.N. Ryzhenko, and I.L. Khodakovsky. 1974. *Handbook of Thermodynamic Data*. USGS-WRD-74-001, trans. NTIS-PB-226 722/AS. Springfield, VA:National Technical Information Service.
- Oetting, F.L., M.H. Rand, and R.J. Ackerman. 1976. *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 1. The Actinide Elements*. Vienna, Austria: IAEA.
- O'Hare, P.A.G., B.M. Lewis, S.N. Nguyen. 1988. *Thermochemistry of Uranium Compounds, XVII. Standard Molar Enthalpy of Formation at 298.15 K of Dehydrated Schoepite $UO_3 \cdot 0.9 H_2O$. Thermodynamics of Schoepite + Dehydrated Schoepite + Water*. UCRL-21053 s/c 610-007. Livermore, CA:LLNL.
- Owens, B.B., and S.W. Mayer. 1964. The thermodynamic properties of uranyl sulphate. *J. Inorg. Nucl. Chem.* 26:501-507.
- Pabalan, R. T. 1992. Unsaturated mass transport (Geochemistry): Experimental Studies. *Report on Research Activities for Calendar Year 1991*. W. C. Patrick, ed. CNWRA 91-01A. San Antonio, TX: CNWRA: 2-1 to 2-24.
- Pabalan, R.T., and D.R. Turner. 1992. Sorption modeling for HLW performance assessment. *Report on Research Activities for Calendar Year 1991*. W.C. Patrick, ed. CNWRA 91-01A. San Antonio, TX:CNWRA.
- Payne, T.E., and T.D. Waite. 1991. Surface complexation modeling of uranium sorption data obtained by isotope exchange techniques. *Radiochim. Acta* 52/53:487-493.
- Payne, T.E., K. Sekine, J.A. Davis, and T.D. Waite. 1992. Modeling of radionuclide sorption processes in the weathered zone of the Koongarra ore body. P. Duerden, ed. *Alligator Rivers Analog Project Annual Report, 1990-1991*. Australian Nuclear Science and Technology Organization (ANSTO).
- Phillips, S.L., F.V. Hale, L.F. Silvester, and M.D. Siegel. 1988. *Thermodynamic Tables for Nuclear Waste Isolation: Aqueous Solutions Database*. NUREG/CR-4864. Washington, DC:NRC.
- Rard, J.A. 1983. *Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species*. UCRL-53440. Livermore, CA:LLNL.

- Rard, J.A. 1984. *Errata Sheet to UCRL-53440*. Unpublished Note, March 1984:LLNL.
- Rard, J.A. 1985a. Chemistry and thermodynamics of ruthenium and some of its inorganic compounds and aqueous species. *Chemical Rev.* 85:1-39.
- Rard, J.A. 1985b. Chemistry and thermodynamics of europium and some of its simpler inorganic compounds and aqueous species. *Chemical Rev.* 85:555-582.
- Rard, J.A. 1987a. *Thermodynamic Data Bases for Multivalent Elements: An Example for Ruthenium*. UCRL-96555. Livermore, CA:LLNL.
- Rard, J.A. 1987b. *Update of the Europium Data Base, October, 1987*. Internal Memorandum: LLNL.
- Reardon, E.J. 1981. K_d 's - Can they be used to describe reversible ion sorption reactions in contaminant migration? *Groundwater* 19:279-286.
- Rickard, D.T., and J.O. Nriagu. 1978. Aqueous environmental chemistry of lead. *The Biochemistry of Lead in the Environment*. J.O. Nriagu, ed. New York:Elsevier.
- Robie, R.A., B.S. Hemingway, and J.R. Fisher. 1979. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar (10⁵ Pascals) Pressure and At Higher Temperatures*. USGS Bull. 1452. Reston, VA:USGS.
- Sanchez, A.L., J.W. Murray, and T.H. Sibley. 1985. The adsorption of plutonium IV and V on goethite. *Geochim. Cosmochim. Acta* 49:2297-2307.
- Schwab, A., and A. Felmy. 1982. *Review and Reevaluation of Pu Thermodynamic Data, Draft Manuscript*. PNL-SA-10731. Richland, WA:Pacific Northwest Laboratory (PNL).
- Smith, R.M., and A.E. Martell. 1976. *Critical Stability Constants. Volume 4:Inorganic Complexes*. New York:Plenum Press.
- Smith, R.W., and J.A. Jenne. 1991. Recalculation, evaluation, and prediction of surface complexation constants for metal adsorption on iron and manganese oxides. *Environ. Sci. Technol.* 25:525-531.
- Tripathi, V.S. 1984. *Uranium(VI) Transport Modeling: Geochemical Data and Submodels*. Ph.D. Dissertation. Stanford, CA:Stanford University.
- Turner, D.R. 1991. *Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review*. CNWRA 91-011. San Antonio, TX:CNWRA.
- Viani, B.E., and C.J. Bruton. 1992. Modeling ion exchange in clinoptilolite using the EQ3/6 geochemical modeling code. *Proceedings of the Seventh International Symposium on Water-Rock Interaction. Volume 1: Low Temperature Environments*. Rotterdam, Netherlands:A.A. Balkema: 73-77.

- Wagman, D.D., W.H. Evans, V.B. Parker, R.H. Shumm, I. Halow, and S.M. Bailey. 1982. *The NBS Tables of Chemical Thermodynamic Properties. Selected Values for Inorganic and C1 and C2 Organic Substances in SI Units*. New York, NY:American Chemical Society.
- Westall, J.C. 1982. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 2.0*. Rpt. 82-02. Corvallis, Oregon:Department of Chemistry, Oregon State University.
- Westall, J.C., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.* 12:265-294.
- Westall, J.C., J.L. Zachary, and F.M.M. Morel. 1976. *MINEQL, A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems*. Tech. Note 18. Cambridge, MA:Department of Civil Engineering, Massachusetts Institute of Technology.
- Wolery, T.J., K.J. Jackson, W.L. Bourcier, B.E. Bruton, K.G. Knauss, and J.M. Delany. 1990. *Current Status of the EQ3/6 Software Package for Geochemical Modeling*. Chemical Modeling of Aqueous Systems II. D. Melchior, R. L. Bassett, eds. ACS Symposium Series 416. Washington, DC:104-116.8.1.
- Yeh, G.T., and V.S. Tripathi. 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* 25:93-108.

8 SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

by Roberto T. Pabalan and David R. Turner

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8.1 TECHNICAL OBJECTIVES

A fundamental concern in evaluating the suitability of Yucca Mountain, Nevada, as a repository for high-level nuclear wastes (HLW) is the possibility of radionuclide migration from the repository to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is sorption of radionuclides on minerals encountered along the flow paths. Sorption is specifically referred to in 10 CFR 60.122(b) as a favorable geochemical condition that will tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed [10 CFR 60.122(c)(8)] as a potentially adverse condition that could reduce the effectiveness of the natural barrier system.

To support the U.S. Nuclear Regulatory Commission's (NRC) HLW program, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is conducting research activities under the Sorption Modeling for HLW Performance Assessment Research Project. The broad objectives are to develop sufficient understanding of radionuclide transport issues so that timely precicensing guidance can be provided to the U.S. Department of Energy (DOE) and a sound basis be available for evaluating the DOE license application. Specifically, the results will be used in addressing NRC's needs in evaluating the use of K_d 's in modeling sorption. Results of the completed Task 1 (Literature Review and Development of Approach) have been reported previously. Results of activities undertaken in Task 2 (Hydrogeochemical Modeling) and Task 3 (Sorption Experiments) are discussed below.

8.2 TASK 2—HYDROGEOCHEMICAL MODELING

8.2.1 Introduction

Sorption is generally incorporated into performance assessment models through the use of an empirical linear sorption isotherm, which assumes that sorption of a given radionuclide increases linearly with the concentration in solution. The advantage to this approach lies in its computational simplicity, representing water/rock interaction through a single sorption coefficient (K_d). The limitations to this approach have been discussed in detail elsewhere (Reardon, 1981; Kent et al., 1988; Turner, 1991), and focus on the inability of empirical models to consider changes in solution chemistry and variations in the mineral/water interface. Because many minerals are known to exhibit complex pH-dependent sorption behavior (Kohler et al., 1992), strict application of an empirical approach would require a different K_d value for each change in the physical and/or chemical system. This can quickly lead to excessive experimental burden to represent the heterogeneous conditions likely to be encountered in the geologic environment of interest. As an alternative, more mechanistic approaches to sorption modeling have been developed that are able to consider changes in geochemical conditions and model complex sorption behavior with a relatively small set of parameters (Davis and Kent, 1990). However, the complexity and

computational requirements of these models work against their ready incorporation in performance assessment codes. Therefore, practical application of mechanistic sorption models to performance assessment requires that a balance be struck between model completeness and computational efficiency, streamlining the model where possible. Comparison and evaluation of different modeling approaches is a necessary part of this process.

Surface complexation models (SCMs) represent one type of mechanistic approach that has been used to model contaminant sorption on oxide surfaces over a wide range in chemical conditions (e.g., pH, ionic strength, total concentration of adsorbate) (Sanchez et al., 1985; Girvin et al., 1991; Payne et al., 1992). These models are distinctive in that they attempt to consider the electrostatic interactions at the mineral-water interface. More commonly used SCMs include: Triple-Layer (TLM), Diffuse-Layer (DLM) and Constant Capacitance (CCM) models (Davis and Kent, 1990). These models and their limitations are described in detail elsewhere (Westall and Hohl, 1980; Turner, 1991; Pabalan and Turner, 1992). The application of these models requires a set of model-specific parameters representing the system chemistry and the properties of the adsorbent; the number of parameters varies with the complexity of the model. The values of these parameters are imperfectly known, however, and in practice they have tended to be used as multiple fitting parameters (e.g., Sanchez et al., 1985; Hsi and Langmuir, 1985; LaFlamme and Murray, 1987). Because of both fundamental differences in how the models treat the mineral-water interface and the tendency to use model-specific nonstandard parameters, it is difficult to compare directly the results of different studies, and even more difficult to compare the performance of different models for a given data set (Westall and Hohl, 1980).

One recently advocated approach to addressing this problem is the selection of a standard set of parameters that is uniformly applied in all systems (Davis and Kent, 1990; Hayes et al., 1991; Bradbury and Baeyens, 1992). While this approach may not truly represent the exact physical, electrostatic, and chemical processes operating at the mineral-water interface, it does limit the number of adjustable parameters and serves to establish a baseline that will allow future direct comparison of modeling results and the evaluation of model performance. In addition, such an approach may be desirable from the point of view of developing simple, flexible sorption models with internally consistent databases for performance assessment.

Hayes et al. (1991) derived a set of "standard" input parameters for the TLM, DLM, and CCM models using the FITEQL nonlinear least squares parameter estimation code (Westall, 1982) to perform a sensitivity analysis of potentiometric titration data for different oxide/water systems. As appropriate, the necessary parameters include: Protonation and deprotonation constants (K_+ and K_-); Capacitance (C_1 and C_2); Site density (N_s); and Binding constants (K_{Na+} and K_{NO_3}) for the TLM, DLM, and CCM models. Table 8-1 gives the parameters values derived by Hayes et al. (1991) for goethite (α -FeOOH). Values for K_+ and K_- of the TLM were fixed at the mean values determined by Smith and Jenne (1991) based on an exhaustive literature compilation. These values meet the criteria established by Hayes et al. (1991) that $\Delta pK_a = -[(\log K_+) + (\log K_-)] \geq 4.0$. It is worth noting that the TLM has the largest number of adjustable parameters, while the DLM has the fewest.

8.2.2 Modeling U(VI)-goethite sorption in the UO_2^{+2} - H_2O System

To compare the performance of the different models, the data of Tripathi (1984) for U(VI)-sorption on goethite [specific surface area (A_{sp}) = $50m^2/g$] were re-examined using the FITEQL code and

Table 8-1. Independently fixed SCM parameters for goethite used in this study. Except as noted, data are from Hayes et al. (1991).

Parameter	TLM	CCM	DLM
Log K ₊	5.0 _(a)	6.8	7.1
Log K ₋	-10.9 _(a)	-10.2	-10.2
C ₁ (F/m ²)	0.8	1.0	—
C ₂ (F/m ²)	0.2	—	—
Log K _{Na⁺}	-8.33	—	—
Log K _{NO₃⁻}	8.74	—	—
N _S (sites/nm ²)	10	10	10

(a) TLM values from Smith and Jenne (1991)

the parameters listed in Table 8-1. In addition to the input parameters (Table 8-1) and sorption data, FITEQL requires the input of a chemical equilibrium model for the system under investigation. For this reason, the resultant equilibrium constants for the surface complexation reactions are dependent on the thermodynamic data available for the system of interest. Equilibrium constants for the formation of uranyl aqueous species were taken from the comprehensive NEA uranium database (Grenthe et al., 1992) and corrected for ionic strength effects using the Davies equation (Dzombak and Morel, 1990). Because there is no real theoretical understanding of the activity coefficients of surface species (Westall and Hohl, 1980), unit activity was assumed. Since one objective of this exercise is to develop simple sorption models for performance assessment, uranium sorption for the CO₂-free system was modeled assuming monodentate complexation reactions involving only a single mononuclear uranyl hydroxide species [UO₂(OH)_n²⁻ⁿ] of the general form:



Undoubtedly, the models could be further refined to produce a better fit to the data by invoking more than one surface complex, multidentate sorption, and/or consideration of polynuclear species. However, to satisfy the need to develop simple models for performance assessment, the principal of parsimony has been adopted. While this type of approach may not reflect the actual surface complex that is formed (Manceau and Charlet, 1991), it allows comparison of different modeling strategies.

Table 8-2 lists the equilibrium constants (or binding constants) determined using FITEQL for reactions of the type presented in Eq. (8-1). It is apparent that the resultant values are model dependent. Because both protonation and deprotonation of surface sites and specific adsorption of uranyl species occurs in the same plane for the CCM and DLM models, the electrostatic correction applied to the mass action represented in Eq. (8-1) is the same for like-charged surface complexes. As a result, the binding constants (log K) determined in the fitting exercise are the same (e.g., log K for the CCM or DLM are

Table 8-2. Log K values derived using FITEQL. (Data from Tripathi, 1984; $U(VI)_T = 1.05 \times 10^{-6}$ M, No CO_2 , 0.1 M $NaNO_3$).

Surface Species	Log K		
	TLM	CCM	DLM
$MO-UO_2^+$	-4.1	0.9	1.0
$MOH-UO_2^{+2}$	4.6	8.7	8.8
$MO-UO_2OH^0$	-9.6	-7.0	-7.0
$MOH-UO_2OH^+$	-1.2	0.9	1.0
$MO-UO_2(OH)_2^-$	-15.0	-14.9	-15.0
$MOH-UO_2(OH)_2^0$	-6.9	-7.0	-7.0
$MOH_2-UO_2(OH)_2^+$	1.5	0.9	1.0
$MOH-UO_2(OH)_3^-$	-12.6	-14.9	-15.0
$MOH_2-UO_2(OH)_3^0$	-4.5	-7.0	-7.0
$MOH-UO_2(OH)_4^{-2}$	-18.0	-22.8	-22.9
$MOH_2-UO_2(OH)_4^-$	-10.2	-14.9	-15.0

identical for $MOH-UO_2(OH)_2^0$ and $MO-UO_2OH^0$). Also, the three surface complexes formed assuming a neutral aqueous species $UO_2(OH)_2^0$ result in similar binding constants for all three models. This is due to the fact that for a neutral species, there is no electrostatic correction for specific uranyl adsorption, and the entire surface charge is assumed to be due to protonation and deprotonation. The slight variations (less than an order of magnitude) are due to differences in the charge/potential relationship assumed by the different models.

After generating the values listed in Table 8-2, the MINTEQA2 geochemical code (Allison et al., 1991) with a radionuclide database developed at the CNWRA (Pabalan and Turner, 1992; Turner et al., 1993) was used to model the CO_2 -free U(VI)-goethite system studied by Tripathi (1984). Surface complexation models treat reactions at the surface in a fashion equivalent to aqueous speciation reactions in solution. As a result, surface sites effectively "compete" with the solution for available uranium. Due to mass balance constraints, uranium in solution is reduced by the amount sorbed on the solids. Since a surface such as goethite acts as a uranium sink over at least part of the pH range considered, the aqueous speciation predicted in the presence of a solid will differ from that predicted for a pristine $U(VI)-H_2O \pm CO_2$ system.

The resultant fit to the data calculated using MINTEQA2 for the different SCMs is shown in Figure 8-1. For clarity, and because the CCM and DLM considers like-charged surface complexes to be the same, only one example of each type of charged surface complex (i.e., +2, +1, -1, -2) is shown. The TLM model fits the observed data very well assuming a single complex of the form $\text{MOH-UO}_2(\text{OH})_4^{-2}$ and provides the best fit to the data for all the models. This is understandable given the greater complexity and larger number of parameters in the TLM. However, the simplest model, the DLM, produces a reasonable fit to the data assuming the formation of $\text{MOH-UO}_2(\text{OH})_4^{-2}$. The fit to the data is reasonable up to a pH of about 6, but falls short of the sorption maximum, Γ_{max} . Because such a reasonable fit is achieved using such a simple model, we investigated the DLM more in depth. At first, an attempt was made to vary the binding constant $K_{\text{MOH-UO}_2(\text{OH})_4^{-2}}$ systematically (Figure 8-2a). It is apparent that for a log K slightly greater than that determined by FITEQL (-22 versus -22.9), the model provides a feasible fit to the data. Although the sorption edge is slightly overpredicted and Γ_{max} is slightly underpredicted, the model is able to reproduce the general aspects of the observed sorption behavior over a pH range (4 to 10) that spans the entire range of pH values measured in waters at Yucca Mountain.

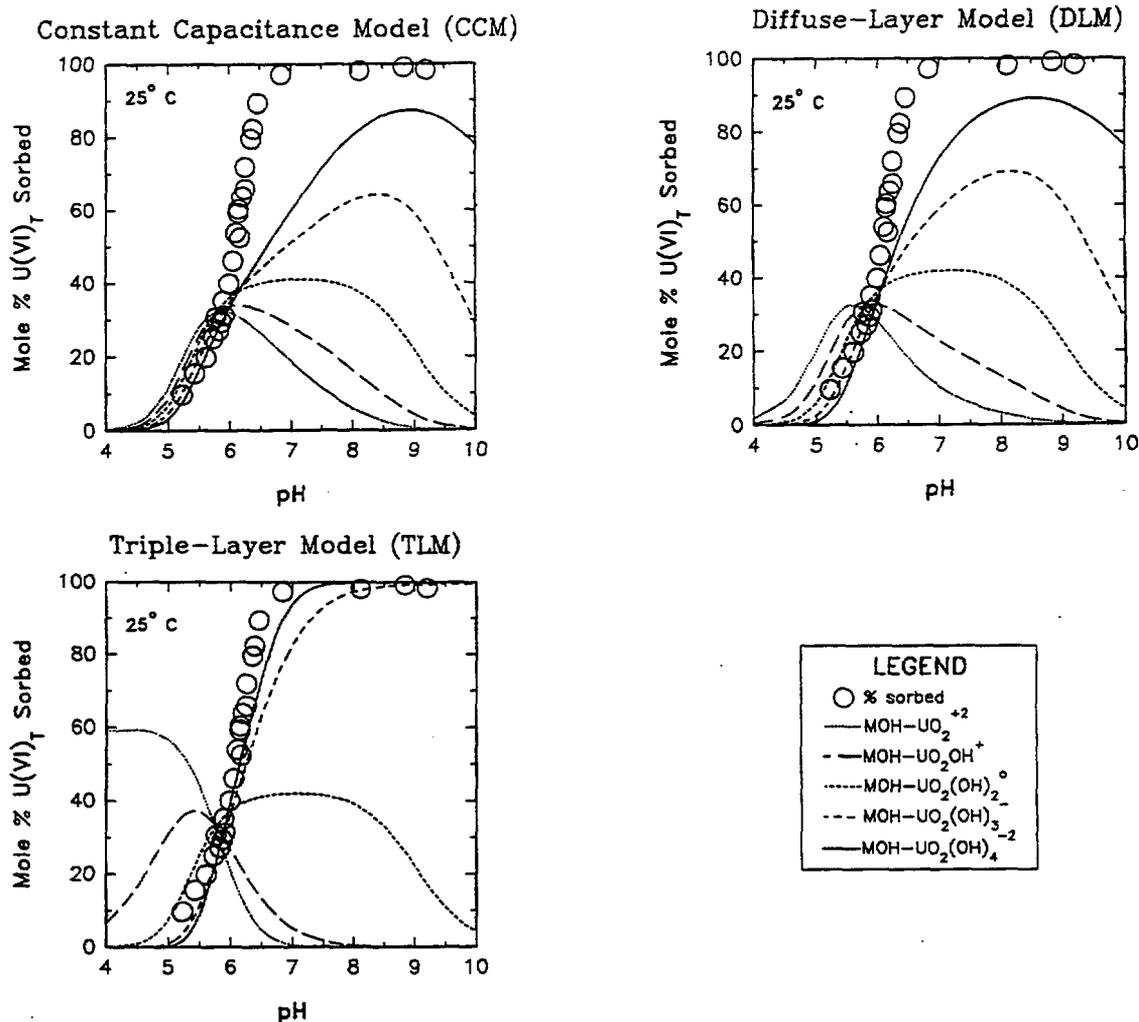


Figure 8-1. SCM modeling results. Parameters from Tables 8-1 and 8-2. Sorption data from Tripathi (1984). $U(\text{VI})_{\text{T}} = 1.05 \times 10^{-6}$ M, No CO_2 , 0.1 M NaNO_3 .

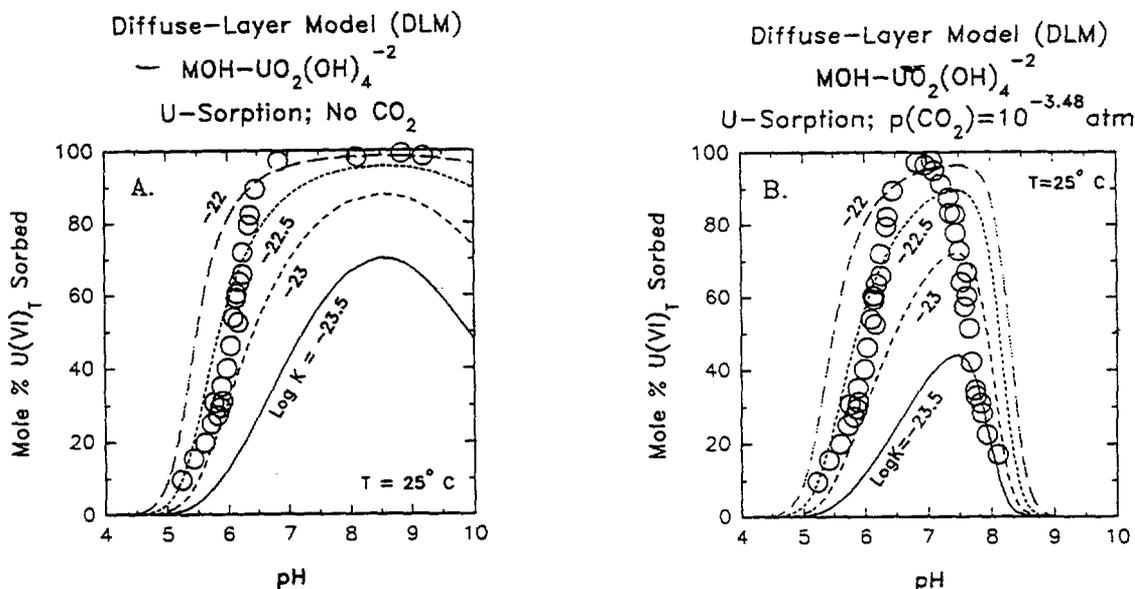


Figure 8-2. Effect of varying log K. $U(VI)_T = 1.05 \times 10^{-6}$ M, 0.1 M $NaNO_3$. (A) No CO_2 (B) $p(CO_2) = 10^{-3.48}$ atm.

8.2.3 Modeling U(VI)-goethite sorption in the UO_2^{+2} - H_2O - CO_2 System

Several studies of actinide sorption (Hsi and Langmuir, 1985; Tripathi, 1984; LaFlamme and Murray, 1987; Kohler et al., 1992; Payne et al., 1992) have shown that introduction of CO_2 leads to the development of a desorption edge at higher pH. This desorption has been attributed to both competition for sites by CO_3^{2-} and HCO_3^- (LaFlamme and Murray, 1987) and the competition for uranium by uranyl-(hydroxy)-carbonate complexes (Tripathi, 1984; Kohler et al., 1992). Payne et al. (1992) were able to provide an excellent fit to U(VI)- CO_2 sorption data for ferrihydrite using the two-site double-diffuse layer model of Dzombak and Morel (1990) without invoking site competition. Zachara et al. (1987) suggest that sorption of CO_3^{2-} , HCO_3^- , and H_2CO_3 reduces chromate (CrO_4^{2-}) adsorption at $p(CO_2) = 10^{-2.46}$ atm, indicating that competition for sorption sites by carbonate species may be significant in soils where $p(CO_2)$ is elevated. Dzombak and Morel (1990) conclude that CO_3^{2-} and HCO_3^- sorb only weakly if at all, unless total carbonate concentrations are much greater than that which would occur in a system open to atmospheric CO_2 [$p(CO_2) = 10^{-3.48}$ atm].

The approach described above (and the parameters listed in Table 8-1) were used with the DLM to investigate the feasibility of modeling the effect of CO_2 on U(VI)-sorption on goethite (Tripathi, 1984). First, an attempt was made to fit the data using the $MOH-UO_2(OH)_4^{-2}$ surface complex used in the CO_2 -free system (Figure 8-2a). Systematically varying values for the binding constant show that, within the constraints of the conceptual model used, the sorption/desorption edges and Γ_{max} cannot be well fitted simultaneously (Figure 8-2b). Nevertheless, it is important to note that the general aspects of the sorption/desorption behavior are reproduced using such a simple model. Uranium speciation calculations for the U(VI)- CO_2 - H_2O system indicate the formation of several uranyl-hydroxy-carbonato species over the pH range represented by Tripathi's data (Turner et al., 1993; Figure 8-7). To address the possible incorporation of these species in surface complexes, the formation of a single monodentate surface complex was assumed and FITEQL was used with the parameters in Table 8-1 to determine equilibrium constants (Table 8-3).

Table 8-3. $\text{Log } K$ values derived using FITEQL. (Data from Tripathi, 1984; $U(\text{VD})_T = 1.05 \times 10^{-6}$ M, $p(\text{CO}_2) = 10^{-3.48}$ atm, 0.1 M NaNO_3).

Surface Species	DLM - Log K
$\text{MOH-UO}_2\text{CO}_3^{\circ}$	14.9
$\text{MOH}_2\text{-UO}_2(\text{CO}_3)_2^{-}$	28.5
$\text{MOH}_2\text{-UO}_2(\text{CO}_3)_3^{-3}$	34.1
$\text{MOH}_2\text{-(UO}_2)_2\text{CO}_3(\text{OH})_3^{\circ}$	10.5
$\text{MOH-UO}_2(\text{OH})_4^{-2}$	-23.3

The sorption-pH curves, calculated using MINTEQA2 and the parameters in Tables 8-1 and 8-3, are illustrated in Figure 8-3. None of the curves reproduce the fit exactly, although assuming the formation of $\text{MOH}_2\text{-UO}_2(\text{CO}_3)_3^{-3}$ simulates the general aspects of the data. Doubtless, an improved fit could be obtained using more species, especially invoking mononuclear and polynuclear uranyl hydroxy species at lower pH. For example, Kohler et al. (1992) obtained an excellent fit to U(VI)-goethite data using a TLM and assuming the formation of four surface complexes, $\text{MO-UO}_2\text{OH}^{\circ}$, $\text{MO-(UO}_2)_3(\text{OH})_5^{\circ}$, $\text{MOH}_2\text{-UO}_2(\text{CO}_3)_2^{-}$, and $\text{MOH}_2\text{-UO}_2(\text{CO}_3)_3^{-3}$. Although such an approach has been demonstrated to provide an improved fit to the data set, the complexity of the sorption model would be likely to restrict its practical application in performance assessment.

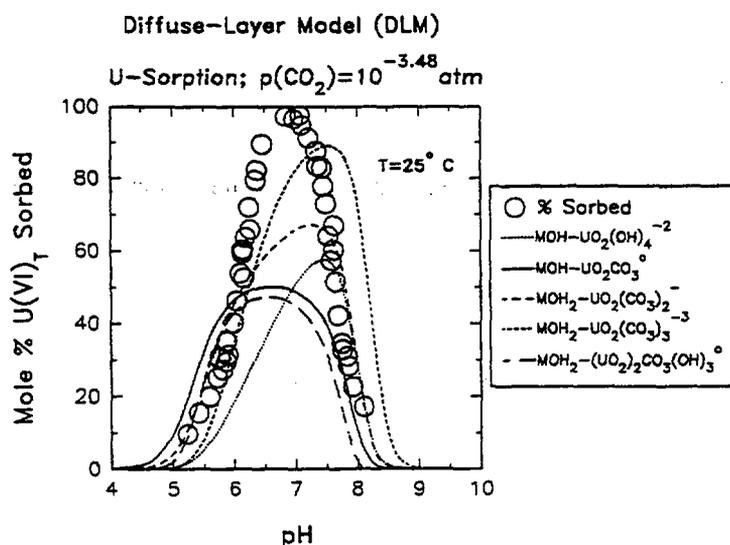


Figure 8-3. DLM modeling of sorption data of Tripathi (1984). $U(\text{VD})_T = 1.05 \times 10^{-6}$ M, $p(\text{CO}_2) = 10^{-3.48}$ atm, 0.1 M NaNO_3 . Parameters from Tables 8-1 and 8-3.

Table 8-4. Effect of number of measurements on Log K estimated using FITEQL. (Data from Tripathi, 1984; $U(VI)_T = 1.05 \times 10^{-6}$ M, No CO_2 , 0.1 M $NaNO_3$).

Surface Species	DLM - Log K			
	m=25	m=13	m=9	m=5
MO- UO_2^+	0.95	0.93	0.93	0.89
MOH- UO_2^{+2}	8.84	8.79	8.78	8.74
MO- UO_2OH^0	-6.96	-6.96	-6.94	-7.01
MOH- UO_2OH^+	0.95	0.93	0.93	0.89
MO- $UO_2(OH)_2^-$	-14.95	-14.94	-14.92	-14.96
MOH- $UO_2(OH)_2^0$	-6.96	-6.96	-6.94	-7.01
MOH ₂ - $UO_2(OH)_2^+$	0.95	0.93	0.93	0.89
MOH- $UO_2(OH)_3^-$	-14.95	-14.94	-14.92	-14.96
MOH ₂ - $UO_2(OH)_3^0$	-6.96	-6.96	-6.94	-7.01
MOH- $UO_2(OH)_4^{-2}$	-22.94	-22.93	-22.91	-22.93
MOH ₂ - $UO_2(OH)_4^-$	-14.95	-14.94	-14.92	-14.96

8.2.4 Effect of Data Set Size

Another concern of performance assessment is that the number of data points that are necessary to allow an adequate description of the system under consideration is excessive. As a first order attempt to address this concern, the pH-percent U(VI) sorbed data of Tripathi (1984) was divided into smaller subsets and FITEQL was used to calculate DLM binding constants for the U(VI)- H_2O -goethite (no CO_2) system. In an attempt to avoid bias towards a particular pH range, the original 25 data points (see Figure 8-1) were arranged from lowest to highest pH; progressively smaller subsets were then extracted, first by selecting every other data point (m=13 points), every third data point (m=9), and every fifth data point (m=5). This initial approach is simplistic, but it does assure that most of the experimental pH range is sampled. The binding constants calculated using FITEQL are listed in Table 8-4. All other parameters were held constant at the values listed in Table 8-1 for the DLM. Calculated Log K values were similar for all data sets.

From this analysis, it is clear that a few carefully selected data points are sufficient to determine the location of the sorption edge for the uranyl- H_2O system. Similar sorption behavior has been observed for other important actinides (Am, Np, Pu, Th), and it may be reasonable to expect similar results for these systems (Sanchez et al., 1985; LaFlamme and Murray, 1987; Girvin et al., 1991). Although the uncertainty in the calculated binding constants is necessarily greater for smaller data sets, this does offer some guidance in the ability to predict complex sorption behavior with a reasonable number of data points. It is critical that experiments are performed over a broad enough range in pH to adequately

"sample" all aspects of the sorption behavior under consideration. This is especially important in the presence of CO_2 , as this has been shown to produce a desorption edge at higher pH.

8.2.5 Modeling U(VI)-Clinoptilolite Sorption - A First Order Approximation

Many minerals are known to exhibit pH-dependent sorption behavior similar to goethite, with the sorption edge shifted to different pHs, dependent on the mineral (Kohler et al., 1992). This also opens up the possibility that if one mineral such as goethite dominates sorption behavior, it may be possible to model sorption in mixtures of minerals using parameters determined from single mineral experiments (Bradbury and Baeyens, 1992; Payne et al., 1992). Taking the analogy of a standard set of parameters one step farther (see Bradbury and Baeyens, 1992), the coefficients determined by fitting the $\text{UO}_2^{+2}\text{-H}_2\text{O-CO}_2$ data of Tripathi (1984) (Tables 8-1 and 8-3) were used to model the pH-dependent U(VI)-clinoptilolite sorption data of Pabalan and Turner (1992). The results of the MINTEQA2 calculations using the DLM are shown in Figure 8-4 with the forward sorption data of Pabalan and Turner (1992). Only the total uranium concentration, specific surface area and the solid/water ratio were modified to reflect the clinoptilolite experiment conditions. The fit is surprisingly good considering all of the assumptions that are made. The sorption envelope and Γ_{max} calculated by the model is consistently greater than those shown for U(VI)-goethite sorption in Figure 8-3. This is due to the higher specific surface area ($700 \text{ m}^2/\text{g}$) assumed for clinoptilolite. This probably includes intracrystalline surface area, much of which is inaccessible to larger uranyl species at $\text{pH} > 5$ (Pabalan and Turner, 1992). If a smaller A_{SP} , similar to that for other silicates ($1\text{-}10 \text{ m}^2/\text{g}$) is used, the sorption envelope is much smaller, reducing the calculated Γ_{max} , and the fit to the data deteriorates. Independently fitting clinoptilolite sorption data using FITEQL with the reduced A_{SP} values and the parameters listed in Table 8-1 will increase calculated $\log K$ values to compensate for decreased A_{SP} , and the resultant fit to the data is the same as in Figure 8-4. For example, decreasing A_{SP} from $700 \text{ m}^2/\text{g}$ to $50 \text{ m}^2/\text{g}$ results in an increase in $\log K$ of one order of magnitude for the formation of $\text{MOH-UO}_2\text{CO}_3^0$. This underscores the need to establish a baseline parameter set before an internally consistent mechanistic database of binding constants can be developed.

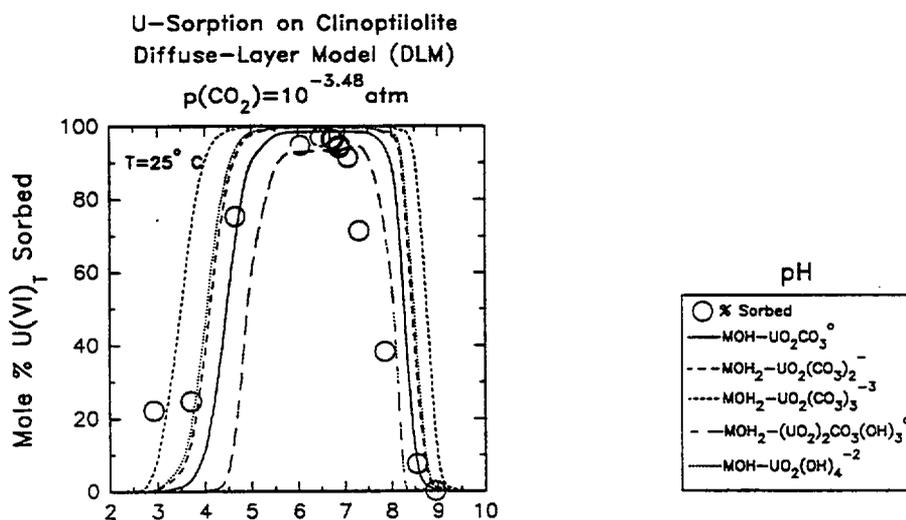


Figure 8-4. DLM modeling of clinoptilolite sorption data of Pabalan and Turner (1992). Model parameters are from Tables 8-1 and 8-3. $\text{U(VI)}_T = 2 \times 10^{-6} \text{ M}$, 0.1 M NaNO_3 .

Again, it must be emphasized that this approach is a great simplification and probably does not present a realistic picture of what is actually occurring at the clinoptilolite-water interface. Because clinoptilolite is an aluminosilicate, instead of the ferrinol (FeOH) sites associated with goethite, a more realistic approach would be to use a multi-site model with aluminol (AlOH) and silanol (SiOH) surface functional groups in stoichiometric proportions. Using this approach with the TLM, Kohler et al. (1992) achieved good fits modeling Np(V)-sorption on albite and kaolinite. The sensitivity analysis of Hayes et al. (1991) provides values for DLM, CCM, and TLM for α -Al₂O₃ that are similar to those for α -FeOOH and which may be applicable. TLM parameters were determined for pyrogenic SiO₂ by James and Park (1982), but these are based on a particular set of assumed parameters (e.g., C₁, C₂, N₃) and there has been no systematic sensitivity analysis performed to develop a similar "standard" set of different model parameters for silicates.

8.2.6 Summary and Conclusions

In order to compare the performance of different candidate surface complexation models, it is desirable to minimize the amount of nonstandard, data set-specific parameters used. Minimizing the amount of manipulation necessary to fit a particular data set establishes a consistent baseline against which model performance can be evaluated. Adoption of this approach will serve two purposes: it will encourage development of simple flexible mechanistic models for performance assessment, and it will lead to the evolution of a comprehensive, internally consistent set of parameters that is necessary for the incorporation of SCMs in contaminant transport models (Yeh and Tripathi, 1989). The work of Dzombak and Morel (1990) has undertaken to do this for transition metals using FITEQL and assuming a two-site double diffuse layer model. A similar approach is needed for the application of SCMs to radionuclide (particularly actinide) sorption.

A first attempt has been made to apply a standard set of parameters (Hayes et al., 1991) for three commonly used surface complexation models to U(VI)-sorption on goethite (Tripathi, 1984). This modeling attempt is relevant to the HLW repository at Yucca Mountain since uranium is anticipated to be an important radionuclide in assessing repository performance (Kerrisk, 1985), and the relatively well characterized uranium system (Grenthe et al., 1992) is considered to be analogous to other important actinides (Pu, Np, Am, Th). In addition, goethite is a ubiquitous mineral in many natural systems, and equilibrium speciation calculations indicate that J-13 well water is saturated with regard to several iron oxyhydroxides (Baca et al., 1992).

The FITEQL parameter estimation code of Westall (1982) was used to determine the necessary equilibrium constants for possible surface complexation reactions. The resultant constants were model-specific. Within the constraints of the conceptual model, the TLM was best able to fit data in the CO₂-free system. However, the DLM was able to reproduce the general aspects of uranyl sorption behavior while using a far simpler representation of the mineral/water interface than the TLM. Such simple mechanistic approaches may be preferred in performance assessment models.

From the point of view of describing the mineral/water interface, it must be emphasized that the results given here are dependent on the assumptions used in constructing the conceptual model. For the purposes of performance assessment, a principal of parsimony was adopted in defining possible surface complexes in the U(VI)-H₂O-CO₂ system. This may be preferred where simpler models are desirable to strike a balance between accuracy of the conceptual model and the computational resources required by geochemistry in performance assessment calculations (Yeh and Tripathi, 1989). The fit to

the data could be improved by invoking additional surface complexes as has been done in other studies (Hsi and Langmuir, 1985; Kohler et al., 1992), but without independent analysis, the validity of the postulated complexes would be uncertain. As can be seen from examining Table 8-2, different surface complexes result in identical values for binding constants in the DLM and CCM. For this reason, these models are not able to distinguish between like-charged surface complexes. Although EXAFS work indicates the formation of bidentate mononuclear uranyl-hydroxy surface complexes (Manceau and Charlet, 1991), this work only exists for fairly concentrated solutions (millimolar) at single pH values. Additional EXAFS work will be required to ascertain the extent to which SCMs represent the mineral/water interface (Sposito, 1992). It must also be stressed that the parameters calculated in the fitting exercise are dependent on the uranium data used in the geochemical equilibrium model. Although the data used is the extensively evaluated NEA database (Grenthe et al., 1992; Turner et al., 1993), several studies (Tripathi, 1984; 1992; Fuger, 1992) suggest that there is some uncertainty in the value used for $\text{UO}_2(\text{OH})_2^0$.

Although dependent on the thermodynamic data available, the result of this exercise is a first step towards developing the database necessary for consistent application of mechanistic SCMs in a predictive way for performance assessment. The exercise also demonstrates that, unlike an empirical K_d approach, a relatively simple SCM such as the Diffuse-Layer Model can reproduce the general aspects of chemistry-dependent complex sorption behavior using a single set of only a few parameters.

8.3 TASK 3—SORPTION EXPERIMENTS

To develop an understanding of radionuclide sorption processes and the important physical and chemical parameters that affect sorption behavior in the Yucca Mountain environment, experiments are under way to investigate the sorption behavior of uranium on geologic media. Because thick, laterally-extensive horizons of zeolite-rich (predominantly clinoptilolite) tuffs exist underneath the proposed HLW repository at Yucca Mountain and could provide important geologic barriers to radionuclide migration, sorption experiments are being conducted on the zeolite mineral clinoptilolite.

The favorable selectivity of natural zeolites, such as clinoptilolite, for alkali and alkaline earth radionuclides (e.g., ^{137}Cs and ^{90}Sr) through an intracrystalline ion exchange mechanism is well-known (Ames, 1960, 1964a, 1964b; Chelischev, 1973). This property has made these minerals suitable for use in reducing the concentration of those radionuclides in aqueous solutions of various origins (Mumpton, 1978; Vavrova et al., 1991). However, the sorptive properties of these zeolites for actinides, which have a more complex aqueous chemistry than Cs and Sr, is not well-known. Although experimental studies indicated good correlation of Cs and Sr sorption ratios with the clinoptilolite content of zeolitized tuffs (Daniels et al., 1982; Meyer et al., 1991), there were no trends observed in the amount of sorbed uranium, neptunium, and plutonium with increased zeolitization of silicic tuffs (Daniels et al., 1982). On the other hand, uranium-bearing clinoptilolite occurs as an ore mineral in the uranium deposit of Tono, Japan (Katayama et al., 1974; Doi et al., 1975). This indicates that under certain geochemical conditions clinoptilolite can be an important sorber of an actinide element.

The ongoing experiments were designed to understand fundamental controls on uranium sorption on clinoptilolite, including the effects of pH, aqueous uranium speciation, and solution concentration of uranium. The experimental procedures and some of the results were presented and discussed in a previous CNWRA semiannual report (Pabalan and Turner, 1992). Additional data and discussion are given next.

8.3.1 Results and Discussion

To determine the time required to reach sorption equilibrium, kinetics experiments were conducted. The results are given in Figure 8-5, which shows the amount of uranium sorbed on clinoptilolite and the solution pH as functions of time. The data indicate that it takes about 300 hours to reach a constant pH and percent U sorbed. The equilibrium sorption mixtures were therefore allowed to equilibrate for at least 14 days. Additional data from other experiments indicate that the increase in pH with time is mainly due to ion exchange between H^+ in solution and Na^+ initially in the intracrystalline sites of clinoptilolite.

The results of the equilibrium sorption experiments are summarized in Figures 8-6A and 8-6B, for mixtures with initial ΣU of 2.0×10^{-5} and 2.0×10^{-6} m, respectively. Control experiments, which checked for potential losses of uranium from solution to container walls, indicated that uranium loss was negligible; thus, the %U sorbed was calculated from the initial and final solution concentrations of uranium. Initial uranium concentrations of 2.0×10^{-5} and 2.0×10^{-6} m, which were calculated from the mass of uranyl nitrate reagent used to prepare the U stock solution, agree with values measured by polarographic methods within analytical uncertainty. Final uranium concentrations were based on polarographic measurements. The results indicate that uranium sorption on clinoptilolite is strongly dependent on pH. The amount of uranium lost from solution increases sharply with increasing pH at values above about 3.5 ('adsorption edge'). At near neutral pH (~ 6.5), almost complete removal (> 90 percent) of uranium from solution occurs. However, at $pH > 6.5$, the amount of uranium sorbed on the solid phase sharply decreases with increasing pH ('desorption edge').

The circles and squares in Figure 8-6 represent, respectively, data from the first and second sets of equilibrium sorption experiments. The second set of experiments was designed to determine the reproducibility and/or reversibility of the sorption reactions. The good agreement between the two data sets indicates that uranium sorption on clinoptilolite is reproducible. The squares at pH less than about 6.5 represent reversals along the adsorption edge and demonstrate that the uranium sorption reactions are reversible. In addition, a comparison of data in Figures 8-6A and 8-6B indicates that the adsorption edge shifts to lower pH with a decrease in total uranium concentration. This is consistent with the trends in uranium sorption observed by Tripathi (1984) and by Payne et al. (1992) in their studies using goethite and ferrihydrite, respectively. There is also a slight, but discernible, shift of the desorption edge to higher pH at lower total uranium concentration, which is similar to that observed by Tripathi (1984). Payne et al. (1992) also observed this trend in their data on ferrihydrite, but the pH shift in their adsorption and desorption edges with changes in uranium concentration are almost equal in magnitude.

Aqueous uranium speciation for solutions analogous to those in the sorption experiments is illustrated in Figure 8-7. The figure shows the relative stabilities of the aqueous uranyl species as a function of pH for solutions in equilibrium with atmospheric $CO_2(g)$. The uranium speciation was calculated using the EQ3NR geochemical code (Wolery et al., 1990), with its associated thermodynamic database (version R16.com), and the uranium thermodynamic database recommended by the Nuclear Energy Agency (NEA) (Grenthe et al., 1992). A comparison of Figures 8-6 and 8-7 indicates that the decrease in the amount of uranium sorbed at alkaline pH can be related to the increasing importance of carbonate- and hydroxy-carbonate-complexes of uranium at higher pH. This is consistent with published sorption data on other geologic material such as clays (Siegel et al., 1990) and iron oxides/oxyhydroxides (Hsi and Langmuir, 1985; Payne et al., 1992). In addition, it appears that uranium sorption on clinoptilolite becomes important in the pH range where $UO_2(OH)_2(aq)$ is the predominant aqueous

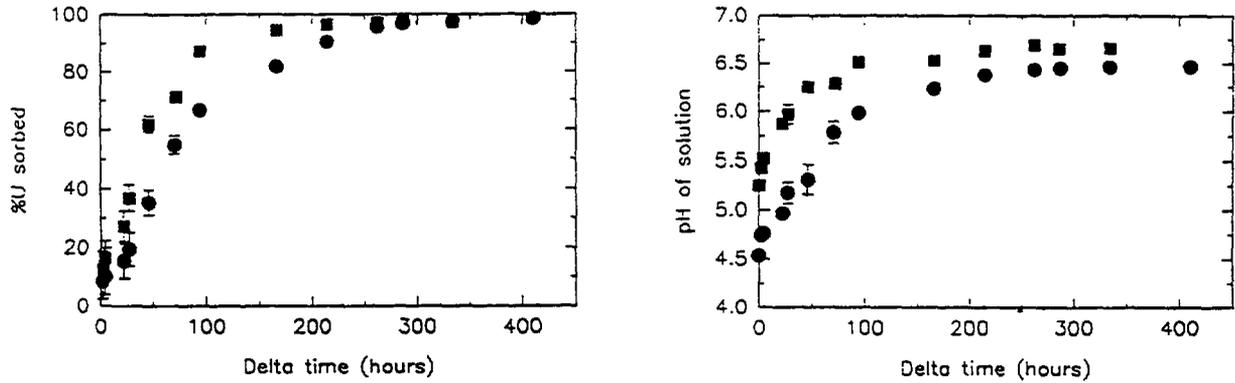


Figure 8-5. Results of kinetics experiments. Initial uranium concentration is 2.1×10^{-6} m. Circles and squares represent data for mixtures with initial pH of 4.54 and 5.26, respectively. Error bars in %U sorbed were calculated based on an estimated $\pm 5\%$ uncertainty in uranium analyses. Error bars in pH are based on measurements on duplicate sets of solutions.

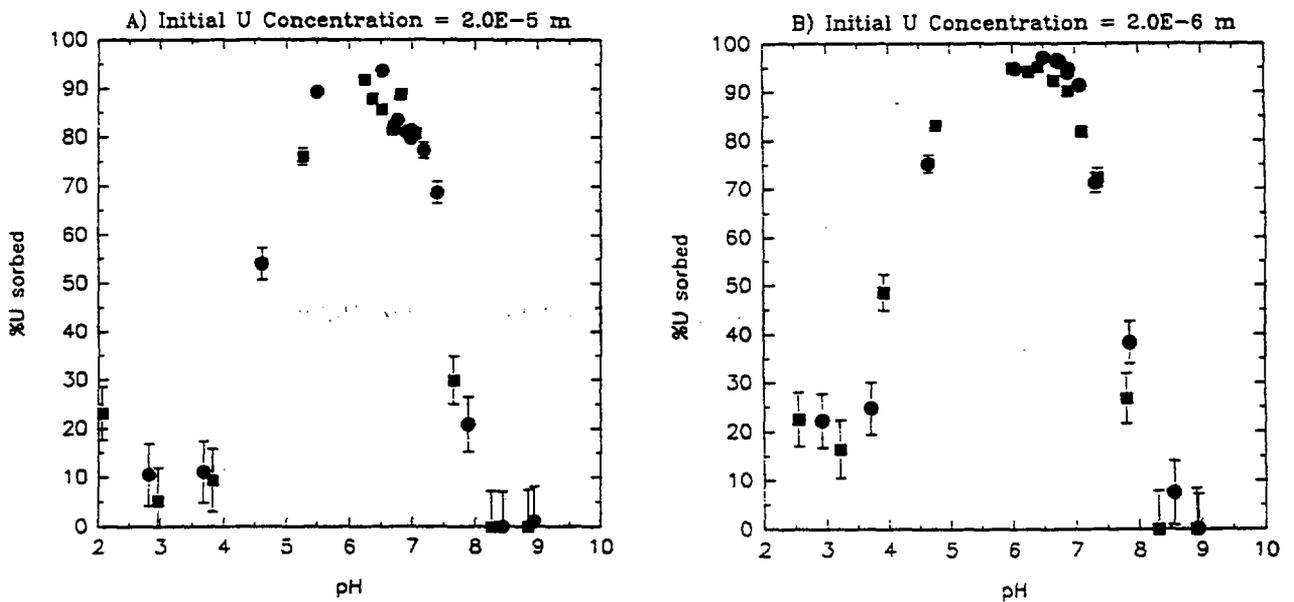


Figure 8-6. Uranium sorption on clinoptilolite versus equilibrium pH for solutions with initial uranium concentrations of: (A) 2.0×10^{-5} and (B) 2.0×10^{-6} m. The circles and squares represent data from the first and second set of equilibrium sorption experiments, respectively. Error bars were calculated based on an estimated $\pm 5\%$ uncertainty in uranium analyses.

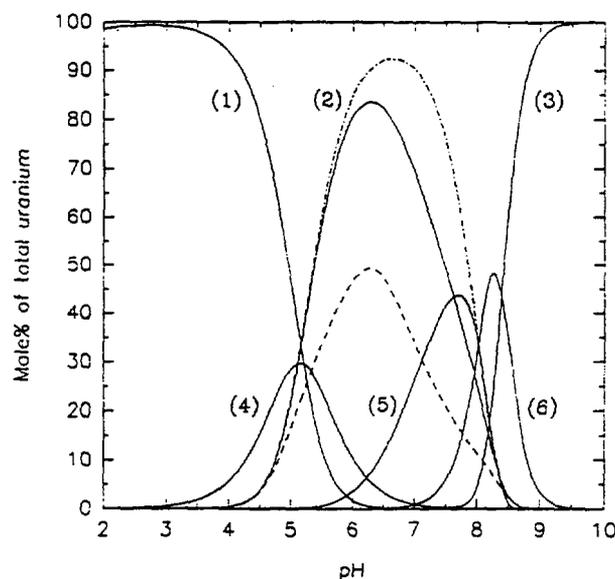


Figure 8-7. Aqueous uranyl speciation at 25°C as a function of pH for a 2.0×10^{-6} m $\text{UO}_2(\text{NO}_3)_2$ solution (solid curves) and $\log p\text{CO}_2 = -3.5$ atm. Dashed and dotted-dashed lines represent mole% of $\text{UO}_2(\text{OH})_2^\circ(\text{aq})$ species for $\Sigma\text{U} = 2.0 \times 10^{-5}$ and 2.0×10^{-7} m, respectively. Minor species with maximum mole% less than 5 are not shown. (1) UO_2^{2+} , (2) $\text{UO}_2(\text{OH})_2^\circ$, (3) $\text{UO}_2(\text{CO}_3)_4^{4-}$, (4) $\text{UO}_2(\text{OH})^+$, (5) $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, and (6) $\text{UO}_2(\text{CO}_3)_2^{2-}$.

uranium species. It is possible that $\text{UO}_2(\text{OH})_2^\circ$ could be an important species sorbed on the surface of clinoptilolite, although spectroscopic (e.g., EXAFS) data is required to determine if this is correct.

The results shown in Figure 8-6 indicate that at pH less than 3.5, the amount of uranium lost from solution appears to increase with decreasing pH. In this pH range most of the aqueous uranium is present as the UO_2^{2+} species as shown in Figure 8-7. The $\text{O}=\text{U}=\text{O}$ group is linear in both crystalline compounds and in solution, with the $\text{U}=\text{O}$ distance ranging from about 1.6-2.0 Å (Cotton and Wilkinson, 1980). On the other hand, the intracrystalline channels in clinoptilolite have dimensions of 4.0×5.5 , 4.1×4.7 , and 4.4×7.2 Å (Meier and Olson, 1978). This suggests that an ion exchange reaction is possible between UO_2^{2+} in solution and Na^+ initially in the zeolite intracrystalline cation exchange sites. The experimental data of Andreeva and Chernyavskaya (1982) on uranium sorption on clinoptilolite at pH of 2 to 4 also suggest that the sorption reaction has an intracrystalline ion exchange character.

8.3.2 Conclusions

Sorption experiments involving uranium solutions in equilibrium with atmospheric $\text{CO}_2(\text{g})$ indicate that uranium(6+) species are strongly sorbed on the zeolite mineral clinoptilolite at near-neutral pH's. The amount of uranium sorbed is strongly dependent on pH and, to some extent, on the total concentration of uranium. Uranium sorption on clinoptilolite is important in the pH range where $\text{UO}_2(\text{OH})_2^\circ(\text{aq})$ is the predominant uranium aqueous species, whereas sorption is inhibited at pH's where carbonate- and hydroxy-carbonate-complexes are the primary uranyl aqueous species. Surface adsorption appears to be the main sorption mechanism, although at $\text{pH} < 4$ the results suggest that ion exchange may

occur between the UO_2^{2+} ions in solution and the cations in the intracrystalline cation exchange sites of clinoptilolite.

The effectiveness of zeolite-rich horizons beneath Yucca Mountain as barriers to actinide transport through sorption processes will depend strongly on groundwater chemistry. Reliable predictions of radionuclide transport will need to account for changes in solution chemistry. Because the sorption reactions are reversible, uranium sorbed on clinoptilolite may later be desorbed due to changes in groundwater chemistry (e.g., increase in pH). However, a comparison with sorption data on other minerals (e.g., clays, iron oxides/oxyhydroxides) indicates that the dependence of uranium sorption on various parameters is similar for different geologic materials, which may help in modeling sorption processes involving mineral mixtures (i.e., rocks). Experiments to understand the effects of other factors such as solid/liquid ratio and ionic strength on uranium sorption on clinoptilolite are currently under way.

8.4 REFERENCES

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: Version 3.0 user's manual*. EPA/600/3-91/021. Athens, GA: U.S. Environmental Protection Agency (EPA).
- Ames, L.L. Jr. 1960. The cation sieve properties of clinoptilolite. *Amer. Mineral.* 45: 689-700.
- Ames, L.L. Jr. 1964a. Some zeolite equilibria with alkali metal cations. *Amer. Mineral.* 49: 127-145.
- Ames, L.L. Jr. 1964b. Some zeolite equilibria with alkaline earth metal cations. *Amer. Mineral.* 49: 1099-1110.
- Andreeva, N.R. and N.B. Chernyavskaya. 1982. Uranyl ion sorption by mordenite and clinoptilolite. *Radiokhimiya* 24:9-13.
- Baca, R.G., D. Turner, and B. Sagar. 1993. Transport of radionuclides in colloidal form. *NRC High-Level Radioactive Waste Research at CNWRA: January-June 1992*. W.C. Patrick, ed. CNWRA 92-01S, NUREG/CR-5817, Vol. 3, No. 1. San Antonio, TX: CNWRA.
- Bradbury, M.H., and B. Baeyens. 1992. A mechanistic approach to the generation of sorption databases. *Radionuclide Sorption From the Safety Evaluation Perspective. Proceedings of an NEA Workshop*. Nuclear Energy Agency (NEA). Paris: Organization for Economic Cooperation and Development (OECD): 121-162.
- Chelischev, N.F., B.G. Berenschtein, T.A. Berenschtein, H.K. Grebanova, and H. Martynova. 1973. Ion exchange properties of clinoptilolites. *Dokl. Akad. Nauk SSSR* 210: 1110-1112.
- Cotton, F.A., and G. Wilkinson. 1980. *Advanced Inorganic Chemistry*. New York: John Wiley and Sons.
- Daniels, W.R., K. Wolfsberg, R.S. Rundberg, A.E. Ogard, J.F. Kerrisk, C.J. Duffy, T.W. Newton, S.D. Knight, F.O. Lawrence, V.L. Rundberg, M. Sykes, G. Thompson, B. Travis,

- E. Treher, R. Vidale, G. Walter, R. Aguilar, M. Cisneros, S. Maestas, A. Mitchell, P. Oliver, N. Raybold, and P. Wanek. 1982. *Summary Report on the Geochemistry of Yucca Mountain and Environs*. LA-9328-MS. Los Alamos, NM: Los Alamos National Laboratory (LANL).
- Davis, J.A., and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Reviews in Mineralogy: Volume 23. Mineral-Water Interface Geochemistry*. M.F. Hochella, Jr. and A.F. White, eds. Washington, DC: Mineralogical Society of America: 177-260.
- Doi, K., S. Hirono, and Y. Sakamaki. 1975. Uranium mineralization by groundwater in sedimentary rocks. *Econ. Geol.* 70:628-646.
- Dzombak, D.A., and F.M.M. Morel. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons.
- Fuger, J. 1992. Thermodynamic properties of actinide aqueous species relevant to geochemical problems. *Radiochim. Acta* 58/59:81-91.
- Girvin, D.C., L.L. Ames, A.P. Schwab, and J.E. McGarrah. 1991. Neptunium adsorption on synthetic amorphous iron oxyhydroxide. *J. Coll. Interface Sci.* 141:67-78.
- Grenthe, I., J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. 1992. *Chemical Thermodynamics Series, Volume 1: Chemical Thermodynamics of Uranium*. NEA. New York: Elsevier.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1991. Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *J. Coll. Interface Sci.* 142:448-469.
- Hsi, C.-K.D. and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* 49: 1931-1941.
- James, R.O., and G. Parks. 1982. Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical properties. *Surf. Coll. Sci.* 12:119-216.
- Katayama, N., K. Kubo, and S. Hirono. 1974. Genesis of uranium deposits of the Tono Mine, Japan. *Symposium on the Formation of Uranium Ore Deposits*. IAEA-SM-183/11. Vienna: International Atomic Energy Agency: 437-452.
- Kent, D.B., V.S. Tripathi, N.B. Ball, J.O. Leckie, and M.D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. NUREG/CR-4807. Washington, D.C: U.S. Nuclear Regulatory Commission (NRC).
- Kerrisk, J.F. 1985. *An Assessment of the Important Radionuclides in Nuclear Waste*. LA-10414-MS. Los Alamos, NM: LANL.

- Kohler, M., E. Wieland, and J.O. Leckie. 1992. Metal-ligand-surface interactions during sorption of uranyl and neptunyl on oxides and silicates. *Proceedings of the 7th International Symposium on Water-Rock Interaction - WRI-7. Volume 1: Low Temperature Environments*. Y.K. Kharaka and A.S. Maest, eds. Rotterdam: A.A. Balkema.
- LaFlamme, B.D., and J.W. Murray. 1987. Solid/Solution Interaction: The effect of carbonate alkalinity on adsorbed thorium. *Geochim. Cosmochim. Acta* 51:243-250.
- Manceau, A. and L. Charlet. Sorption and speciation of heavy metals at the oxide/water interface: From microscopic to macroscopic. *Environ. Poll.* 1:401-408.
- Meier, W.M. and D.H. Olson. 1978. *Atlas of Zeolite Structure Types*. Pittsburgh, PA: Polycrystal Book Service.
- Meyer, R.E., W.D. Arnold, F.I. Case, G.D. O'Kelley, and J.F. Land. 1991. Effects of mineralogy on sorption of strontium and cesium onto Calico Hills tuff. T.A. Abrajano, Jr. and L.H. Johnson, eds. *Scientific Basis for Nuclear Waste Management XIV*. MRS Symp. Proc. 212. Pittsburgh, PA: Materials Research Society (MRS): 569-576.
- Mumpton, F.A. 1978. Natural zeolites: A new industrial mineral commodity. *Natural Zeolites: Occurrence, Properties, Use*. L.B. Sand, and F.A. Mumpton, eds. New York: Pergamon Press: 3-37.
- Pabalan, R.T. and D.R. Turner. 1993. Sorption Modeling for HLW Performance Assessment. *NRC High-Level Radioactive Waste Research at CNWRA: January-June 1992*. W.C. Patrick, ed. CNWRA 92-01S, NUREG/CR-5817, Vol. 3, No. 1. San Antonio, TX: CNWRA: 8-1 to 8-24.
- Payne, T.E., K. Sekine, J.A. Davis, and T.D. Waite. 1992. Modeling of radionuclide sorption processes in the weathered zone of the Koongarra ore body. P. Duerden, ed. *Alligator Rivers Analogue Project Annual Report, 1990-1991*. Australian Nuclear Science and Technology Organization (ANSTO): 57-85.
- Reardon, E.J. 1981. K_d 's - Can they be used to describe reversible ion sorption reactions in contaminant migration? *Ground Water* 19:279-286.
- Sanchez, A.L., J.W. Murray, and T.H. Sibley. 1985. The adsorption of plutonium IV and V on goethite. *Geochim. Cosmochim. Acta* 49:2297-2307.
- Siegel, M.D., J.O. Leckie, S.W. Park, S.L. Phillips and T. Sowards. 1990. Studies of radionuclides sorption by clays in the Culebra Dolomite at the Waste Isolation Pilot Plant site, southeastern New Mexico. SAND89-2387. Albuquerque, NM: Sandia National Laboratories (SNL).
- Smith, R.W., and E.A. Jenne. 1991. Recalculation, evaluation, and prediction of surface complexation constants for metal adsorption on iron and manganese oxides. *Environ. Sci. Technol.* 25:525-531.

- Sposito, G. 1992. Experimental validation of surface speciation models. *American Geophysical Union 1992 Annual Meeting*. American Geophysical Union (AGU). Washington, DC: 597.
- Tripathi, V.S. 1992. Factors governing reliability of stability constants. *Materials Research Society 1992 Fall Meeting*. MRS. Pittsburgh, PA: 597.
- Tripathi, V.S. 1984. *Uranium(VI) Transport Modeling: Geochemical Data and Submodels*. Unpub. Ph.D. Dissertation. Stanford, CA: Stanford University.
- Turner, D.R. 1991. *Sorption Modeling for High-Level Waste Performance Assessment: A Literature Review*. CNWRA 91-011. San Antonio, TX: CNWRA.
- Turner, D.R., T. Griffin, and T.B. Dietrich. 1993. Radionuclide sorption modeling using the MINTEQA2 speciation code. C. Interrante and R. Pabalan, eds. *Materials Research Society Symposium Proceedings. Scientific Basis for Nuclear Waste Management - XVI*. Pittsburgh, PA: MRS (In Press).
- Vavrova, M., O. Musatovova, and S. Bartha. 1991. In vitro studies on the ability of natural zeolites to sorb some radionuclides. *Isotopenpraxis* 27:325-327.
- Westall, J.C. 1982. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 2.0*. Rpt. 82-02. Corvallis, OR: Department of Chemistry, Oregon State University.
- Westall, J.C., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Adv. Colloid Interface Sci.* 12:265-294.
- Wolery, T.J., K.J. Jackson, W.L. Bourcier, B.E. Bruton, K.G. Knauss, and J.M. Delany. 1990. *Current Status of the EQ3/6 Software Package for Geochemical Modeling*. Chemical Modeling of Aqueous Systems II. D. Melchior and R.L. Bassett, eds. ACS Symposium Series 416. Washington, DC: American Chemical Society: 104-116.
- Yeh, G.T., and V.S. Tripathi. 1989. A critical evaluation of recent developments in hydrogeochemical transport models of reactive multichemical components. *Water Resour. Res.* 25:93-108.
- Zachara, J.M., D.C. Girvin, R.L. Schmidt, and C.T. Resch. 1987. Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. *Environ. Sci. Technol.* 21:589-594.

8 SORPTION MODELING FOR HIGH-LEVEL WASTE PERFORMANCE ASSESSMENT

by Roberto T. Pabalan and David R. Turner

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8.1 TECHNICAL OBJECTIVES

A fundamental concern in evaluating the suitability of Yucca Mountain, Nevada, as a repository for high-level nuclear wastes (HLW) is the possibility of radionuclide migration from the repository to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is sorption of radionuclides on minerals encountered along the flow paths. Sorption is specifically referred to in 10 CFR 60.122(b) as a favorable geochemical condition that will tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed [10 CFR 60.122(c)(8)] as potentially adverse conditions that could reduce the effectiveness of the natural barrier system.

To support the U.S. Nuclear Regulatory Commission (NRC) HLW program, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is conducting research activities under the Sorption Modeling for HLW Performance Assessment Research Project. The broad objectives are to develop sufficient understanding of radionuclide transport issues so that timely prelicensing guidance can be provided to the U.S. Department of Energy (DOE) and a sound basis can be available for evaluating the DOE license application. The results will be used to support the NRC License Application Review Plan (LARP), particularly Sections 3.2.3.2 and 3.2.3.5 pertaining to favorable and potentially adverse geochemical conditions and processes at a potential repository site, and Section 3.4, which addresses the effectiveness of natural barriers against the release of radioactive material to the environment. Laboratory and modeling studies of radionuclide transport, sorption, and retardation, which are central to the Sorption Research Project, will provide an independent basis for addressing Key Technical Uncertainties (KTU) identified during development of Compliance Determination Strategies (CDS), which are an integral part of the LARP. Specifically, a KTU regarding parametric representation of retardation processes will be addressed by this research project. This KTU is relevant to the regulatory requirement topic (RRT) regarding geochemical conditions that favor inhibition of radionuclide migration, i.e., those that is: (i) promote precipitation or sorption of radionuclides; (ii) inhibit the formation of particulates, colloids, and inorganic and organic complexes that increase the mobility of radionuclides; or (iii) inhibit the transport of radionuclides by particulates, colloids, and complexes. This KTU is also related to the RRT on potentially adverse conditions concerning geochemical processes that would reduce sorption of radionuclides. Compliance Determination Methods (CDM) for evaluating compliance with the regulatory requirements associated with the RRT will be developed using data and models, including those arising from this research project.

Results arising from this project will be integrated with those from other CNWRA activities. For example, data on uranium sorption will be used in interpreting data on uranium distribution and migration at the Peña Blanca field site of the Geochemical Natural Analog Research Project (Chapter 7),

as well as in developing conceptual models for radionuclide transport/retardation in near-field and far-field environments related to the Performance Assessment Research Project (Chapter 9) and the Iterative Performance Assessment (IPA) Phase 3. Results of activities undertaken during the first half of 1993 are discussed in the following.

8.2 TASK 2 — SORPTION MODELING

8.2.1 Introduction

Many studies have been conducted during the past several decades to examine the complex sorption behavior of toxic elements such as Zn^{2+} , Cd^{2+} , Pb^{2+} , and Hg^{2+} on a number of different mineral surfaces. Given the increasing concern with radioactive waste, similar experiments have begun to be performed for key radionuclides, with the results only recently reaching the peer-reviewed literature. Because of the acknowledged limitations of empirical methods (Kent et al., 1988; Davis and Kent, 1990), mechanistic modeling approaches to data interpretation are necessary to take full advantage of this research (Bradbury and Baeyens, 1992).

Surface complexation models (SCM) represent one type of mechanistic approach that has been used to interpret contaminant sorption on oxide surfaces over a wide range of chemical conditions (e.g., pH, ionic strength, total concentration of adsorbate). Three commonly used types of SCM include the Constant Capacitance (CCM), Diffuse-Layer (DLM), and Triple-Layer (TLM) models. These models rely on a set of model-dependent parameters to represent the acid-base and electrostatic behavior of the mineral surface. Unfortunately, SCM have tended to be applied in an *ad hoc* fashion, adjusting a number of different model parameters to fit a specific data set. This has made uniform application and comparison of model results difficult, if not impossible (Westall and Hohl, 1980; Pabalan and Turner, 1993).

One recently advocated approach is the development of a standard set of parameters that is uniformly applied in all systems (Davis and Kent, 1990; Hayes et al., 1991; Bradbury and Baeyens, 1992; Mesuere, 1992). While this approach may not truly represent the exact physical, electrostatic, and chemical processes operating at the mineral-water interface, it does limit the number of adjustable parameters and serves to establish a baseline that will allow future direct comparison of modeling results and evaluation of model performance. In addition, such an approach is desirable from the point of view of developing simple, flexible sorption models with internally consistent databases for performance assessment.

To date, this type of uniform approach has largely been limited to one model and one surface. Dzombak and Morel (1990) present an extensive tabulation, evaluation, and application of the DLM to heavy and transition metal sorption on ferrihydrite [$Fe(OH)_3$]. Based on the literature available on ferrihydrite, Dzombak and Morel (1990) established a constant value for site density (N_s in sites/nm²). This value was then applied to available potentiometric titration data to derive a single standard set of DLM equilibrium constants for the reactions that represent the acid-base chemistry of the ferrihydrite surface. These parameters were used in turn to interpret available sorption data for a number of contaminant elements. Hayes et al. (1990; 1991) performed a series of sensitivity analyses for goethite, α - Al_2O_3 , and rutile to determine the relative importance of different parameters in determining constants for the DLM, CCM, and TLM surface complexation models.

Radionuclide sorption data are available for a number of minerals (e.g., SiO_2) that have not received the same amount of attention. Therefore, to take advantage of the data available for different surfaces and to compare different SCM, the approaches of Dzombak and Morel (1990) and Hayes et al. (1990; 1991) need to be extended to provide the necessary model constants for different minerals. This is also important for common rock-forming minerals such as feldspar and kaolinite where it may be possible to model the sorption characteristics assuming a combination of different sites such as aluminol (AlOH°) and silanol (SiOH°) (Benjamin and Leckie, 1981; Kent et al., 1988; Siegel et al., 1992).

Although the ultimate goal of this research is to use a uniform approach to obtain the necessary equilibrium (or binding) constants for sorption reactions that involve the radionuclides themselves, a more basic first step is necessary. This involves deriving acidity constants that describe the acid-base chemistry of the mineral surface that is responsible for generating the sorption sites. Therefore, to demonstrate the feasibility of a uniform approach, the objectives of research presented in this report were to obtain potentiometric titration data from readily available peer-reviewed literature for different relevant minerals and to interpret these data following, where possible, the techniques developed by Dzombak and Morel (1990) and Hayes et al. (1990; 1991). In this fashion, a consistent set of constants that characterize the acid-base behavior of each mineral was developed for each of the three surface complexation models listed above. These parameters are necessary to construct the mass balance/mass action equations used by geochemical sorption/speciation programs such as MINTQA2 (Allison et al., 1991) and HYDRAQL (Papelis et al., 1988). Once these parameters are in place, it will be possible to move to the next step of obtaining binding constants for the sorption of radionuclides.

8.2.2 Potentiometric Titration Data

Potentiometric titration is commonly used to determine the acid-base behavior of a surface. Procedures are described in detail elsewhere (e.g., Dzombak and Morel, 1990), but titration generally involves the incremental addition of known amounts of acid or base to a solid suspension of the mineral of interest, while monitoring changes in solution pH. The ionic strength (I) of the suspension is adjusted to a desired value using a supporting background electrolyte such as NaNO_3 , NaClO_4 , or KCl ; the experiment is performed under closed atmosphere conditions, purging the solution with an inert gas such as nitrogen or argon to eliminate CO_2 and the formation of carbonate and bicarbonate species that would otherwise contaminate the surface. Changes in pH between acid/base additions are monitored potentiometrically; pH equilibration is generally assumed when the pH drift falls below some threshold value (pH units/min). Ideally, the time between additions is kept short (on the order of minutes) to focus on surface protonation/deprotonation. Longer times allow proton exchange with the interior of the solid or dissolution, and result in continuous pH drift and hysteresis in the titration curves (Dzombak and Morel, 1990).

Potentiometric titration data and point-of-zero charge data were identified through several compilations (e.g., James and Parks, 1982; Smith and Jenne, 1988; Kent et al., 1988) and a search of the peer-reviewed literature. Several data sets identified were not used (e.g., Breeuwsma and Lyklema, 1973) due to uncertainty regarding experimental conditions that were necessary for data interpretation. This was particularly true for solid concentrations (c_s) and specific surface area (A_{SP}), which were necessary to convert charge data to total H^+ but not always reported. The sources for potentiometric titration data used in this study are listed in Table 8-1. In most cases, the original data were obtained, although in some cases, data compiled in survey reports were used [e.g., ferrihydrite titration data reported in Dzombak and Morel (1990)]. Generally, data were presented in graphical form only; an

Table 8-1. Mineral properties used in interpreting potentiometric titration (25 °C) with data sources

Mineral	A_{SP} (m^2/g)	pH_{ZPC} ($\pm 1 \sigma$)	Reference(s)
Goethite	50	8.0 ± 0.8 (n=11)	Hsi and Langmuir (1985); Hayes et al. (1990); Yates and Healy (1975); Balistrieri and Murray (1981); Mesuere (1992)
Ferrihydrite	600 ^(a)	8.0 ± 0.1 (n=9)	Hsi and Langmuir (1985); Davis (1977); Swallow (1978); Yates (1975)
Magnetite	5	6.7 ± 0.1 (n=2)	Regazzoni et al. (1983)
amorphous-SiO ₂	175	2.8 ± 0.3 (n=3)	Abendroth (1970); Bolt (1957)
α -Al ₂ O ₃	12	8.9 ± 0.4 (n=4)	Hayes et al. (1990)
γ -Al ₂ O ₃	120	8.4 ± 0.3 (n=3)	Huang and Stumm (1972); Sprycha (1989)
δ -MnO ₂	270 ^(b)	1.9 ± 0.5 (n=7)	Murray (1974); Balistrieri and Murray (1982); Catts and Langmuir (1986)
TiO ₂ (anatase)	125	6.1 ± 0.2 (n=2)	Sprycha (1984); Berube and de Bruyn (1968)
TiO ₂ (rutile)	30	5.9 ± 0.3 (n=4)	Berube and de Bruyn (1968); Yates (1975)

(a) Value recommended in Dzombak and Morel (1990).

(b) Although the same methods were used, Balistrieri and Murray (1983) report 74 m^2/g , Murray (1974) reports 263 m^2/g , and Catts and Langmuir (1986) report 290 m^2/g .

electronic digitizing tablet linked to a personal computer was used to convert graphical data to numerical values in the appropriate coordinates [typically pH versus surface charge ($\mu C/cm^2$)]. Surface charge data were then converted to total H^+ with a spreadsheet application based on procedures described in Dzombak (1985).

8.2.3 Data Interpretation

The strengths and limitations of surface complexation theory and models are described in detail elsewhere (Westall and Hohl, 1980; Hayes et al., 1990; Pabalan and Turner, 1992 a,b) and will only be covered briefly here. All SCM assume a mineral surface comprised of a finite number of amphoteric sites (XOH°) that can become positively charged (XOH_2^+) by sorption of H^+ , or negatively charged (XO^-) through desorption of a proton (Table 8-2). If the equilibrium (or acidity) constants K_+ and K_- , and site concentrations for these reactions can be determined, sorption of protons can be modeled as an equilibrium process using the mass balance/mass action approach common to many geochemical programs.

Table 8-2. Summary of surface complexation model parameters (modified from Hayes et al., 1991)

MODEL EQUATION/REACTION (MASS ACTION)	CHARGE/POTENTIAL RELATIONSHIPS (25 °C)	MODEL-SPECIFIC ADJUSTABLE PARAMETERS (a)
<p><u>1. Diffuse-Layer (DLM):</u></p> $\text{XOH}^\circ + \text{H}^+ = \text{XOH}_2^+ \quad (K_+)$ $\text{XOH}^\circ = \text{XO}^- + \text{H}^+ \quad (K_-)$ $\text{XOH}^\circ + \text{M}^+ = \text{XO} \cdot \text{M}^\circ + \text{H}^+ \quad (K_{M^+})$	$-\sigma_o = \sigma_d = -0.1174\sqrt{I} \sinh\left(\frac{zF\Psi_d}{2RT}\right)$ $\Psi_o = \Psi_d$	K_+, K_-, K_{M^+}
<p><u>2. Constant Capacitance (CCM):</u></p> <p>Same as DLM</p>	$\sigma_o = C_1\Psi_d$	K_+, K_-, C_1, K_{M^+}
<p><u>3. Triple-Layer (TLM):</u></p> $\text{XOH}^\circ + \text{H}^+ = \text{XOH}_2^+ \quad (K_+)$ $\text{XOH}^\circ = \text{XO}^- + \text{H}^+ \quad (K_-)$ $\text{XOH}^\circ + \text{C}^+ = \text{XO} \cdot \text{C}^\circ + \text{H}^+ \quad (K_{\text{Cation}})$ $\text{XOH}^\circ + \text{A}^- + \text{H}^+ = \text{XOH}_2 \cdot \text{A}^\circ \quad (K_{\text{Anion}})$ $\text{XOH}^\circ + \text{M}^+ = \text{XO} \cdot \text{M}^\circ + \text{H}^+ \quad (K_{M^+})$	$-\sigma_o = \sigma_d = -0.1174 \sqrt{I} \sinh\left(\frac{zF\Psi_d}{2RT}\right)$ $\sigma_o = (\Psi_o - \Psi_\beta) C_1$ $\sigma_o + \sigma_\beta = -\sigma_d = (\Psi_\beta - \Psi_d) C_2$	$K_+, K_-, K_{\text{Cation}}, K_{\text{Anion}}, C_1, C_2, K_{M^+}$

(a) Adjustable parameters are: K_+, K_- = Protonation and Deprotonation equilibrium constants, respectively; K_{M^+} = Intrinsic equilibrium constant for sorption of contaminant M^+ ; $K_{\text{Cation}}, K_{\text{Anion}}$ = Intrinsic equilibrium constant for cations and anions in background electrolyte, respectively; C_1, C_2 = Capacitance for inner and outer electrostatic layers (Farads/m²). Parameters not specific to each model include: N_s = surface site density (sites/nm²).

The data selected for this study covered a range in ionic strength from 0.0004 to 1 M. In constructing the geochemical equilibrium problem, the mass action was corrected for ionic strength effects on activity using the Davies Equation (e.g., Dzombak and Morel, 1990). For reactions involving a surface species such as XOH_2^+ , an additional correction is added for the electrostatic effects of the charged surface using the exponential Boltzmann relationship

$$a_{i,s} = a_i \left[e^{\frac{-\Psi_j F}{RT}} \right]^z \quad (8-1)$$

where $a_{i,s}$ is the activity of a given ion i in the aqueous phase near the charged surface, a_i is the activity in the bulk solution, $e^{-\Psi_j F/RT}$ is the Boltzmann factor, Ψ_j is electrostatic potential of the J th layer (volt), z is the valence of the ion, F and R are the Faraday (J/volt equiv) and ideal gas (J/K·mole) constants, respectively, and T is absolute temperature (K). The relationship between surface charge as derived from the titration data and potential at the surface differs among SCM models (Westall and Hohl, 1980).

Surface complexation models differ in how the mineral/water interface is represented. For this reason, different adjustable parameters are necessary for each model (Table 8-2). Drawing on the recommendations of several recent studies (Hayes et al., 1990; Dzombak and Morel, 1990; Davis and Kent, 1990), it was attempted in this study to fix several of these parameters *a priori* to minimize the number of fitted parameters and to establish a baseline to facilitate comparison between models.

To consider mass balance constraints on site availability, all SCM require a single value for A_{SP} . However, surface area, generally determined in titration experiments by BET/ N_2 techniques, is subject to uncertainty and can vary from study to study, depending on grain size, how the mineral was prepared, and how long the mineral was allowed to age. Since one objective of this research is the development of a simplified uniform approach to modeling titration data, a single generalized A_{SP} has been assumed for each mineral and applied consistently for each SCM considered (Table 8-1). This maintains the distinction in A_{SP} between minerals, and in most cases the use of similar mineral preparation techniques between studies provides some support for this assumption.

In the case of magnetite and $\alpha\text{-Al}_2\text{O}_3$, only one data set was modeled, and the reported A_{SP} , rounded to the nearest whole number, was used. In most cases where several studies were interpreted, each study reported following the same mineral preparation procedures. For example, each of the five goethite studies listed in Table 8-1 reported using the methods of Atkinson et al. (1967; 1968; 1972), leading to relatively close agreement in A_{SP} (48 to 66 m^2/g). In other cases, however, such as $\delta\text{-MnO}_2$, surface area measurements differ markedly, even though identical methods of synthesis were reported. Other surface area measurements for $\delta\text{-MnO}_2$ support assuming a higher surface area (270 m^2/g). Finally, in some cases (e.g., $\gamma\text{-Al}_2\text{O}_3$, am-SiO_2), commercial grade materials were used and reported surface area measurements agreed closely.

8.2.3.1 Fixed Model Parameters

Site Density (N_S). Based on a sensitivity analysis of titration data using the CCM, DLM, and TLM models, Hayes et al. (1990) suggested that model results were relatively insensitive to differences in site density and proposed a constant site density of 10 sites/ nm^2 . The study of Mesuere (1992), however, suggested that for a broader pH range, goethite titration data was sensitive to N_S and better modeled assuming a small site density of 1.5 sites/ nm^2 for the DLM and 5 sites/ nm^2 for the TLM. Based

on a literature survey, Dzombak and Morel (1990) recommended a total site density of 2.31 sites/nm² for ferrihydrite. Since the goal of this study was a uniform application rather than taking a best fit approach, the recommendation of Davis and Kent (1990) was followed and the site density of Dzombak and Morel (1990) has been assumed for all minerals. Because there does not appear to be a physical reason for assuming different site densities for different models, the same site density has also been maintained for the different SCM.

Also implicit in the approach taken here is the equivalence of all sites. Other studies (Benjamin and Leckie, 1981; Dzombak and Morel, 1990) have employed heterogeneous sites to explain observed sorption behavior. Since simplification is one desired goal of this study, and because of a lack of data on site heterogeneities for many of the minerals considered here, a single site type is assumed.

Capacitances. All three models require values for N_s and A_{sp} to construct the mass balance relationships. In addition, the CCM and TLM require capacitances to describe the charge-potential relationships across one or more model-defined planes at the mineral/water interface. The CCM requires a single value. Based on the sensitivity analysis of Hayes et al. (1990), this has been set at 1.0 F/m². The TLM requires capacitances for its two inner layers. By convention (Hayes et al., 1990), the outer β -layer capacitance (C_2) is set at 0.2 F/m². As with the CCM, the sensitivity analysis of Hayes et al. (1990) has been used to set the inner α -layer capacitance at 0.8 F/m². The DLM does not require capacitance values.

8.2.3.2 Parameter Estimation Using FITEQL

Several studies advocating a uniform approach to SCM applications (Dzombak and Morel, 1990; Hayes et al., 1990; Mesuere, 1992) have used Version 2.0 of the FITEQL parameter estimation code (Westall, 1982) to determine acidity constants (K_+ and K_-) and cation/anion binding constants (K_{Cation} and K_{Anion}). This study also used FITEQL to interpret the titration data. For the DLM and CCM models, values were determined for $\text{Log } K_+$ and $\text{Log } K_-$ simultaneously. However, unlike the single layer DLM and CCM, the TLM allows for sorption of the background electrolyte (Na^+ and NO_3^- for example). This leads to four equilibrium constants, K_+ , K_- , K_{Cation} , and K_{Anion} to describe the interface. While FITEQL can, in theory, fit these four constants simultaneously, in practice the code does not converge unless two of these can be specified. The relationship between K_+ , K_- , and pH_{ZPC} can be expressed

$$(\text{Log } K_+ - \text{Log } K_-)/2 = \text{pH}_{\text{ZPC}} \quad (8-2)$$

and the sensitivity analysis of Hayes et al. (1990) recommended a value for ΔpK such that

$$\Delta\text{pK} = |\text{Log } K_+ + \text{Log } K_-| = 4.0 \quad (8-3)$$

In this fashion, if pH_{ZPC} is known for a given mineral, values can be set for the TLM acidity constants and FITEQL can be used to solve for K_{Cation} and K_{Anion} . Turning again to the peer-reviewed literature, values for pH_{ZPC} were obtained for the different minerals considered. In general, the differences between values reported for a given mineral were small, and a mean value was chosen for pH_{ZPC} . The values used are reported in Table 8-1. It should also be noted that $\delta\text{-MnO}_2$ and amorphous- SiO_2 have such low pH_{ZPC} that most of the available titration data is at $\text{pH} > \text{pH}_{\text{ZPC}}$. In this range, only deprotonation and adsorption of cations are assumed to be significant (Kent et al., 1988), and the FITEQL runs were set up to determine equilibrium constants (K_- and K_{Cation}) for only these reactions.

Output from FITEQL includes a "goodness-of-fit" parameter and standard deviations for the estimated parameters (Westall, 1982). These values are determined based on the experimental error specified in the optimization run and the size of the data set. For example, because the chemical system is not as well constrained, goodness-of-fit and parameter uncertainty generally deteriorate for smaller data sets (Dzombak and Morel, 1990). In most cases, error is not reported for potentiometric titration data, and the approach of Hayes et al. (1990) has been adopted with only slight modification. Relative error has been assumed to be ± 1 percent (0.01), while absolute error has been assumed to be 1×10^{-8} M instead of the 2×10^{-8} M used by Hayes et al. (1990). Their sensitivity analyses indicated that the dissimilarities in acidity constants due to differences in experimental error are negligible, but the calculated uncertainty in the estimated values increases with increasing error. The goodness-of-fit parameter generated by FITEQL can be used as a measure of how well the data are described by the assumed chemical and adsorption models. In a strict sense, however, goodness-of-fit cannot be compared directly unless the experimental error limits imposed on the problem are known.

8.2.4 Discussion of Results

After interpretation of the data, the chief objective of this parameter estimation exercise was to combine the results for separate potentiometric titration data sets into a single set of weighted values for the desired SCM parameters (K_+ , K_- , K_{Cation} , and K_{Anion}). This involved combining experiments performed at different ionic strengths using different background electrolytes. In a strict sense, this approach is not valid for the CCM. This is because there is no ionic strength correction in the charge-potential relationship (Table 8-2) and, in theory, the capacitance used should be adjusted for each ionic strength (Hayes et al., 1990; 1991). By arbitrarily fixing the capacitance used in the model at a single value, the calculated equilibrium constants are adjusted by FITEQL to fit the data. The resultant values are therefore valid only for the ionic strength at which the data were measured. Also implicit in this approach is the assumption that different background electrolytes behave in an identical manner and have no effect on the modeling results. While this is probably reasonable for the simple CCM and DLM models that assume an inert background electrolyte, it is likely to be an oversimplification in the TLM.

The values resulting from the FITEQL analysis were tabulated for each study at each ionic strength considered. In some cases, the numerical scheme did not converge. For the DLM and TLM, the method of Dzombak and Morel (1990) was used to obtain convergence for one of the values. This involves fixing one of the constants using values obtained from runs at other ionic strengths in the data set, and rerunning the input file to fit the remaining parameter. In almost all cases, convergence was achieved quickly. Because of its lack of ionic strength dependence, however, this was not done for the CCM. For some data sets, however, plotting the Log of the acidity constants ($\text{Log } K_+$ and $\text{Log } K_-$) versus the base-10 logarithm of the ionic strength resulted in a linear relationship. The correlation was generally strong ($r^2 \geq 0.9$) and could be used to extrapolate acidity constants for ionic strengths outside of the range of the experiments.

Dzombak and Morel (1990) proposed a scheme for deriving a single set of acidity constants for the DLM. This approach relies on using the standard deviation calculated by FITEQL to develop a weighting factor (w_i) according to the following relationship

$$w_i = \frac{(1/\sigma_{\text{Log } K})_i}{\sum (1/\sigma_{\text{Log } K})_i} \quad (8-4)$$

The weighting factor is then used to derive a "best-estimate" of the equilibrium constant of interest

$$\overline{\text{Log } K} = \sum w_i (\text{Log } K)_i \quad (8-5)$$

In this fashion, a value with a lower standard deviation (i.e., a better fit) is more heavily weighted and will have more influence on the final value. Dzombak and Morel (1990) used this approach to combine acidity constants for different ferrihydrite data sets at different ionic strengths. This technique is valid for the DLM, which contains an ionic strength term in the charge-potential relationship. Because it also adjusts potential to reflect ionic strength, a similar approach should be valid for the TLM. Again, however, for the reasons given earlier, this approach is not valid for the CCM, and was not used. The weighted results (DLM and TLM only) are presented in Table 8-3. The values reported for the CCM are for $I = 0.1$ M. Generally, constants calculated at different ionic strengths within a given data set agreed very closely. This holds true even for different background electrolytes at the same concentration. For example, for the $\gamma\text{-Al}_2\text{O}_3$ data of Sprycha (1989), DLM-Log K_+ ranged from 6.17 to 7.02 and DLM-Log K_- varied from -8.82 to -9.75 . This was despite ionic strengths ranging from 0.001 to 0.1 M and background electrolytes ($I = 0.1$ M) that included NaBr, NaCl, KCl, CsCl, and NaI. Agreement between data sets was not as good, which is not surprising given the differences in data set size, laboratory procedure, equipment, and sample preparation (perhaps exemplified in differences in measured A_{SP}) that were noted for the different studies.

One factor complicating data comparison was the different pH ranges covered in the experiments. If the coverage is not as extensive on one side of the pH_{ZPC} , the chemical equilibrium model will not be well constrained and FITEQL will have more difficulty converging on equilibrium constants. One extreme example of this is $\delta\text{-MnO}_2$, where there are no data available below its low $\text{pH}_{ZPC} \sim 2.0$. In this case, as noted earlier, the protonation reaction and the anion adsorption reaction for the TLM (Table 8-2) are not constrained at all, and attempting to include them in the optimization leads to convergence problems.

One of the trade-offs inherent in the simplified uniform approach adopted here is the implicit assumption of similar mineral morphology between studies embodied in using a single A_{SP} for a given mineral. Although a systematic analysis has not been performed here, it is important to recognize the uncertainty inherent in estimated acidity constants due to differences in surface area measurements. It would be possible to construct a more complete model by maintaining the exact A_{SP} reported for each of the titration studies through the data interpretation. However, because of the uncertainty in A_{SP} measurements, a single generalized value was used. This assumption is supported by the similarity in reported mineral preparation techniques and the generally close agreement between measured A_{SP} values.

Similarity in mineral synthesis methods provides some justification for assuming a single A_{SP} . In addition, although some information is lost in this simplification, the general distinctions in A_{SP} between minerals are preserved. Also, relative to empirical models, the addition of geochemical considerations such as aqueous speciation, pH, and partial gas pressures to sorption models is the benefit received.

8.2.5 Conclusions

Despite disparities in experimental conditions, the agreement in acidity constants (and binding constants for background electrolytes in the TLM) between different data sets for several minerals (e.g.,

Table 8-3. Best estimate values for SCM constants (T = 25 °C)

Mineral	Model	N_S (sites/nm ²)	Log K ₊	Log K ₋	Log K _{Anion}	Log K _{Cation}
Goethite	CCM(0.1M)	2.31	6.47	-9.03	n.a.	n.a.
	DLM	"	7.35	-9.17	n.a.	n.a.
	TLM ^(a)	"	6.00	-10.00	8.78	-7.64
Ferrihydrite	CCM(0.1M)	2.31	7.35	-8.45	n.a.	n.a.
	DLM	"	7.29 ^(b)	-8.93 ^(b)	n.a.	n.a.
	TLM ^(a)	"	6.00	-10.00	8.43	-7.66
Magnetite	CCM(0.1M)	2.31	6.26	-7.32	n.a.	n.a.
	DLM	"	6.72	-6.37	n.a.	n.a.
	TLM ^(a)	"	4.70	-8.70	7.95	-5.47
am-SiO ₂	CCM(0.1M)	2.31	(c)	-7.05	n.a.	n.a.
	DLM	"	(c)	-7.20	n.a.	n.a.
	TLM ^(a)	"	0.90	-4.90	(c)	-6.29
α-Al ₂ O ₃	CCM(0.1M)	2.31	9.08	-8.32	n.a.	n.a.
	DLM	"	8.33	-9.73	n.a.	n.a.
	TLM ^(a)	"	6.80	-10.80	10.12	-7.73
γ-Al ₂ O ₃	CCM(0.1M)	2.31	6.92	-9.00	n.a.	n.a.
	DLM	"	6.85	-9.05	n.a.	n.a.
	TLM ^(a)	"	6.40	-10.40	8.28	-7.95
δ-MnO ₂	CCM(0.1M)	2.31	(c)	-2.14	n.a.	n.a.
	DLM	"	(c)	-3.27	n.a.	n.a.
	TLM ^(a)	"	-0.10	-3.9	(c)	-1.60
TiO ₂ (anatase)	CCM(0.1M)	2.31	3.26	-8.98	n.a.	n.a.
	DLM	"	3.40	-8.67	n.a.	n.a.
	TLM ^(a)	"	4.10	-8.10	5.45	-7.55
TiO ₂ (rutile)	CCM(0.1M)	2.31	3.91	-7.79	n.a.	n.a.
	DLM	"	4.23	-7.49	n.a.	n.a.
	TLM ^(a)	"	3.90	-7.90	5.24	-6.42

- n.a. Parameters not applicable to CCM and DLM models.
(a) Log K₊ and Log K₋ fixed by convention. See text for discussion.
(b) Dzombak and Morel (1990) constants for ferrihydrite.
(c) Not considered for δ-MnO₂ and am-SiO₂. See text for discussion.

goethite, ferrihydrite, $\gamma\text{-Al}_2\text{O}_3$, and am- SiO_2) for a given SCM was often within two orders of magnitude. This supports combining these results into a single set of parameters. The similarity between the DLM and TLM constants calculated for goethite and ferrihydrite suggests that ferrinol (FeOH^0) sites behave similarly for these two minerals despite differences in crystallinity, and indicates that they may be modeled using the same SCM parameters.

This modeling exercise pointed up some of the limitations in the different SCM. The CCM is perhaps the most restrictive of the three models in that it requires knowledge of the dependence of capacitance on ionic strength. For this reason, the type of generalized approach outlined here is not strictly applicable for the CCM. The TLM can model different ionic strengths, but it has a larger number of parameters and requires some means of fixing $\text{Log } K_+$ and $\text{Log } K_-$ to model titration data using FITEQL. This extra level of complexity tends to work against the ready incorporation of the TLM in performance assessment codes (Hayes et al., 1990; 1991). The simplest model, the DLM, is also able to model ionic strength changes, and also has the fewest number of parameters to fit. Examination of the values listed in Table 8-3 for the acidity constants and mineral pH_{ZPC} indicates that the values for both the CCM and DLM are reasonable, meeting the constraint set in Eq. (8-2).

Values determined in this study are necessary before data on radionuclide sorption on these minerals can be interpreted using surface complexation models. It is important to remember, however, that in an effort to establish a baseline, the constants in Table 8-3 were determined using fixed site density, capacitances, and, in the case of the TLM, acidity constants. Although these parameters were selected where possible, based on surveys of mineral properties, they may not be the same as properties reported for a given set of experimental data. For this reason, results cannot be compared directly to constants determined using a different set of parameters (Dzombak and Hayes, 1992). However, while there is some loss of conceptual (and numerical) accuracy in using a single set of parameters to model sorption data, this type of uniform approach is to be favored in trying to strike a balance between model completeness and performance assessment needs for efficient modeling.

8.3 SORPTION EXPERIMENTS

To develop an understanding of radionuclide sorption processes and the important physical and chemical parameters that affect actinide sorption behavior in the Yucca Mountain environment, experiments are being conducted to investigate the sorption behavior of uranium on geologic media. Results reported previously (Pabalan et al., 1993) regarding uranium (6+) sorption on clinoptilolite, which is the predominant zeolite mineral in the proposed HLW repository at Yucca Mountain, indicate that sorption of uranium is strongly dependent on pH and, to some extent, on uranium concentration in solution. Uranium sorption on clinoptilolite is important at near-neutral pH where $\text{UO}_2(\text{OH})_{2(\text{aq})}$ is the predominant aqueous species calculated using the EQ3 geochemical code, whereas sorption is inhibited at alkaline pH where carbonate- and hydroxy-carbonate-complexes are the calculated primary uranium aqueous species. Those results indicate that, under certain geochemical conditions, the zeolite mineral clinoptilolite can be an important sorber of an actinide element, but quantitative prediction of uranium transport through zeolite-rich rocks will need to account for changes in solution chemistry.

Because the objective of this research project is to understand fundamental controls on radionuclide sorption on rocks, which are essentially mixtures of minerals, new uranium sorption experiments were initiated during this reporting period using the clay mineral montmorillonite, which is another important mineral phase present underneath Yucca Mountain, as the sorbing phase. In contrast

to zeolites, which are tectosilicates with relatively open three-dimensional pore structures, montmorillonite is a phyllosilicate with a layer-type crystal structure. These experiments were designed to evaluate the effects of pH, aqueous uranium speciation, and aqueous uranium concentration on uranium sorption on clays, and also to determine differences in uranium sorption behavior on different types of minerals. The results may help identify simplified approaches to modeling radionuclide sorption, which can be used in performance assessment calculations.

Additional uranium sorption experiments were also initiated using alpha-alumina as the sorbent phase. The primary objective of these experiments is to evaluate the effect of sorbent-surface-area/solution-volume ratio, recognizing that surface adsorption is the predominant uranium sorption mechanism, even for zeolites like clinoptilolite (Pabalan et al., 1993), and that the ratio of fluid-volume to mineral surface-area can vary significantly along a fluid flowpath. A secondary objective is to compare uranium sorption on clinoptilolite and montmorillonite with that on alpha-alumina, which is an oxide with very different structure and surface properties.

8.3.1 Experimental Procedures

Uranium sorption on Na-montmorillonite

The sorption experiments were conducted by reacting 0.1 g of Na-montmorillonite with 50 ml of uranium solutions in polypropylene bottles at 25 °C. In contrast to the experiments on clinoptilolite, which had initial uranium concentrations (as ^{238}U) of 476 or 4,760 ppb, the solutions used in these experiments had initial uranium concentrations of 5, 50, or 500 ppb (mostly as ^{233}U) in an 0.1 M NaNO_3 matrix. The Na-montmorillonite was prepared from montmorillonite powder (source locality: Cheto, Arizona) obtained from the Source Clay Minerals Repository (University of Missouri-Columbia) by ion-exchange with 3 M NaCl solutions. Prior to addition of the solid phase, the initial pH of each solution was adjusted to a value in the range 2.5 to 9.0 at approximately 0.25 pH intervals by addition of HNO_3 or NaHCO_3 . The amount of reagent needed to achieve the desired initial pH of the uranium solution was estimated using the EQ3NR geochemical code (version 3245.R124) with database Data0.com.R12 (Wolery et al., 1990). The solutions, which were kept open to atmospheric $\text{CO}_2(\text{g})$ throughout the experiment, were agitated using gyratory shakers.

The Na-montmorillonite powder was added after all solutions had attained a constant pH. For uranium solutions with added NaHCO_3 , it took at least 10 days to equilibrate with atmospheric $\text{CO}_2(\text{g})$ and reach a constant pH. Control experiments consisting of uranium solutions (in an 0.1 M NaNO_3 matrix and initial pH adjusted to 2, 4, 6, 8, or 9.5) without added clay were used to determine potential losses of uranium to the container walls. After about 2 weeks, samples were taken from each mixture using polypropylene syringes tipped with 0.2 μm DynaGard filters. Initial and final uranium concentrations of the experimental mixtures and control solutions were analyzed with a liquid scintillation analyzer. The equilibrium pH of each solution was also measured.

Uranium sorption on alpha-alumina

The sorption experiments on alpha-alumina were conducted by reacting 0.2 g of the solid with 100 ml of uranium solutions in polypropylene bottles at 25 °C. The solutions all had initial concentrations of 5 ppb (mostly as ^{233}U) in an 0.1 M NaNO_3 matrix. The sorbent phase used consisted of alpha-alumina issued by the National Institute of Standards and Technology (NIST) as certified reference materials for

measurements of specific surface-area of powders, specifically Reference Materials (RM) 8005, 8006, and 8007, with reported surface-areas of 2.09, 0.23, and 0.0686 m²/g, respectively. The experiments were conducted at a constant solid-mass/solution-volume, but variable sorbent-surface-area/solution-volume ratio. In a manner similar to the montmorillonite experiments described earlier, the initial pH of the uranium solutions was adjusted by addition of HNO₃ or NaHCO₃. The alpha-alumina was added after all solutions attained a constant pH. The solutions were agitated using gyratory shakers and were kept open to atmospheric CO₂(g) throughout the experiment. After about 2 weeks, samples were taken using filter-tipped syringes for liquid scintillation analysis and the equilibrium pH of each solution was measured.

8.3.2 Results and Discussion

Initial results of the sorption experiments on Na-montmorillonite and alpha-alumina are presented in Figures 8-1 and 8-2. Figure 8-1 shows the percent of uranium lost from solution (initial uranium concentration = 50 ppb) versus the equilibrium pH in the Na-montmorillonite experiments. Figure 8-2 shows the percent of uranium lost from solution (initial uranium concentration = 5 ppb) versus the equilibrium pH in the alpha-alumina experiments. The solid circles in these figures, which represent data from the experimental mixtures, illustrate the strong dependence of uranium sorption on pH. This dependence is similar to that observed for uranium sorption on clinoptilolite (Pabalan et al., 1993), on iron oxides/oxyhydroxides (Tripathi, 1984; Payne et al., 1992), and on the clay mineral corrensitite (Siegel et al., 1990). The data represented by the solid circles, however, are not corrected for uranium losses to the container walls or filters. The open circles in Figures 8-1 and 8-2, which are data from the control experiments, show that significant amounts of uranium are lost to the container and the filter. The control data also show that the losses to the container and filter mimic the pH-dependence of the results from the experimental mixtures. The significant losses of uranium from solution in the control experiments preclude meaningful interpretation of the results from the experimental mixtures. Although possible uranium losses to the containers and to syringe filters were anticipated based on data published in the literature and the low initial uranium concentrations used in this study, the uranium losses observed in the control experiments were higher than expected. For example, Tripathi (1984) assessed the possible loss of uranium from his experiments due to sorption on a syringe-Nucleopore filter assembly from solutions having initial concentrations of 20 ppb to 5 ppm uranium and reported that no significant losses were observed.

The experiments on uranium sorption on Na-montmorillonite and alpha-alumina are currently being redone. These new experiments use teflon (FEP), instead of polypropylene, bottles to minimize losses to the container walls, and filtration of aqueous samples was eliminated. Separation of sorbent from aqueous phase is being done only by centrifugation. A greater number of control solutions (ten, instead of the usual four) is also being used to determine the pH-dependence of uranium loss to the containers. Results of these experiments will be presented in the next semi-annual research report.

8.4 ASSESSMENT OF PROGRESS TOWARDS MEETING PROJECT OBJECTIVES

Electrostatic SCM have been used recently to describe complex sorption behavior for a number of contaminants. Each model employs a set of model-specific adjustable parameters to describe the mineral/water interface. Traditionally, several of these parameters have been adjusted simultaneously to achieve a best fit to a specific data set. This lack of uniformity has made comparison between different

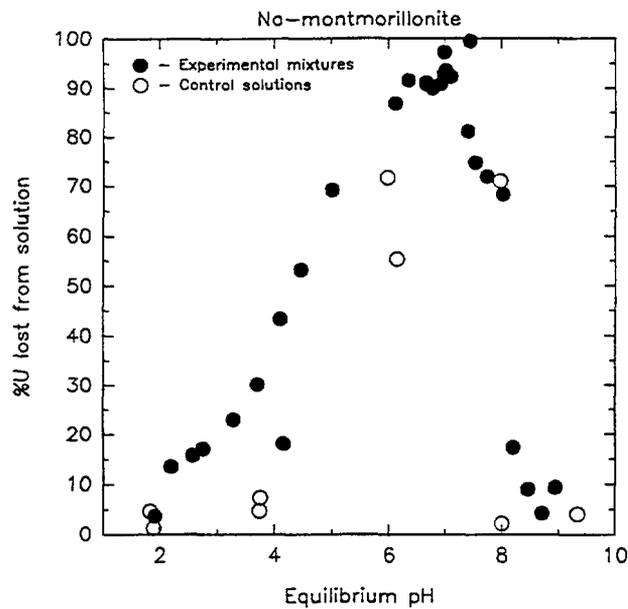


Figure 8-1. Data from the experiments on uranium sorption on Na-montmorillonite in terms of percent of uranium lost from solution versus equilibrium pH. Initial uranium concentration in solution is 50 ppb. The solid and open circles are data from the experimental and control mixtures, respectively.

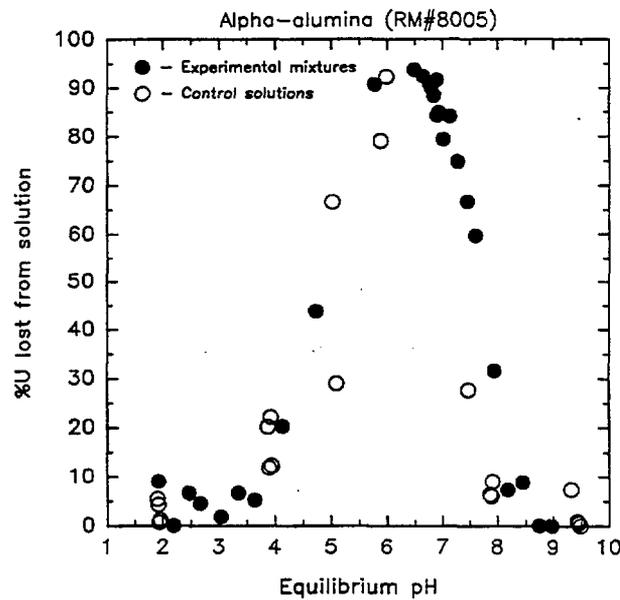


Figure 8-2. Data from experiments on uranium sorption on alpha-alumina in terms of percent of uranium lost from solution versus equilibrium pH. Initial uranium concentration in solution is 5 ppb. The solid and open circles are data from the experimental and control mixtures, respectively.

models and studies difficult, if not impossible. For three commonly used SCM, the current study has developed a uniform set of model parameters to provide a consistent baseline from which to determine the equilibrium constants needed to describe the acid-base chemistry of a number of different minerals. With these parameters in place, it is now possible to use surface complexation models to describe available radionuclide sorption data for these minerals. It may also be possible to combine values for different oxides to describe sorption site characteristics for common rock-forming minerals such as feldspar and clay. Because a uniform approach has been used, modeling results can be compared and the performance of the different models evaluated. These initial efforts have identified some of the strengths and weaknesses of the different SCM.

Results of laboratory experiments on uranium sorption have begun to provide an understanding of the important parameters that control the sorption behavior of an actinide element. For example, the results reported previously on uranium sorption on clinoptilolite (Pabalan et al., 1993) indicated that uranium(6+) species are strongly sorbed at near-neutral pH. However, the amount of uranium sorbed is strongly dependent on pH and decreases steeply away from near-neutral pH. Some dependence on total uranium concentration in solution was also observed. Because of the strong dependence on pH, modeling of sorption processes will likely require that changes in groundwater chemistry be properly accounted for in performance assessment calculations if retardation by sorption processes is included. Information derived from the laboratory experiments has been useful in developing CDS 3.2.3.3 and 3.2.3.5.

The similarity in the dependence of uranium sorption on parameters such as pH and uranium concentration observed for the zeolite mineral clinoptilolite and iron oxides/oxyhydroxides and clays is important. This may help identify simplified approaches to modeling sorption and thus help in developing CDM relevant to the KTU identified in Section 8.1, and in developing conceptual models related to the Performance Assessment Research Project and the IPA Phase 3. The information derived from the laboratory experiments may also help interpret data on uranium distribution and migration at the Peña Blanca field site of the Geochemical Natural Analog Research Project.

Experience gained and lessons learned from both sorption modeling and sorption experiments, including problems encountered such as uranium losses to containers and filters, will be useful in reviewing DOE study plans and prelicensing submittals on sorption studies. The experience will also be necessary to identify potential problems in sorption experiments and modeling exercises conducted by the DOE. Although losses of radionuclides to container walls and filters are mentioned in some publications, the strong pH-dependence of these losses is not discussed. Thus, sorption experiments that do not properly account for these losses are flawed.

8.5 PLANS FOR NEXT REPORTING PERIOD

Available information on the acid-base chemistry and surface area of minerals important at Yucca Mountain will be examined for incorporation into surface complexation approaches. Sorption modeling will continue, using the parameters determined in this study. Radionuclide sorption data will be obtained from the peer-reviewed literature and experimental studies at the CNWRA, and modeled using different surface complexation approaches. Comparison of model results will allow evaluation of SCM performance, and should further indicate how these models can be simplified for practical incorporation into hydrogeochemical transport codes. In addition, calibration of sorption models will provide an understanding of what chemical conditions control radionuclide sorption.

Experiments studying uranium sorption on Na-montmorillonite, alpha-alumina, and clinoptilolite will continue. In order to obtain data on the surface properties of these minerals such as pH_{zpc} , a Mettler potentiometric titrator is being set up for acid-base titration of mineral samples, as well as a Micromeritics Zeta Potential Analyzer for electrophoretic measurements. Because the batch sorption experiments on single minerals only provide phenomenological information, that is, how much radionuclide is lost from solution, an attempt will be made to utilize molecular dynamics simulation to provide more mechanistic information by computer simulation of sorption of different aqueous species.

8.6 REFERENCES

- Abendroth, R.P. 1970. Behavior of pyrogenic silica in aqueous electrolytes. *Journal of Colloid and Interface Science* 34: 591-596.
- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. EPA/600/3-91/021. Athens, GA: U.S. Environmental Protection Agency.
- Atkinson, R.J., A.M. Posner, and J.P. Quirk. 1967. Adsorption of potential determining ions at the ferric oxide-aqueous electrolyte interface. *Journal of Physical Chemistry* 71: 550-558.
- Atkinson, R.J., A.M. Posner, and J.P. Quirk. 1968. Crystal nucleation in Fe(III) solutions and hydroxide gels. *Journal of Inorganic Nuclear Chemistry* 30: 2371-2381.
- Atkinson, R.J., A.M. Posner, and J.P. Quirk. 1972. Kinetics of isotopic exchange of phosphate at the α -FeOOH-aqueous solution interface. *Journal of Inorganic Nuclear Chemistry* 34: 2201-2211.
- Balistreri, L., and J.W. Murray. 1981. The surface chemistry of goethite (α -FeOOH) in major ion sea water. *American Journal of Science* 281: 788-806.
- Balistreri, L., and J.W. Murray. 1982. The surface chemistry of δ -MnO₂ in major ion sea water. *Geochimica et Cosmochimica Acta* 46: 1253-1265.
- Benjamin, M.M., and J.O. Leckie. 1981. Multiple site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *Journal of Colloid and Interface Science* 79: 209-221.
- Berube, Y.G., and P.L. de Bruyn. 1968. Adsorption at the rutile-solution interface. 1. Thermodynamic and experimental study. *Journal of Colloid and Interface Science* 27: 305-318.
- Bolt, G.H. 1957. Determination of the charge density of silica soils. *Journal of Physical Chemistry* 61: 1166-1169.
- Bradbury, M.H., and B. Baeyens. 1992. A mechanistic approach to the generation of sorption databases. *Radionuclide Sorption From the Safety Evaluation Perspective. Proceedings of an NEA Workshop*. Nuclear Energy Agency (NEA). Paris: Organization for Economic Cooperation and Development: 121-162.

- Breeuwsma, A., and J. Lyklema. 1973. Physical and chemical adsorption of ions in the electrical double layer on hematite ($\alpha\text{-Fe}_2\text{O}_3$). *Journal of Colloid and Interface Science* 43: 437-448.
- Catts, J.G., and D. Langmuir. 1986. Adsorption of Cu, Pb and Zn by $\delta\text{-MnO}_2$: Applicability of the site binding surface complexation model. *Applied Geochemistry* 1: 255-264.
- Davis, J.A. 1977. *Adsorption of Trace Metals and Complexing Ligands at the Oxide/Water Interface*. Ph.D. Dissertation Stanford, CA: Stanford University.
- Davis, J.A., and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Reviews in Mineralogy: Volume 23. Mineral-Water Interface Geochemistry*. M.F. Hochella, Jr. and A.F. White, eds. Washington, DC: Mineralogical Society of America: 177-260.
- Dzombak, D.A. 1985. *Toward a Uniform Model for the Sorption of Inorganic Ions on Hydrous Oxides*. Ph.D. Dissertation Cambridge, MA: Massachusetts Institute of Technology.
- Dzombak, D.A., and K.F. Hayes. 1992. Comment on recalculation, evaluation, and prediction of surface adsorption constants for metal adsorption on iron and manganese oxides. *Environmental Science and Technology* 26:1251-1253.
- Dzombak, D.A., and F.M.M. Morel. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1990. *Application of Surface Complexation Models for Radionuclide Adsorption: Sensitivity Analysis of Model Input Parameters*. NUREG/CR-5547. Washington, DC: U.S. Nuclear Regulatory Commission.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1991. Surface complexation models: An evaluation of model parameter estimation using FITEQL and oxide mineral titration data. *Journal of Colloid and Interface Science* 142: 448-469.
- Hsi, C.-K.D., and D. Langmuir. 1985. Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site-binding model. *Geochimica et Cosmochimica Acta* 49: 1931-1941.
- Huang, C.P., and W. Stumm. 1972. The specific surface area of $\gamma\text{-Al}_2\text{O}_3$. *Surface Science* 32: 287-296.
- James, R.O., and G. Parks. 1982. Characterization of aqueous colloids by their electrical double-layer and intrinsic surface chemical properties. *Surface and Colloid Science* 12: 119-216.
- Kent, D.B., V.S. Tripathi, N.B. Ball, J.O. Leckie, and M.D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. NUREG/CR-4807. Washington, D.C: U.S. Nuclear Regulatory Commission.
- Mesuer, K.L.G. 1992. *Adsorption and Dissolution Reactions Between Oxalate, Chromate, and an Iron Oxide Surface: Assessment of Current Modeling Concepts*. Ph.D. Dissertation. Beaverton, OR: Oregon Graduate Institute of Science and Technology.

- Murray, J.W. 1974. The surface chemistry of hydrous manganese dioxide. *Journal of Colloid and Interface Science* 46: 357-371.
- Pabalan, R.T., and D.R. Turner. 1992(a). *Sorption Modeling for HLW Performance Assessment. Report on Research Activities for Calendar Year 1991*. W.C. Patrick, ed. CNWRA 91-01A. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-66.
- Pabalan, R.T., and D.R. Turner. 1992(b). *Sorption Modeling for HLW Performance Assessment. NRC High-Level Radioactive Waste Research at CNWRA January 1 Through June 30, 1992*. W.C. Patrick, ed. CNWRA 92-01S. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-24.
- Pabalan, R.T., and D.R. Turner. 1993. *Sorption Modeling for HLW Performance Assessment. NRC High-Level Radioactive Waste Research at CNWRA July 1 Through December 31, 1992*. W.C. Patrick, ed. CNWRA 92-02S. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-18.
- Pabalan, R.T., J.D. Prikryl, P.M. Muller, and T.B. Dietrich. 1993. Experimental study of uranium (6+) sorption on the zeolite mineral clinoptilolite. C.G. Interrante and R.T. Pabalan, eds. *Scientific Basis for Nuclear Waste Management XVI. MRS Symp. Proc. 212*, Pittsburgh, PA: Materials Research Society: 777-782.
- Papelis, C., K. F. Hayes, and J. O. Leckie. 1988. *HYDRAQL: A Program for the Computation of Chemical Equilibrium Composition of Aqueous Batch Systems Including Surface-Complexation Modeling of Ion Adsorption at the Oxide/Solution Interface*. Technical Report No. 306., Stanford, CA: Stanford University.
- Payne, T.E., K. Sekine, J.A. Davis, and T.D. Waite. 1992. Modeling of radionuclide sorption processes in the weathered zone of the Koongarra ore body. *Alligator Rivers Analogue Project Annual Report, 1990-1991*. P. Duerden, ed. Menai, New South Wales, Australia: Australian Nuclear Science and Technology Organization: 57-85.
- Regazzoni, A.E., M.A. Blesa, and A.J.G. Maroto. 1983. Interfacial properties of zirconium dioxide and magnetite. *Journal of Colloid and Interface Science* 91: 560-570.
- Siegel, M.D., J.O. Leckie, S.W. Park, S.L. Phillips, and T. Sowards. 1990. *Studies of Radionuclides Sorption by Clays in the Culebra Dolomite at the Waste Isolation Pilot Plant Site, Southeastern New Mexico*. SAND89-2387. Albuquerque, NM: Sandia National Laboratories.
- Siegel, M.D., V.S. Tripathi, M.G. Rao, and D.B. Ward. 1992. Development of a multi-site model for adsorption of metals by mixtures of minerals: 1. Overview and preliminary results. *Water-Rock Interaction: Proceedings 7th International Symposium on Water-Rock Interaction*. Y.F. Kharaka and A.S. Maest eds. Rotterdam, Netherlands: A.A. Balkema.

- Smith, R.W., and E.A. Jenne. 1988. *Compilation, Evaluation, and Prediction of Triple-Layer Model Constants for Ions on Fe(III) and Mn(IV) Hydrous Oxides*. PNL-6754. Richland, WA: Pacific Northwest Laboratory.
- Sprycha, R. 1984. Surface charge and adsorption of background electrolyte ions at anatase/electrolyte interface. *Journal of Colloid and Interface Science* 102: 173-185.
- Sprycha, R. 1989. Electrical double layer at alumina/electrolyte interface. *Journal of Colloid and Interface Science* 127: 1-11.
- Swallow, K.C. 1978. *Adsorption of Trace Metals by Hydrous Ferric Oxide*. Ph.D. Dissertation. Cambridge, MA: Massachusetts Institute of Technology.
- Tripathi, V.S. 1984. *Uranium(VI) Transport Modeling: Geochemical Data and Submodels*. Ph.D. Dissertation. Stanford, CA: Stanford University.
- Westall, J.C. 1982. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 2.0*. Rpt. 82-02. Corvallis, OR: Oregon State University.
- Westall, J.C., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Advances in Colloid and Interface Science* 12: 265-294.
- Wolery, T.J., K.J. Jackson, W.L. Bourcier, C.J. Bruton, B.E. Viani, K.G. Knauss, and J.M. Delany. 1990. Current status of the EQ3/6 software package for geochemical modeling. D.C. Melchior and R.L. Bassett, eds. *Chemical Modeling of Aqueous Systems II. ACS Symp. Series 416*. Washington, DC: American Chemical Society: 104-116.
- Yates, D.A. 1975. *The Structure of the Oxide/Aqueous Electrolyte Interface*. Ph.D. Dissertation. Melbourne, Australia: University of Melbourne.
- Yates, D.A., and T.W. Healy. 1975. Mechanism of anion adsorption at the ferric and chromic oxide/water interfaces. *Journal of Colloid and Interface Science* 52: 222-228.

6 SORPTION MODELING FOR HLW PERFORMANCE ASSESSMENT

by Roberto T. Pabalan and David R. Turner

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6.1 TECHNICAL OBJECTIVES

A fundamental concern in evaluating the suitability of Yucca Mountain, Nevada, as a repository for high-level nuclear waste (HLW) is the possibility of radionuclide migration from the repository to the accessible environment as dissolved constituents in groundwaters. An important mechanism for attenuating radionuclide migration is sorption of radionuclides on minerals encountered along the flow paths. Sorption is specifically referred to in 10 CFR 60.122(b) as a favorable geochemical condition that would tend to inhibit radionuclide migration and "favorably affect the ability of the geologic repository to isolate the waste." Conversely, geochemical processes that "would reduce sorption of radionuclides" are listed [10 CFR 60.122(c)(8)] as potentially adverse conditions that could reduce the effectiveness of the natural barrier system.

To support the U.S. Nuclear Regulatory Commission (NRC) HLW program, the Center for Nuclear Waste Regulatory Analyses (CNWRA) is conducting research activities under the Sorption Modeling for HLW Performance Assessment (PA) Research Project. The broad objective is to develop a sufficient understanding of radionuclide transport issues so that timely precicensing guidance can be provided to the U.S. Department of Energy (DOE) and a sound basis be available for evaluating the DOE license application. The results will be used to support the NRC License Application Review Plan (LARP), particularly Sections 3.2.3.2, 3.2.3.3, and 3.2.3.5 pertaining to favorable and potentially adverse geochemical conditions and processes at a potential repository site, and Section 3.4, which addresses the effectiveness of natural barriers against the release of radioactive material to the environment. Laboratory and modeling studies of radionuclide sorption, retardation, and transport, which are central to the Sorption Research Project, will provide independent bases for addressing Key Technical Uncertainties (KTUs) identified during development of Compliance Determination Strategies (CDSs), which are an integral part of LARP. Specifically, the following KTUs will be addressed by this research project:

- Identity and magnitude of the effects of geochemical processes that reduce radionuclide retardation
- Parametric representation of retardation processes
- Capacity of alteration mineral assemblages to inhibit radionuclide migration
- Effect of degree of saturation on radionuclide sorption and transport

In addition, development of Compliance Determination Methods (CDMs) for evaluating compliance with the regulatory requirements will use data and models generated from this research project.

Results arising from this project will be integrated with those from other CNWRA activities. For example, data on uranium sorption will be used in interpreting data on uranium distribution and migration at the Peña Blanca field site of the Geochemical Natural Analog Research Project (Chapter 5), as well as in developing conceptual models for radionuclide transport/retardation in near- and far-field environments related to the PA Research Project (Chapter 7) and the Iterative Performance Assessment (IPA) Phase 3. Results of activities undertaken during the second half of 1993 are discussed in the sections that follow.

6.2 HYDROGEOCHEMICAL MODELING

6.2.1 Introduction

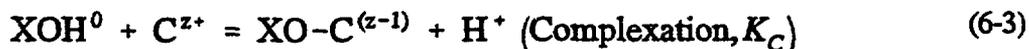
Traditional approaches have modeled radionuclide retardation using parametric models that rely on purely empirical parameters. One KTU in evaluating the suitability of Yucca Mountain as a site for a geologic HLW repository is the ability of such models to accurately represent geochemical processes that could contribute to radionuclide sorption and retardation. Surface complexation models (SCM) have been largely developed and refined as a mechanistic approach to investigating the pH-dependent sorption behavior of toxic species such as Zn^{2+} , Cd^{2+} , Pb^{2+} , and CrO_4^{2-} on simple (hydr)oxides such as goethite (α -FeOOH), rutile (TiO_2) and ferrihydrite [$Fe(OH)_3$], (Davis and Leckie, 1978; Rai et al., 1988; Dzombak and Morel, 1990). Similar studies have begun to be performed to study the sorption of key radionuclides (especially actinides) on a variety of minerals, including both simple (hydr)oxides and more complex minerals such as micas and clays (Riese, 1982; Tripathi, 1984; Kent et al., 1988; Kohler et al., 1992). To take full advantage of this research for PA, there is a need to apply SCMs to radionuclide sorption. Recent work (Pabalan and Turner, 1993) has focused on using a uniform approach to develop a set of consistent parameters for commonly used SCMs for different simple (hydr)oxides. With these parameters in place, it is possible to use SCMs to interpret existing data and to compare model performance in predicting radionuclide sorption on these different simple minerals as a function of changes in system chemistry. It may also be possible to use the SCM approach to examine radionuclide sorption on more complex rock-forming minerals such as zeolites, feldspar, and mica.

Three commonly used SCMs include the Diffuse Layer (DLM), Constant Capacitance (CCM), and Triple Layer (TLM) Models. The conceptual bases and assumptions for these models are discussed in detail elsewhere (Westall and Hohl, 1980; Davis and Kent, 1990; Pabalan and Turner, 1993). In brief, all SCMs employ equilibrium reactions involving protonation/deprotonation of amphoteric surface functional groups (XOH^0) to describe the acid-base behavior of a mineral surface.



where K_+ and K_- are referred to as intrinsic surface acidity constants. Sorption is represented by postulating the formation complexes at the mineral/water interface between these sites and the cations and

anions in solution. Surface reactions are assumed to be analogous to aqueous speciation reactions. This requires an additional assumption regarding the stoichiometry of the surface reactions(s). A typical surface reaction (for the sorbing cation C^{z+} in this case) takes the general form



where $XO-C^{(z-1)}$ represents the surface complex with a total charge of $z-1$.

The electrostatic attraction and repulsion of these sites for charged species in solution form the basis for surface complexation models. For surface species, activity expressions are corrected for electrostatic effects by assuming an exponential Boltzmann relationship. The total number of available surface sites in mineral- H_2O systems (sites/L) is calculated based on the product of specific surface area (A_{SP} in m^2/g), site density (N_S in sites/ nm^2), and solid concentration (c_S in g/L) in the liquid. In a given system, mass action, mass balance, and model-specific charge/potential constraints can be used in a manner analogous to that employed by geochemical aqueous speciation programs (Westall and Hohl, 1980; Allison et al., 1991) to determine distribution of the element of interest between the dissolved and sorbed phases.

The DLM and CCM both assume that protonation/deprotonation and adsorption occur in one plane at the surface/solution interface, and that only those ions specifically adsorbed in this "o-plane" contribute to the total surface charge. In the DLM, the Stern-Grahame extension of the Gouy-Chapman relationship for symmetrical electrolytes is used to describe the interdependence between electrolyte concentration (ionic strength), charge, and electrostatic potential. In contrast to the DLM, the CCM assumes that the charged surface is separated from the bulk solution by a layer of constant capacitance; surface charge is related to surface potential through a simple linear equation. In its formulation, the CCM does not explicitly consider ionic strength effects. Therefore, in a strict sense, CCM acidity constants are only valid at one ionic strength; new values are necessary if conditions change. More elaborate than the DLM and CCM, the TLM divides the mineral/water interface into three layers. In its original construction (see Davis and Kent, 1990), protonation/deprotonation of surface sites (K_+ and K_-) is restricted to the innermost o-plane, and specifically adsorbed ions are assigned to the β -plane (i.e., outer-sphere complexes). Subsequent modifications provide for inner-sphere complexes to describe strongly bound metals. The outermost layer, the d-plane, is made up of a diffuse region of counterions extending into the bulk solution. Like the DLM, the TLM uses the Gouy-Chapman relationship and is applicable at different ionic strengths. The TLM also handles ionic strength effects through provisions for background electrolyte adsorption.

Although the SCM approach is not an explicit mechanistic model of processes at the mineral surface at the atomistic level, it incorporates aspects of thermodynamic principles to describe the mineral/water interface. As such, the difference SCM use a set of parameters that describe an idealized, but physically reasonable model of the electrostatic and acid-base behavior of a given mineral. While there is still uncertainty in the complexes formed at the surface, current research is under way using spectroscopic techniques to determine surface species (e.g., Manceau and Charlet, 1991) and provide some independent support of modeling efforts. In spite of these limitations, theoretically based SCMs represent a critical step toward more mechanistic models and are able to predict for the effects of changes in the solution and surface chemistry in a quantitative way that most purely empirical methods such as a linear K_d model cannot.

The major drawback of the models is the complexity inherent in their construction, which limits practical applications in PA. This complexity is reflected in the number of parameters used in each model. The DLM is the simplest model, requiring only four types of adjustable parameters: protonation (K_+); deprotonation (K_-); binding constants (such as $K_{\text{UO}_2^{2+}}$); and site density (N_s). The CCM shares these four parameters plus a capacitance term (C_1) for charge/potential relationships. As the most elaborate model, the TLM requires eight types of adjustable parameters: the four used by the DLM, and binding constants for sorbing background electrolytes (K_{Cation} and K_{Anion} such as K_{Na^+} , $K_{\text{NO}_3^-}$); and capacitances for the inner and outer layers (C_1 and C_2 , respectively).

Parameter values are imperfectly known and, in practice, have been used as multiple fitting parameters specific to a particular data set. Because of fundamental differences in how the models treat the mineral/water interface and the tendency to use model-specific parameters, it is difficult to directly compare the results of different studies (Westall and Hohl, 1980). One recently advocated approach is the characterization of the mineral surface using "standard" values for parameters such as acidity constants, site density, and capacitances that are uniformly applied in all contaminant systems (Davis and Kent, 1990; Dzombak and Morel, 1990; Hayes et al., 1990). While this approach may not represent the exact processes operating at the mineral/water interface, once the mineral surface is characterized, the number of adjustable parameters is limited to the binding constant(s) for the assumed surface complexes. This serves to establish a baseline for future comparison of modeling results and also provides for future development of a consistent sorption database for PA.

Using this uniform approach to interpret available potentiometric titration data and the nonlinear least squares parameter optimization program FITEQL, Version 2.0 (Westall, 1982), Pabalan and Turner (1993) established a set of consistent parameters for the DLMs, CCMs, and TLMs for nine different (hydr)oxides. The following discussion uses these parameters to examine actinide sorption on different types of surfaces. All sorption modeling results were calculated using MINTEQA2, Version 3.11 (Allison et al., 1991) and the radionuclide database developed at the CNWRA (Turner et al., 1993; Turner, 1993). The reader is referred to these studies and the references therein for more details on the methods employed and thermodynamic data sources.

6.2.2 Modeling Radionuclide Sorption on Simple (Hydr)oxides—Effects of Surface-Area/Solution Volume Ratio

To examine sorption as a function of mineral surface area, recent studies at the CNWRA have focused on uranium(6+) [also UO_2^{2+} or uranium(6+)] sorption on α -alumina ($\alpha\text{-Al}_2\text{O}_3$). Efforts were undertaken to investigate the ability of surface complexation models to predict the observed changes in sorption using the model parameters developed previously (Pabalan and Turner, 1993). Because it is the simplest SCM, attention was focused on the DLM.

In addition to data on the mineral properties and the acidity constants to describe acid-base behavior of the surface, FITEQL requires the input of a chemical equilibrium model for the system under investigation. For readily hydrolyzable elements such as UO_2^{2+} , the chemical system quickly becomes complicated with the inclusion of equilibrium constants for the formation of aqueous uranyl-hydroxy-carbonato species. For this reason, the resultant binding constants are dependent on the quality and extent of the thermodynamic data available for the system of interest. Implicit in this statement is that binding constants derived using FITEQL are valid only for the thermodynamic data used in constructing the chemical equilibrium model. For uranium, the equilibrium constants used in the chemical equilibrium

models submitted to FITEQL were selected from the internally consistent NEA Thermodynamic Database (Grenthe et al., 1992). All data were corrected for ionic strength effects using the Davies equation. If the same data sources are used, the binding constants can be applied in sorption/speciation codes such as MINTQA2 (Allison et al., 1991) to model uranium sorption once corrected to a reference state of $I=0$ M. To maintain simple models as much as possible, a single monodentate uranium surface species was assumed.

The input parameters used in setting up the FITEQL run to interpret the alumina sorption data are given in Table 6-1. The data sets for each of the three surface-area/solution-volume ratios considered were interpreted using FITEQL, and the resulting binding constants were combined, based on the standard deviation reported by FITEQL (see Dzombak and Morel, 1990 for details), to yield a weighted best estimate. Based on the statistical measure of goodness-of-fit provided by FITEQL (see Westall, 1982 for details), assuming the formation of the surface species $XO-(UO_2)_2CO_3(OH)_3^0$ was able to reproduce the observed sorption behavior quite well (Figure 6-1). Not surprisingly, the binding constants determined for each individual data set (solid lines) provide the best fit to the observed data. However, the binding constants for the different data sets do not differ appreciably (Table 6-1), and the weighted value (dashed lines) also provides a reasonable fit to the data. The fact that the binding constants are similar for all three data sets suggests that fitting only one data set would predict the sorption behavior of the other two data sets well. For example, the binding constant determined for the 2.09 m²/g data set (Log K=12.64) is quite close to the weighted value (Log K=12.73) and results in a fit similar to that shown by the dashed line in Figure 6-1. For the highest surface-area/solution-volume ratio, the model predicts a steep sorption edge that diverges from the observed values at pH less than about 5. This suggests that noncarbonate uranyl species such as UO_2^{2+} or UO_2OH^+ may be necessary to fine-tune the model at lower pH and produce the best fit to the data. For PA, the benefits of achieving improved accuracy in this fashion should be weighed against the additional computational time required by the added level of complexity.

6.2.3 Modeling Radionuclide Sorption on Complex Rock-Forming Minerals

Radionuclide sorption data are available for a number of common rock-forming minerals such as clays, micas, and zeolites, which, because of their abundance, may contribute significantly to sorption processes at Yucca Mountain. Typically, these minerals have a fixed-charge component due to Al^{3+} substitution for tetrahedral Si^{4+} , but many also exhibit a pH-dependent variable surface charge similar to simple (hydr)oxides (Kent et al., 1988; Siegel et al., 1992). In contrast to simple (hydr)oxides, only rarely are potentiometric titration data available for these minerals (e.g., Riese, 1982). However, because these minerals are more complex, the development of a pH-dependent surface charge may be due to more than one type of site.

Recent studies have proposed modeling radionuclide sorption on complex rock-forming minerals assuming a heterogeneous surface composed of different site types with acid-base behavior controlled independently of one another (Brady and Walther, 1992). For example, using a TLM, Rai et al. (1988) modeled chromate (CrO_4^{2-}) adsorption on kaolinite assuming a heterogeneous surface composed of stoichiometric proportions of silanol ($SiOH^0$) and aluminol ($AlOH^0$) sites. Similar approaches have been proposed to model radionuclide sorption on kaolinite, including uranium (Kohler et al., 1992), thorium, and radium (Riese, 1982).

The uranium(6+)-kaolinite sorption data of Payne et al. (1992) and neptunium(5+)-biotite sorption data of Nakayama and Sakamoto (1991) were investigated using this approach. Surface areas for

Table 6-1. DLM binding constants (Log K) for forming the indicated surface complex, determined using FITEQL, Version 2.0 (Westall, 1982) and sorption data for the uranium(6+)- α -alumina system. Acidity constants are from Pabalan and Turner (1993). $N_S=2.31$ sites/nm²; Reported A_{SP} (m²/g) are: RM 8005=2.09; RM 8006=0.229; RM 8007=0.0686. Uranium(6+)_T=95 ppb (4.4×10^{-7} M). Values corrected to I=0 M using Davies equation.

Uranium(6+)- α -alumina ^(a)	
Surface Complex	DLM: Log K ^(b)
AlOH ₂ ⁺	8.33 ± 0.15
AlO ⁻	-9.73 ± 0.12
AlO-(UO ₂) ₂ CO ₃ (OH) ₃ ⁰ - [RM 8005]	12.64 ± 0.01
AlO-(UO ₂) ₂ CO ₃ (OH) ₃ ⁰ - [RM 8006]	12.70 ± 0.01
AlO-(UO ₂) ₂ CO ₃ (OH) ₃ ⁰ - [RM 8007]	12.91 ± 0.01
AlO-(UO ₂) ₂ CO ₃ (OH) ₃ ⁰ - Weighted	12.73 ± 0.19
^(a) Data for the chemical equilibrium model are from NEA Thermodynamic Database for Uranium (Grenthe et al., 1992).	
^(b) Reported uncertainties represent 95-percent confidence limit for acidity constants and weighted binding constant. For best-fit surface complexes, listed uncertainty represents standard deviation ($\pm 1\sigma$) reported by FITEQL.	

these minerals were taken from Allard et al. (1983). End-member stoichiometries were assumed for kaolinite (Al₂Si₂O₅) and biotite [K(Mg,Fe)₃AlSi₃O₁₀(OH)₂]. The total number of sites was calculated based on the assigned surface area, solid concentration in suspension, and a site density of 2.31 sites/nm² as recommended by Davis and Kent (1990). These sites were divided between AlOH⁰ and SiOH⁰ based on the stoichiometric proportions for kaolinite and biotite (AlOH⁰:SiOH⁰ = 1:1 and 1:3, respectively). The acid-base behavior of each site type was assumed to be independent of the other site type, and sites were modeled using the acidity constants determined for SiO₂ and α -alumina in earlier studies (Pabalan and Turner, 1993). The thermodynamic data for uranium are from the NEA database (Grenthe et al., 1992), and neptunium data are from the latest release of the EQ3/6 database (Release Data0.com.r16; Lemire, 1984). With these data as input into the chemical equilibrium model, and the sorption data from the two studies, FITEQL, Version 2.0 (Westall, 1982) was used to determine binding constants for the different surface complexation models. For the diffuse-layer model, the estimated binding constants are listed in Table 6-2, and the results are shown in Figure 6-2.

Contaminant speciation (especially for actinides) can vary rapidly as a function of pH (Turner, 1993). For this reason, sorption edges that extend over wider pH ranges, such as those exhibited by the uranium(6+)-kaolinite and neptunium(5+)-biotite data, tend to require more than one surface complex (Davis and Leckie, 1978; Dzombak and Morel, 1990). The approach taken here is greatly simplified

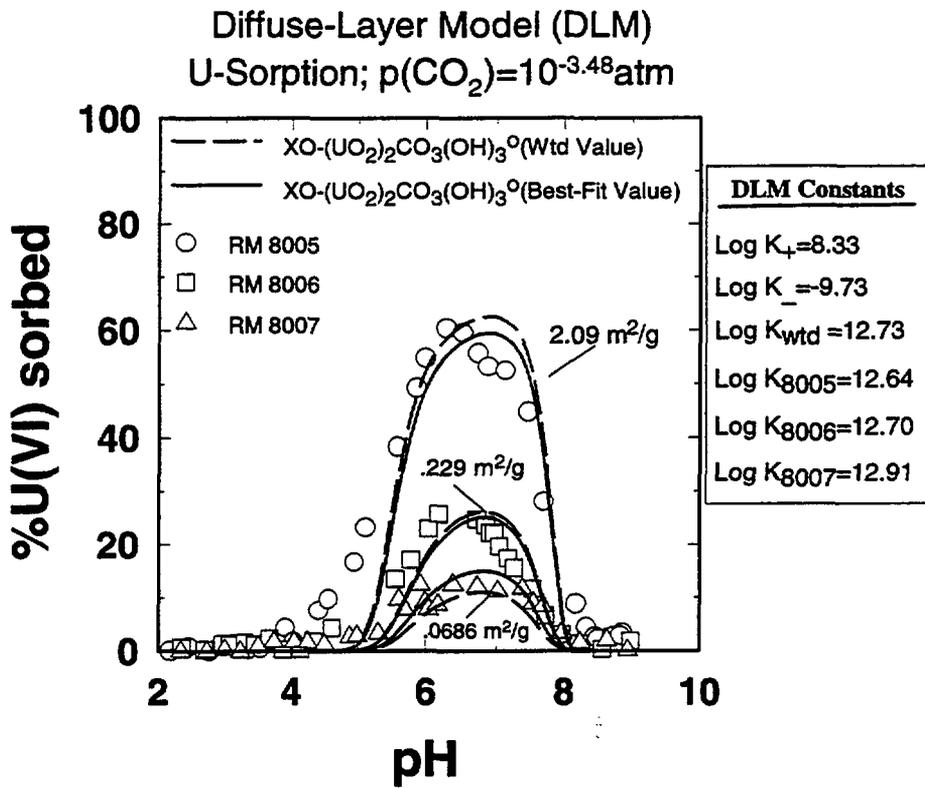


Figure 6-1. DLM modeling results for uranium(6+)- α -alumina sorption (under atmospheric CO_2) assuming the formation of a single surface complex, $\text{XOH}_2\text{-(UO}_2)_2\text{CO}_3(\text{OH})_3$. Model parameters and binding constants are given in Table 6-1.

compared to the heterogeneous binding sites likely to be found at the surface. For both sheet silicates, sorption behavior is likely to be due to a combination of ion exchange at intracrystalline sites and surface complexation along edge sites. For biotite, other site types (e.g., Fe, Mg) probably also contribute to pH-dependent surface charge. Nevertheless, the relatively simple DLM is able to reproduce the observed behavior quite well (Figure 6-2). However, as discussed earlier, the added complexity of multiple surface species tends to make the practical application of SCMs more difficult in PA.

In addition to α -alumina, experiments at the CNWRA have focused on sorption behavior in the uranium(6+)- $\text{H}_2\text{O-CO}_2$ -clinoptilolite system. The data exhibit the same type of sorption behavior as that shown by α -alumina, with a steep sorption edge over a fairly narrow pH range from 4 to 6 with a maximum at about 6.5 and a sharp desorption edge at more basic pH values. A similar approach to that taken for the uranium(6+)-kaolinite and neptunium(5+)-biotite sorption data discussed previously was taken for clinoptilolite. The nominal formula for Na-clinoptilolite is $(\text{Na}_2\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 8\text{H}_2\text{O})$, yielding a Si:Al ratio of 5:1. The clinoptilolite used in the CNWRA experiments is slightly enriched in silica relative to the idealized form $(\text{Na}_{1.807}\text{K}_{0.123}\text{Ca}_{0.0031}\text{Mg}_{0.0349})(\text{Al}_{1.948}\text{Fe}^{3+}_{0.044})(\text{Si}_{10.044}\text{Ti}_{0.0044})\text{O}_{24} \cdot 7.43\text{H}_2\text{O}$, and yields a Si:Al ratio of 5.15:1 (Pabalan et al., 1993). This ratio was used in SCM modeling studies of the sorption data. Because surface area measurements are not yet available for this clinoptilolite a BET surface area of $16\text{ m}^2/\text{g}$ was assumed (Los Alamos National Laboratory, 1993). Site density was fixed at $2.31\text{ sites}/\text{nm}^2$ (Dzombak and Morel, 1990; Davis and Kent, 1990), and as, with kaolinite, the acidity constants for SiO_2 and α -alumina were used with thermodynamic data from the NEA uranium

Table 6-2. DLM binding constants (Log K) for forming the indicated surface complexes, determined using FITEQL, Version 2.0 (Westall, 1982) and sorption data for the uranium(6+)-kaolinite (Payne et al., 1992) and neptunium(5+)-biotite (Nakayama and Sakamoto, 1991) systems. Stoichiometric proportions of SiOH⁰ and AlOH⁰ of 1:1 and 3:1 are assumed for kaolinite and biotite, respectively. Acidity constants are from Pabalan and Turner (1993). N_S=2.31 sites/nm²; A_{SP}=11 m²/g and 8 m²/g for kaolinite and biotite, respectively (Allard et al., 1983). Uranium(6+)_T=10⁻⁶ M; Neptunium(5+)_T=6×10⁻⁶ M. Values corrected to I=0 M using Davies equation.

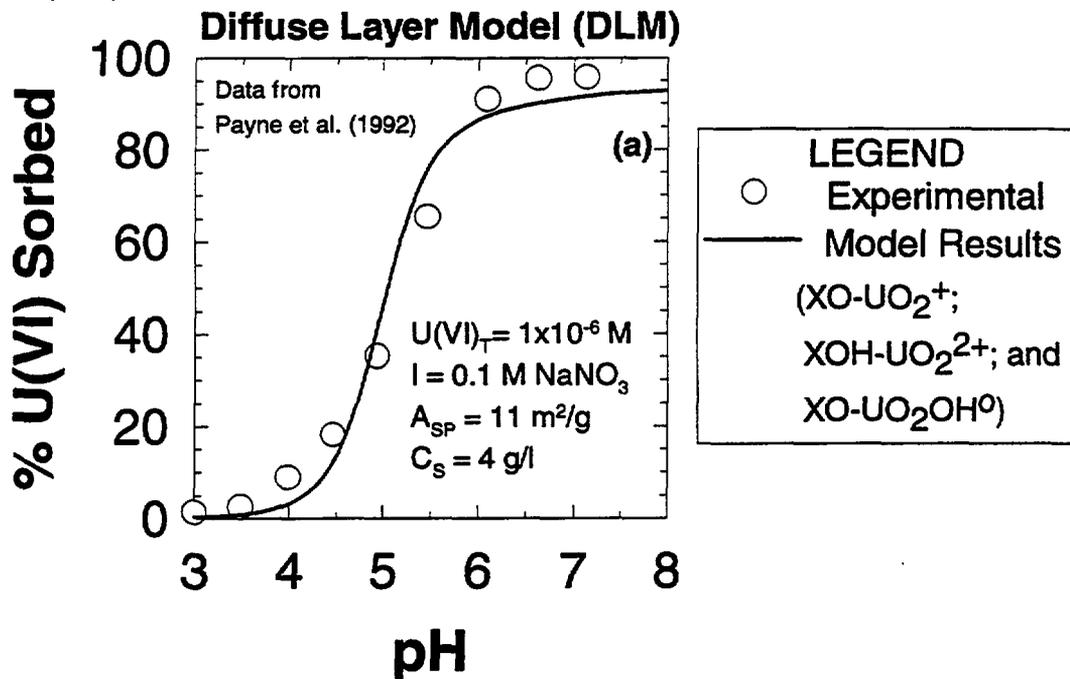
Uranium(6+)-kaolinite (Payne et al., 1992) ^(a)		Neptunium(5+)-biotite (Nakayama and Sakamoto, 1991) ^(a)	
Surface Complex	DLM: Log K _(b)	Surface Complex	DLM: Log K _(b)
SiOH ₂ ⁺ AlOH ₂ ⁺	n.a. 8.33±0.15	SiOH ₂ ⁺ AlOH ₂ ⁺	n.a. 8.33±0.15
SiO ⁻ AlO ⁻	-7.20±0.05 -9.73±0.12	SiO ⁻ AlO ⁻	-7.20±0.05 -9.73±0.12
SiO-UO ₂ ⁺ AlO-UO ₂ ⁺	0.96±0.04 2.18±0.10	SiOH-NpO ₂ ⁺ AlOH-NpO ₂ ⁺	2.86±0.06 4.15±0.03
SiOH-UO ₂ ²⁺ AlOH-UO ₂ ²⁺	5.73±0.16 9.20±0.03	SiO-NpO ₂ OH ⁻ AlO-NpO ₂ OH ⁻	-11.58±0.02 -12.39±0.17
SiO-UO ₂ OH ⁰ AlO-UO ₂ OH ⁰	-5.84±0.44 -4.74±0.59	-- --	-- --

n.a. — pH_{ZPC} ≈ 2.8 for SiO₂; SiOH₂⁺ not considered in this pH range.

^(a)Data for the chemical equilibrium model are from NEA Thermodynamic Database for Uranium (Grenthe et al., 1992); neptunium data are from the EQ3/6 database (Release Data0.com.r16; Lemire, 1984).

^(b)Reported uncertainties represent 95-percent confidence limit for acidity constants. For surface complexes, listed uncertainty represents standard deviation (±1σ) reported by FITEQL.

U(VI) SORPTION ON KAOLINITE



Np(V) SORPTION ON BIOTITE

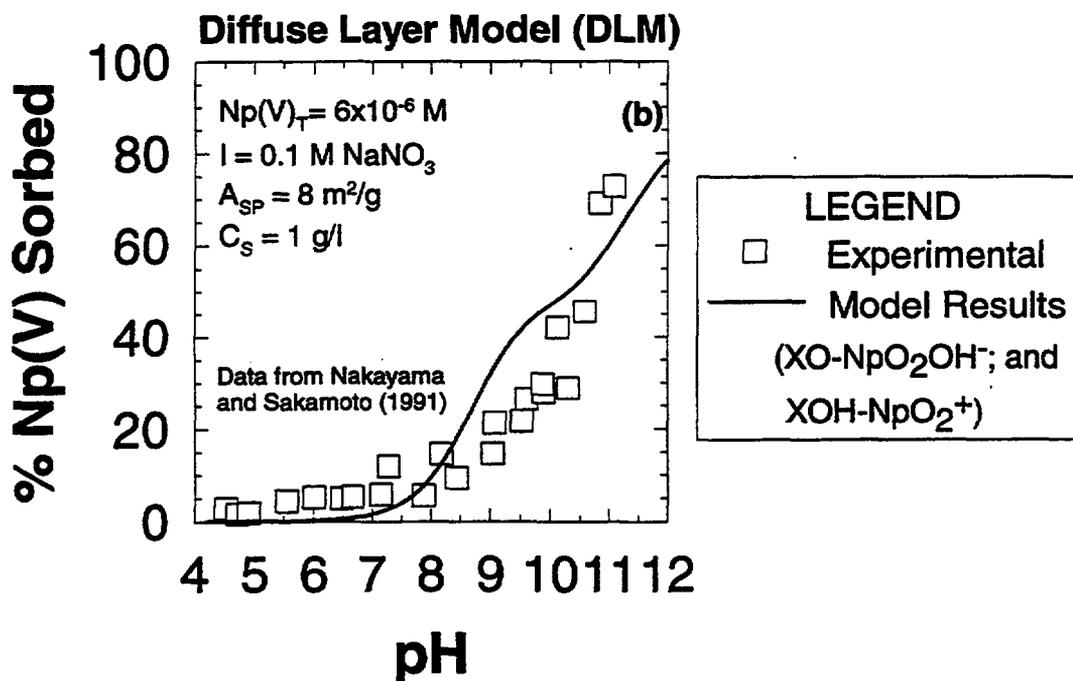


Figure 6-2. DLM modeling results for: (a) uranium(6+)-kaolinite sorption (Payne et al., 1992); (b) neptunium(5+)-biotite sorption (Nakayama and Sakamoto, 1991). Model parameters and binding constants are given in Table 6-2.

database (Grenthe et al., 1992) to construct the chemical equilibrium model for FITEQL. Based on the interpretation of the 50-ppb sorption data, values for the estimated binding constants are given in Table 6-3; these values are typically within 0.1 log units of values determined by fitting the 500-ppb data. Modeling results calculated using the values in Table 6-3 are shown in Figure 6-3.

Given the constraints on the conceptual approach used, the DLM is able to reproduce the sorption and desorption edges for the 5-, 50- and 500-ppb data. For the 5-, and 50-ppb data, the model results for $\text{SiOH-UO}_2\text{CO}_3^0$ and AlOH-UO_2^{2+} fall slightly short of the sorption maximum. For the 500-ppb data, the surface complexes SiO-UO_2^+ and AlO-UO_2^+ predict the maximum fairly well, though the predicted maximum is shifted to a slightly lower pH. These modeling results suggest the formation of different surface species at the silanol and aluminol sites. This assumption is reasonable given the large differences in pH_{ZPC} between SiO_2 and α -alumina (2.8 and 8.9, respectively). Modeling also suggests that different surface species form at the different uranium concentrations. This suggestion is also reasonable given the significant changes in speciation predicted with changes in total uranium(6+) concentration (Turner, 1993).

As in most cases, it is possible to improve the fit to sorption data by postulating additional surface species. It is also possible that sorption involving fixed-charge ion exchangers like clays and zeolite is more complicated than the surface processes assumed in surface complexation models. It is important to remember, however, that the added benefits of improving accuracy in this fashion must be weighed against the additional computational burden imposed by the added complexity.

6.2.4 Summary and Conclusions

Experimental sorption data indicate that radionuclide (especially actinide) sorption is a complex function of the physical and chemical conditions of the system under consideration. Current PA approaches, however, tend to rely on purely empirical methods to model radionuclide sorption. Because these models do not explicitly account for changes in system chemistry, extrapolation of laboratory data beyond experimental conditions is uncertain. The purpose of this study is to move toward a uniform mechanistic model for radionuclide sorption that allows for the prediction of complex sorption behavior and quantitatively accounts for changes in the physical and chemical conditions.

SCMs are one type of mechanistic approach to modeling sorption processes. These models use similar approaches to correct for electrostatic effects at the charged mineral/water interface, but differ in how the interface is conceptualized. The complexity of these models also varies with the types of adjustable parameters, ranging from four for the DLM to eight for the TLM. Traditional applications rely on adjusting different parameters to match a given data set. Because of the number of parameters, this method is likely to result in a nonunique fit and makes comparisons between models and between studies difficult.

A first attempt has been made to develop and apply a standard set of SCM parameters to radionuclide sorption (Pabalan and Turner, 1993). Using available potentiometric titration data, model-specific values for K_+ , K_- , K_{Cation} , and K_{Anion} were developed for the CCMs, DLMs, and TLMs using a uniform approach (Dzombak and Morel, 1990; Hayes et al., 1990). In this way, only a single type of adjustable parameter, the binding constant, remains to model radionuclide sorption data. Since the user can still specify the types of complexes forming at the mineral surface, there is still flexibility in this modeling approach.

Table 6-3. DLM binding constants (Log K) for forming the indicated surface complexes, determined using FITEQL, Version 2.0 (Westall, 1982) and 50-ppb sorption data for the uranium(6+)-clinoptilolite system. Stoichiometric proportions of SiOH⁰ and AlOH⁰ (5.15:1) are assumed for clinoptilolite. Acidity constants are from Pabalan and Turner (1993). N_S=2.31 sites/nm²; A_{SP}=16 m²/g (Los Alamos National Laboratory, 1993). Values corrected to I=0 M using Davies equation.

Uranium(6+)-clinoptilolite ^(a)	
Surface Complex	DLM: Log K ^(b)
SiOH ₂ ⁺ AlOH ₂ ⁺	n.a. 8.33 ± 0.15
SiO ⁻ AlO ⁻	-7.20 ± 0.05 -9.73 ± 0.12
SiOH-UO ₂ ²⁺ AlOH-UO ₂ ²⁺	5.89 ± 0.01 9.24 ± 0.01
SiO-UO ₂ ⁺ AlO-UO ₂ ⁺	0.19 ± 0.01 2.69 ± 0.01
SiO-UO ₂ OH ⁰ AlO-UO ₂ OH ⁰	-6.30 ± 0.01 -4.26 ± 0.01
SiOH-UO ₂ CO ₃ ⁰ AlOH-UO ₂ CO ₃ ⁰	15.58 ± 0.01 19.25 ± 0.01
n.a. — pH _{ZPC} ≈ 2.8 for SiO ₂ ; SiOH ₂ ⁺ not considered in this pH range.	
^(a) Data for the chemical equilibrium model are from NEA Thermodynamic Database for Uranium (Grenthe et al., 1992).	
^(b) Reported uncertainties represent 95-percent confidence limit for acidity constants. For surface complexes, listed uncertainty represents standard deviation (± 1σ) reported by FITEQL.	

These parameters were used in conjunction with the FITEQL code to model other available sorption data. In the case of α-alumina, the DLM and a relatively simple conceptual model invoking a single-surface complex was able to model the effects of variable surface-area/solution-volume ratio reasonably well. In addition to simple (hydr)oxides, it is also possible to apply these models to more complex rock-forming minerals. Assumption of stoichiometric proportions of different site types enabled the DLM to be used to model relatively complex sorption behavior for several different types of complex multioxides including clay, mica, and zeolite, all minerals that are present at Yucca Mountain.

From this study, it is apparent that the application of SCMs to radionuclide sorption behavior proceeds through a logical progression of steps from mineral properties to acidity constants to

U(VI)-SORPTION ON CLINOPTILOLITE
Diffuse-Layer Model (DLM)
 $\text{SiOH}^{\circ}:\text{AlOH}^{\circ} = 5.15:1$

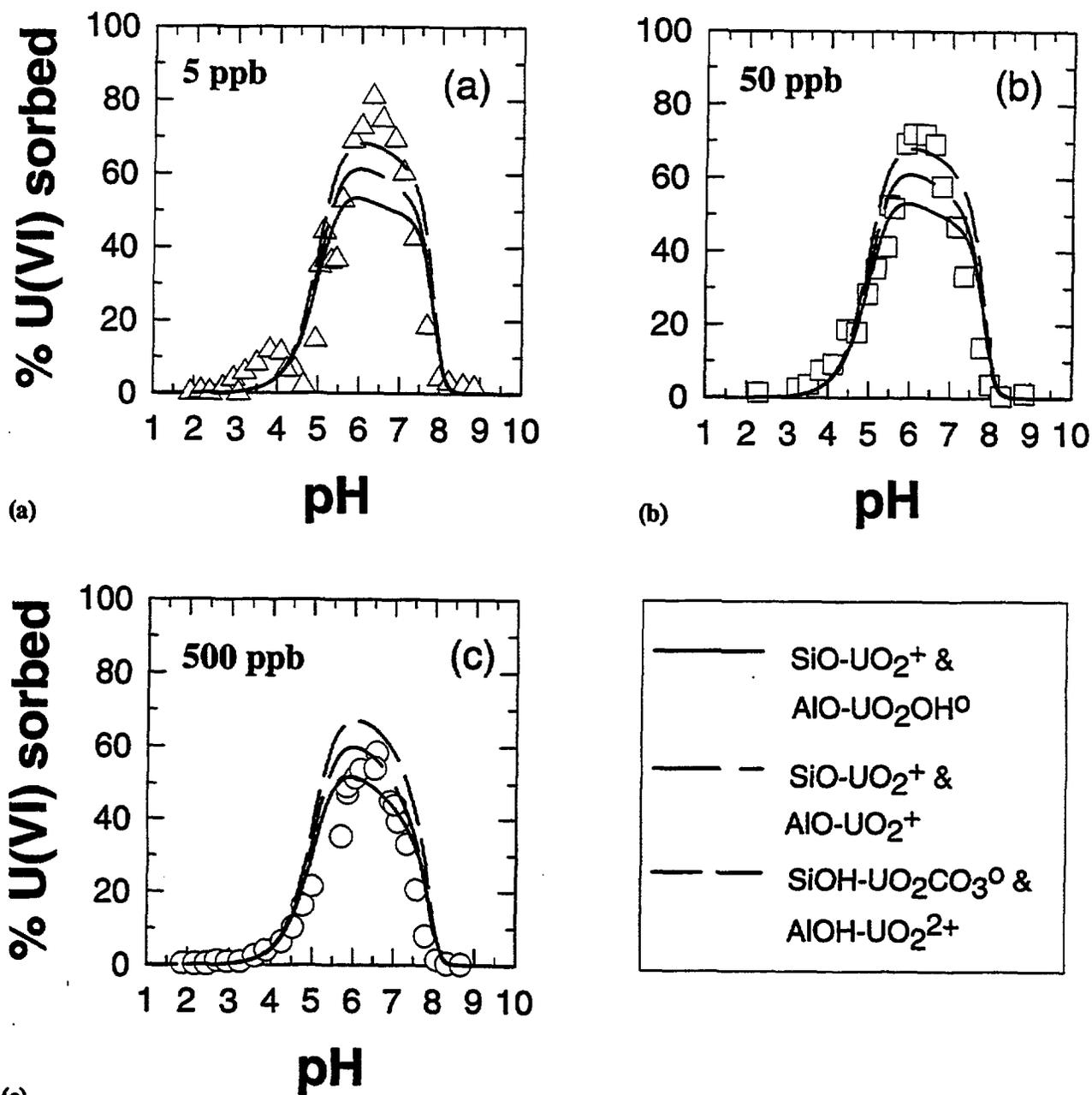


Figure 6-3. DLM modeling results for uranium(6+)-clinoptilolite sorption (under atmospheric CO_2) for: total uranium = (a) 5 ppb; (b) 50 ppb; (c) 500 ppb. Model parameters and binding constants are given in Table 6-3.

radionuclide binding constants. For this reason, any radionuclide binding constants are dependent on the acidity constants used in the FITEQL optimization run; if these acidity constants are modified by the incorporation of new potentiometric titration data or changes in parameter values assumed while interpreting the present data, all radionuclide binding constants must be re-evaluated. In addition, the tabulated binding constants are dependent on the thermodynamic data available. Any significant changes in the data likewise require a recalculation of the necessary parameters.

From the point of view of describing the mineral/water interface, it must be emphasized that the results given here are dependent on the assumptions used in constructing the conceptual model, particularly in selecting the complexes formed at the surface. In some cases, especially for single-layer models such as the CCM and DLM, the model is unable to distinguish between like-charged surface complexes; independent lines of evidence such as proton release data or spectroscopic information are necessary to identify likely choices. Although some spectroscopic data such as EXAFS are available for actinides, due to analytical limitations they typically exist for fairly concentrated solutions (millimolar) at single pH values. Additional EXAFS work will be required to ascertain the extent to which SCMs best represent the mineral/water interface.

For the purposes of PA, a principle of parsimony was adopted where possible in defining possible surface complexes. Within this framework, the DLM was able to reproduce the general aspects of actinide sorption behavior while using a far simpler representation of the mineral/water interface than the TLM. This method may be preferred where simpler models are desirable to strike a balance between accuracy of the conceptual model and the computational resources required by geochemistry in PA calculations. Despite these limitations, the SCM approach is able to quantitatively incorporate the effects of changes in solution and surface chemistry to an extent that is well beyond the capabilities of a purely empirical method such as the linear k_d model. As additional data become available for characterizing mineral surfaces, the SCMs represent a crucial step toward a mechanistic model of sorption at the mineral/water interface.

6.3 SORPTION EXPERIMENTS

To develop an understanding of radionuclide sorption processes and the important physical and chemical parameters that affect sorption behavior in the Yucca Mountain environment, experiments are being conducted to investigate the sorption behavior of uranium on geologic media. During the second half of 1993, experiments were completed to determine the possible effects of pH, uranium concentration, and ionic strength on the sorption of uranium(6+) on clinoptilolite, which is the predominant zeolite mineral occurring underneath Yucca Mountain. In addition, because surface adsorption is the predominant mechanism for uranium sorption, even for zeolites like clinoptilolite (Pabalan et al., 1993), and because the ratio of fluid-volume to mineral-surface-area can vary significantly along a fluid flow-path, experiments were also conducted to determine the effect of solid-surface-area to solution-volume ratio on uranium(6+) sorption. The latter experiments, which used α -alumina as the sorbent phase, also provided information on possible differences in uranium sorption behavior on different types of minerals. Experimental methods and results are discussed in the following section.

6.3.1 Experimental Procedures

6.3.1.1 Uranium Sorption on Na-clinoptilolite

The sorption experiments were conducted by reacting 0.1 g of Na-clinoptilolite (75-150 μm) with 50 ml of uranium solutions in fluorinated ethylene propylene (FEP) Teflon® bottles. The aqueous

solutions had initial uranium concentrations of 5, 50, or 500 ppb and were prepared using a ^{233}U solution standard issued by the DOE New Brunswick Laboratory as Certified Reference Material (CRM) 111-A. This standard solution had a total uranium concentration of 50.5 ppm (99.5% ^{233}U). All uranium solutions were prepared in FEP Teflon® containers. Most of the experiments were conducted at an ionic strength close to 0.1 m using a NaNO_3 matrix. To study the possible effect of ionic strength on uranium sorption, additional experiments were conducted in a 1.0-m NaNO_3 matrix.

Prior to addition of the solid phase, the initial pH of each solution was adjusted to a value in the range 2.0 to 9.0 at approximately 0.25-pH intervals by the addition of HNO_3 or NaHCO_3 . The amount of reagent needed to achieve the desired initial pH of the uranium solutions was estimated using the EQ3NR geochemical code (Version 3245.R124) with database Data0.com.R12. The solutions, which were kept open to atmospheric $\text{CO}_2(\text{g})$ throughout the experiment, were agitated using gyratory shakers. For uranium solutions with added NaHCO_3 , it took at least 10 d to equilibrate with atmospheric $\text{CO}_2(\text{g})$ and reach a constant pH.

After all solutions had attained a constant pH, 500 μl samples were taken from each solution using Eppendorf micropipets to determine initial uranium concentrations. Na-clinoptilolite powder was then added to each solution, and the mixtures were allowed to equilibrate. Control experiments, which consisted of uranium solutions without added clinoptilolite, were used to determine potential losses of uranium to the container walls and to correct for any increase in uranium concentration due to evaporation of experimental solutions. After about 10 d, samples were taken from each solution to determine the final uranium concentration. The equilibrium pH of each solution was also measured. Subsequently, reverse experiments were initiated by adjusting the pH of some of the experimental solutions to lower or higher pH by the addition of HNO_3 or NaHCO_3 . After an additional period of about 10 d, the pH of the solutions was measured, and aqueous samples were taken to determine the uranium concentrations at the end of the reverse experiment. Uranium concentrations of the experimental and control solutions were all analyzed with a Packard Model 1900 TR Liquid Scintillation Analyzer.

6.3.1.2 Uranium Sorption on α -alumina

In these experiments, α -alumina ($\alpha\text{-Al}_2\text{O}_3$), which is issued by the National Institute of Standards and Technology (NIST) as CRM for measurements of specific surface area of powders, was selected as the sorbent phase. Specifically, Reference Materials (RM) 8005, 8006, and 8007, with reported surface areas of 2.09, 0.229, and 0.0686 m^2/g , respectively, were used. The α -alumina powders were considered suitable because their surface areas are relatively well-constrained and their dense structure prevents intracrystalline ion exchange reactions to occur with the uranium in solution. To minimize altering the surfaces of the α -alumina, the powders were not washed or treated in any way before their use in the experiments.

The sorption experiments on α -alumina were conducted at a constant solid-mass/solution-volume, but variable sorbent-surface-area/solution-volume ratio, by reacting 0.1 g of RM 8005, 8006, or 8007 with 40 ml of ^{233}U solutions in 50-mL Teflon® FEP centrifuge tubes. The solutions all had initial concentrations of ~ 95 ppb U in a 0.1-m NaNO_3 matrix. In a manner similar to the clinoptilolite experiments already described, the initial pH of the uranium solutions was adjusted by the addition of HNO_3 or NaHCO_3 , and the solutions were kept open to atmospheric $\text{CO}_2(\text{g})$ through the duration of the experiment. Control solutions were also included to allow corrections for container sorption and evaporation of solution. The α -alumina powder was added after all solutions had attained a constant pH and after aqueous samples had been taken to determine the initial uranium concentration.

After about 2 wk, the mixtures were centrifuged at 13,000 rpm for about 20 min to separate the liquid and solid phases, and aqueous samples were taken for liquid scintillation analysis. The equilibrium pH of each solution was also measured.

6.3.2 Results and Discussion

6.3.2.1 Uranium Sorption on Na-clinoptilolite

Results of the experiments using Na-clinoptilolite are shown in Figures 6-4 to 6-7. Figure 6-4 compares the relative amounts of uranium lost from 5-, 50-, and 500-ppb U solution due to sorption on container walls. This figure shows that significant amounts of uranium are lost from solution to the container, particularly at low initial ΣU . Container sorption is strongly dependent on solution pH and reaches a maximum at pH values between 5 and 6. The pH at which maximum sorption occurs shifts to more acidic conditions with decreasing initial ΣU . Figure 6-5 shows a comparison of the overall %U lost from solution with the %U sorbed on the container from solutions with initial ΣU equal to 5, 50, and 500 ppb. As shown in this figure, the component of the total uranium lost from solution due to container sorption becomes greater with decreasing initial uranium concentration.

Figure 6-6 shows the %U sorbed on clinoptilolite as a function of pH for solutions with initial ΣU equal to 5, 50, and 500 ppb. It is evident from this figure that uranium sorption on clinoptilolite is strongly dependent on pH. The amount of uranium sorbed increases sharply at pH values above about 4 (adsorption edge) and decreases sharply at pH values above about 6.5 (desorption edge). It reaches a maximum value at pH \sim 6.3. In addition, at constant pH the %U sorbed increases with decreasing initial ΣU , although the relative increase in %U sorbed is smaller at lower ΣU . Also shown in Figure 6-6 are the data points for the reverse experiments, which generally plot along the same sorption and desorption trends as the forward data points. This correspondence between forward and reverse data indicates that the uranium sorption reactions are reversible.

In Figure 6-7(a), the overall %U lost from solution is compared with and the %U sorbed on container from an initially 50-ppb U solution in a 0.1- or 1.0-m NaNO_3 matrix. The data show that an increase in ionic strength decreased both the overall sorption and container sorption. Although the total uranium lost from solution is smaller at higher ionic strength, the relative amounts of uranium sorbed on clinoptilolite, which are plotted in Figure 6-7(b) and which have been corrected for container sorption, do not significantly change with variations in ionic strength.

6.3.2.2 Uranium Sorption on α -alumina

The results of the experiments using α -alumina are shown in Figure 6-8. The data show a strong dependence of uranium sorption on α -alumina with pH, which has also been observed for uranium sorption on clinoptilolite. At constant pH, the total uranium sorbed increases as the sorbent-surface-area/solution-volume ratio increases, but the increase is not directly proportional to the reported surface areas of the α -alumina powders. For example, a maximum sorption of 60 percent occurred on the highest surface area powder (RM 8005; 2.09 m^2/g), whereas RM 8006 (0.229 m^2/g) and RM 8007 (0.0686 m^2/g) had maximum uranium sorption of 27 and 14 percent, respectively. Sorption maxima occur between a pH of 6.2 and 6.3, regardless of the surface area of the α -alumina. The adsorption and desorption edges at higher surface-area/solution-volume ratios enclose those at lower ratios. In other words, at a fixed volume of solution, the adsorption edge shifts to more acidic pH with increasing surface area of the solid,

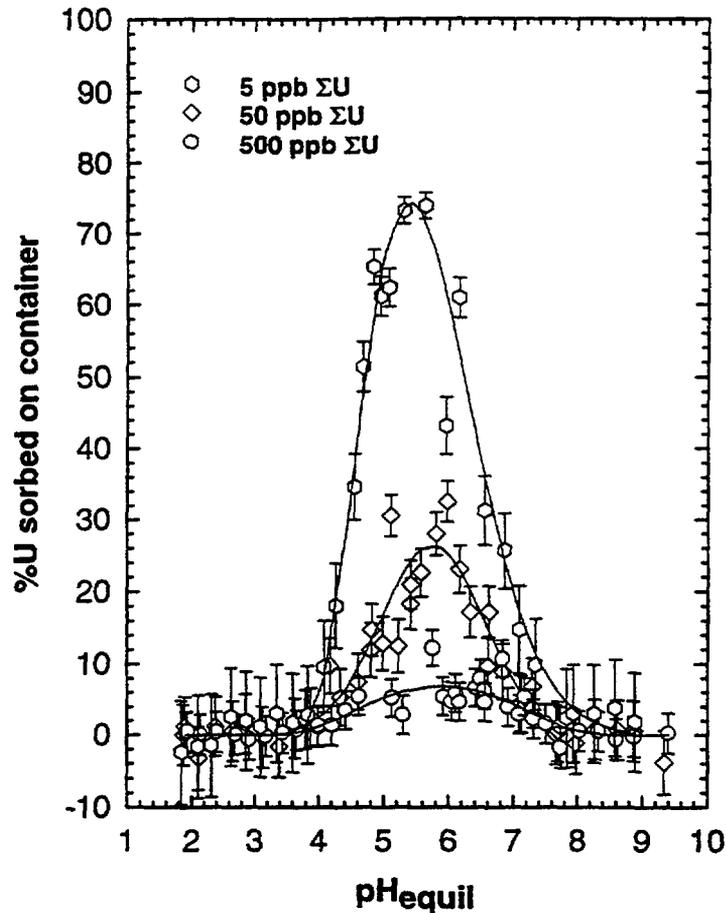


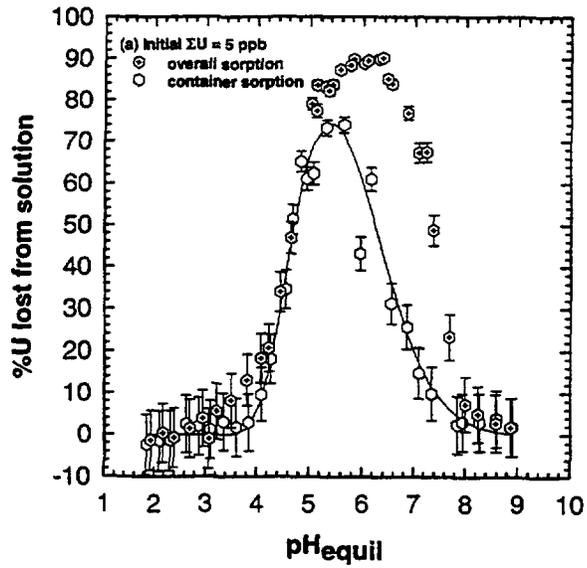
Figure 6-4. %U lost from solution due to sorption on container wall. Best fits to container sorption data, which were used to correct the overall sorption data shown in Figure 6-5, are indicated by the curves.

whereas the desorption edge shifts to more alkaline pH. A similar shift in pH with increasing surface area was reported by Tripathi (1984) for uranium(6+) sorption on the iron oxide mineral goethite.

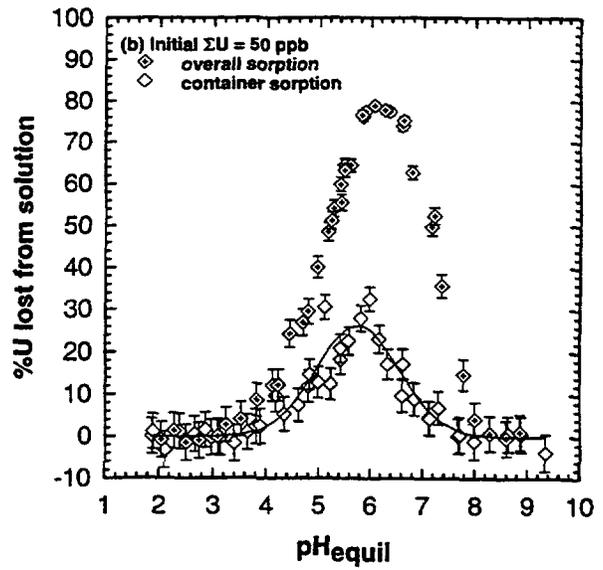
The experimental data discussed previously were evaluated using surface-complexation models as part of the activities in Task 2 of this research project. Some of the results of the modeling effort are given in Section 6.2.

6.4 ASSESSMENT OF PROGRESS TOWARD MEETING PROJECT OBJECTIVES

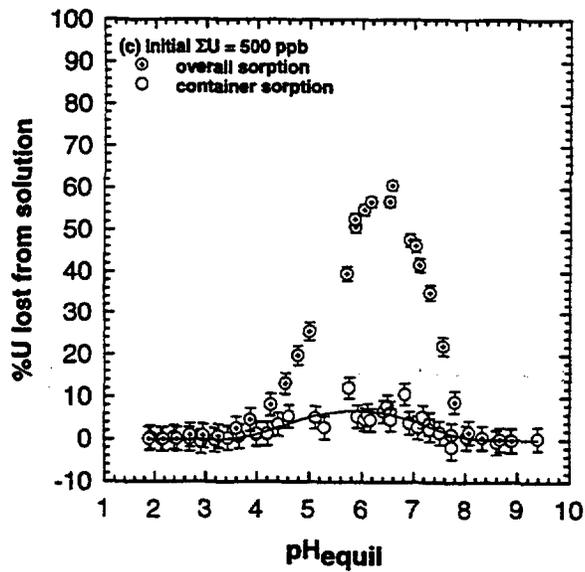
The broad objective of this project is to develop sufficient understanding of issues relevant to radionuclide transport. An important mechanism for attenuating radionuclide transport is sorption of radionuclides on minerals encountered along the flow paths.



(a)

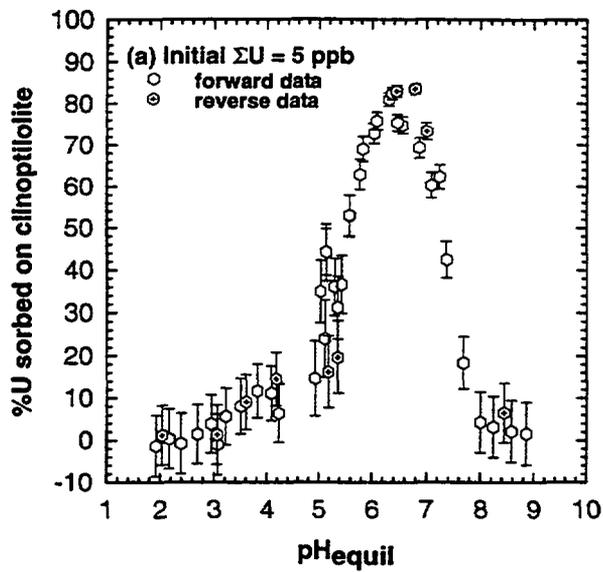


(b)

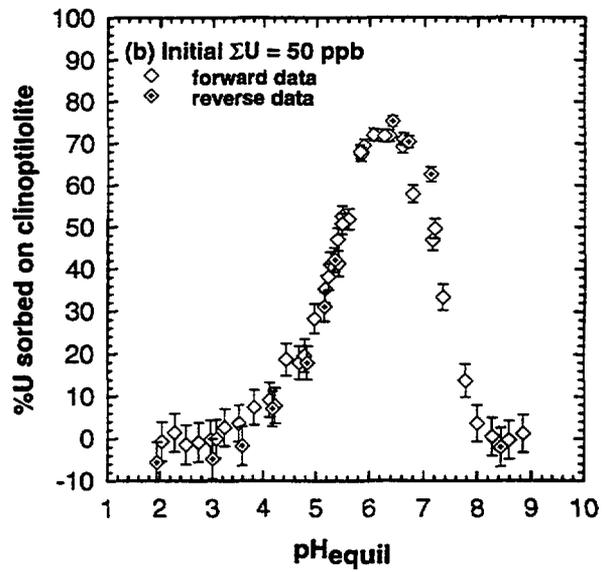


(c)

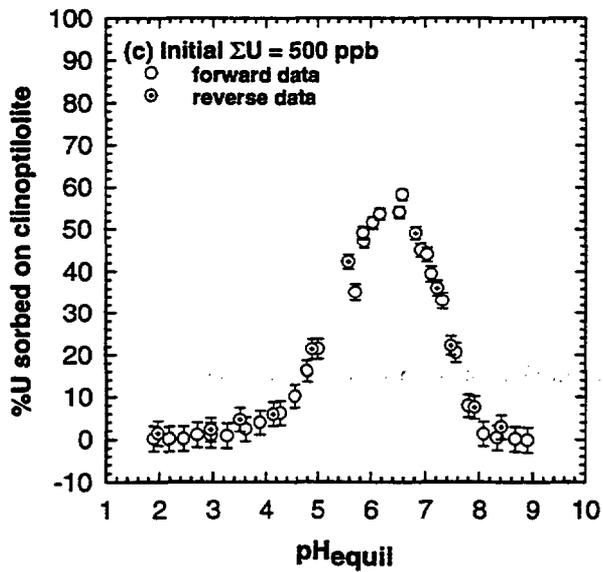
Figure 6-5. Overall %U lost from solution compared with %U sorbed on container for initial $\Sigma U = 5, 50, \text{ and } 500$ ppb



(a)

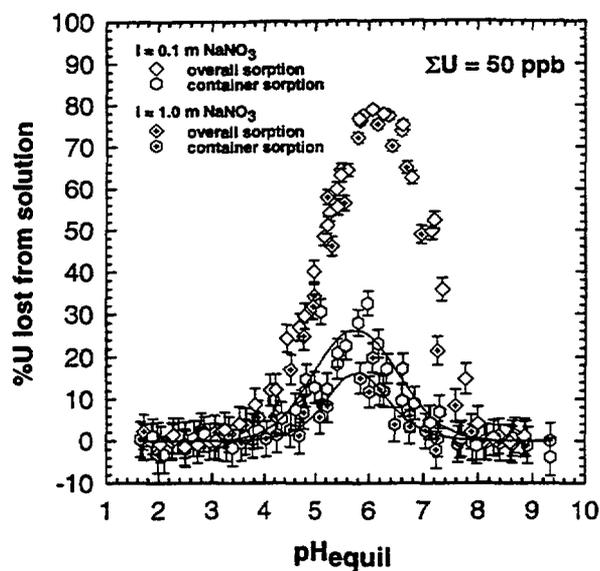


(b)

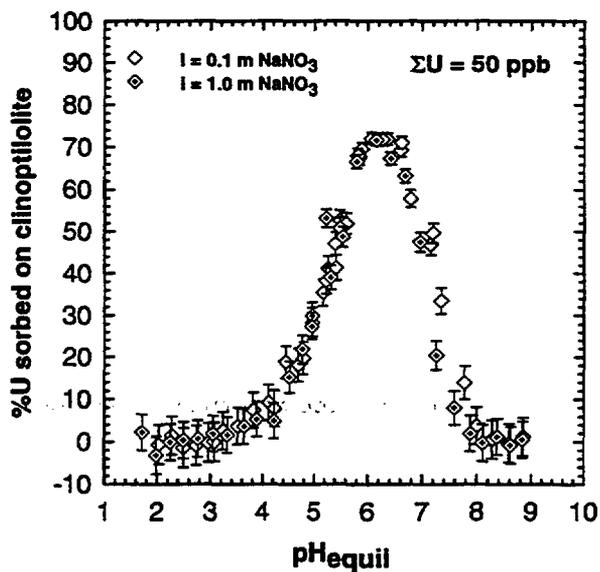


(c)

Figure 6-6. %U sorbed on clinoptilolite calculated from data shown in Figures 6-4 and 6-5. Data from reverse experiments are also shown.



(a)



(b)

Figure 6-7. Effect of ionic strength: (a) Comparison of overall %U lost from solution and %U sorbed on container from an initially 50 ppb U solution in a 0.1- or 1.0-m NaNO₃ matrix. (b) Comparison of %U sorbed on clinoptilolite (corrected for container sorption) from an initially 50 ppb U solution in a 0.1- or 1.0-m NaNO₃ matrix.

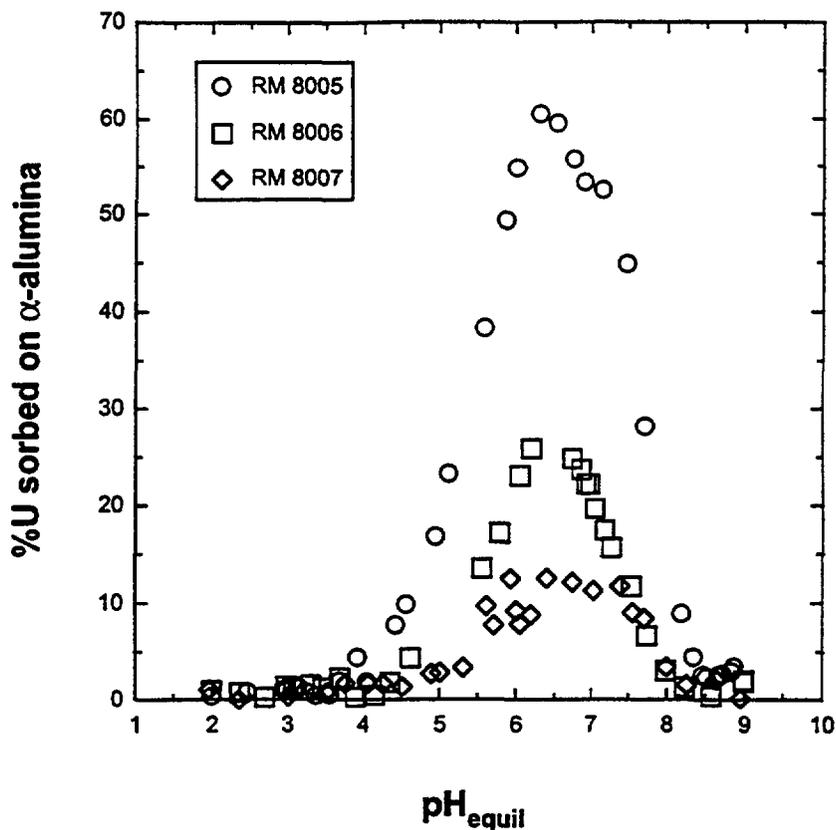


Figure 6-8. Results of sorption experiments on α -alumina. Initial $\Sigma U = 95$ ppb. The circles, squares, and diamonds represent data for solutions that utilized RM 8005 ($2.09 \text{ m}^2/\text{g}$), RM 8006 ($0.229 \text{ m}^2/\text{g}$), and RM 8007 ($0.0686 \text{ m}^2/\text{g}$), respectively.

Modeling efforts using SCM methods for actinide sorption, combined with results of laboratory experiments on uranium sorption, are providing an understanding of the important parameters that control the sorption behavior of uranium. For example, the experimental results reported here demonstrate that uranium sorption on clinoptilolite and α -alumina, which are sorbents of very different mineralogic and surface properties, are strongly sorbed at near-neutral pH (~ 6.3). However, in both systems, the amount of uranium sorbed is strongly dependent on pH and decreases steeply away from near-neutral pH. The ratio of sorbent-surface-area to solution-volume ratio also influences sorption; that is, as the ratio increases, the relative amount of uranium sorbed on the solid also increases. Some dependence on total uranium concentration in solution was also observed. However, it appears that ionic strength has a negligible effect on the sorption behavior of uranium. Because of their theoretical basis, relatively simple surface complexation models are able to account for these behaviors in a quantitative way that exceeds the capability of purely empirical models. Because of the strong dependence on pH and sorbent-surface-area/solution-volume ratio, modeling of sorption processes will likely require that changes in groundwater chemistry and in rock/fluid ratio be appropriately accounted for in PA calculations if retardation by sorption processes is included.

The similarity in the pH-dependence of uranium sorption on clinoptilolite and α -alumina is important. It may help identify simplified approaches to modeling sorption and thus help in the development of CDMs relevant to the KTUs identified in Section 6.1 and in developing conceptual

models related to the PA Research Project and the IPA Phase 3. The information derived from the laboratory experiments may also help interpret data on uranium distribution and migration at the Peña Blanca field site of the Geochemical Natural Analog Research Project.

6.5 PLANS FOR NEXT REPORT PERIOD

Now that a uniform set of SCM parameters has been established, modeling efforts will continue to explore the application of SCM methods to available radioelement sorption data. Particular effort will be focused on using these techniques to model actinide sorption on complex multioxide minerals. After binding constants are determined, it may be possible to predict sorption behavior as a function of changing chemistry such as $p\text{CO}_2$. Where possible, checks will be made using uranium sorption data generated from Task 3 experiments. It may also be feasible to extend SCM methods to mixtures of more than one mineral and natural materials, such as crushed tuff and soils.

Experiments studying uranium sorption on clinoptilolite will continue, but these efforts will focus on the possible effect of $p\text{CO}_2$ on the sorption equilibrium. Additional experiments on α -alumina will also be conducted, but will use mixtures of α -alumina with different surface areas. To develop a better understanding of the effects of mineral properties to sorption processes, new uranium sorption experiments will be initiated using montmorillonite and quartz as the sorbent phases. In order to get data on the surface properties, such as pH_z and pzc , of these various minerals, a Mettler potentiometric titrator is being set up for acid-base titration of mineral samples, as well as a Micromeritics Zeta Potential Analyzer for electrophoretic measurements. Flow experiments using column techniques will also be initiated using uranium as the sorbing radionuclide and quartz sand as the sorbent phase. The data generated from these experiments will continue to be utilized in the modeling activities being conducted under Task 2 of this project. The calculational results presented here for Task 2 were obtained using FITEQL, Version 2.0 (Westall, 1982) and MINTEQA2, Version 3.11 (Allison et al., 1991). These codes are not currently in the CNWRA configuration management system.

6.6 REFERENCES

- Allard, B., M. Karlsson, E.L. Tullborg, and S.A. Larson. 1983. *Ion Exchange Capacities and Surface Areas of Some Major Components and Common Fracture Filling Materials of Igneous Rocks*. KBS 83-64. Göteborg, Sweden: Chalmers University of Technology.
- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual*. EPA/600/3-91/021. Athens, GA: U.S. Environmental Protection Agency.
- Brady, P.V., and J.V. Walther. 1992. Surface chemistry and silicate dissolution at elevated temperatures. *American Journal of Science* 292: 639-658.
- Davis, J.A., and D.B. Kent. 1990. Surface complexation modeling in aqueous geochemistry. *Mineral-Water Interface Geochemistry*. M.F. Hochella, Jr. and A.F. White, eds. Reviews in Mineralogy Volume 23. Washington, DC: Mineralogical Society of America: 177-260.

- Davis, J.A., and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *Journal of Colloid and Interface Science* 67: 90-107.
- Dzombak, D.A., and F.M.M. Morel. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York, NY: Wiley and Sons.
- Grenthe, I., J. Fuger, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. 1992. *Chemical Thermodynamics Series, Volume 1: Chemical Thermodynamics of Uranium*. New York, NY: Elsevier.
- Hayes, K.F., G. Redden, W. Ela, and J.O. Leckie. 1990. *Application of Surface Complexation Models for Radionuclide Adsorption: Sensitivity Analysis of Model Input Parameters*. NUREG/CR-5547. Washington, DC: U.S. Nuclear Regulatory Commission.
- Kent, D.B., V.S. Tripathi, N.B. Ball, J.O. Leckie, and M.D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. NUREG/CR-4807. Washington, DC: U.S. Nuclear Regulatory Commission.
- Kohler, M., E. Wieland, and J.O. Leckie. 1992. Metal-ligand-surface interactions during sorption of uranyl and neptunyl on oxides and silicates. *Proceedings of the 7th International Symposium on Water-Rock Interaction (WRI-7). Volume 1: Low Temperature Environments*. Y.K. Kharaka and A.S. Maest, eds. Rotterdam, Netherlands: A.A. Balkema: 51-54.
- Lemire, R.J. 1984. *An Assessment of the Thermodynamic Behavior of Neptunium in Water and Model Groundwater From 25 to 150 °C*. AECL-7817. Pinawa, Manitoba: Atomic Energy of Canada Limited.
- Los Alamos National Laboratory. 1993. Monthly Activity Report for April 1993.
- Manceau, A., and L. Charlet. 1991. Sorption and speciation of heavy metals at the oxide/water interface: From Microscopic to Macroscopic. *Environmental Pollution 1*: 401-408.
- Nakayama, S., and Y. Sakamoto. 1991. Sorption of neptunium on naturally-occurring iron-containing minerals. *Radiochemica Acta* 52/53: 153-157.
- Pabalan, R.T., and D.R. Turner. 1993. Sorption modeling for HLW performance assessment. *NRC High-Level Radioactive Waste Research at CNWRA January Through June 1993*. B. Sagar, ed. CNWRA 92-02S. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses: 8-1 to 8-18.
- Pabalan, R.T., J.D. Prikryl, P.M. Muller, and T.B. Dietrich. 1993. Experimental study of uranium(6+) sorption on the zeolite mineral clinoptilolite. *Scientific Basis for Nuclear Waste Management XVI MRS Symposium. Proceedings*. C.G. Interrante and R.T. Pabalan, eds. Pittsburgh, PA: Materials Research Society: 294: 777-782.

- Payne, T.E., K. Sekine, J.A. Davis, and T.D. Waite. 1992. Modeling of radionuclide sorption processes in the weathered zone of the Koongarra ore body. *Alligator Rivers Analogue Project Annual Report, 1990-1991*. P. Duerden, ed. Australian Nuclear Science and Technology Organization: 57-85.
- Rai, D., J.M. Zachara, L.E. Eary, C.C. Ainsworth, J.E. Amonette, C.E. Cowan, R.W. Szelmezcza, C.R. Resch, R.L. Schmidt, D.C. Girvin, and S.C. Smith. 1988. *Chromium Reactions in Geologic Materials*. EPRI-EA-5741. Palo Alto, CA: Electric Power Research Institute.
- Riese, A.C. 1982. *Adsorption of Radium and Thorium onto Quartz and Kaolinite: A Comparison of Solution/Surface Equilibria Models*. Ph.D. Dissertation. Golden, CO: Colorado School of Mines.
- Siegel, M.D., V.S. Tripathi, M.G. Rao, and D.B. Ward. 1992. Development of a multi-site model for adsorption of metals by mixtures of minerals: 1. Overview and preliminary results. *Water-Rock Interaction: Proceedings of the 7th International Symposium on Water-Rock Interaction*. Y.K. Kharaka and A.S. Maest, eds. Rotterdam, Netherlands: A.A. Balkema.
- Tripathi, V.S. 1984. *Uranium(6+) Transport Modeling: Geochemical Data and Submodels*. Unpub. Ph.D. Dissertation. Stanford, CA: Stanford University.
- Turner, D.R. 1993. *Mechanistic Approaches to Radionuclide Sorption Modeling*. CNWRA 93-019. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.
- Turner, D.R., T. Griffin, and T.B. Dietrich. 1993. Radionuclide sorption modeling using the MINTEQA2 speciation code. *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management—XVI MRS Symposium*. C.G. Interrante and R.T. Pabalan, eds. Pittsburgh, PA: Materials Research Society: 294: 783-789.
- Westall, J.C. 1982. *FTTEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 2.0*. Rpt. 82-02. Corvallis, OR: Department of Chemistry, Oregon State University.
- Westall, J.C., and H. Hohl. 1980. A comparison of electrostatic models for the oxide/solution interface. *Advances in Colloid and Interface Science* 12: 265-294.