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Scientific Notebook # 394

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CENTER FOR NUCLEAR WASTE
REGULATORY ANALYSES

CNWRA
CONTROLLED
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DJS 6/12/00

20.01402.871
Radionuclide Transport

5/12/00 1
DRJ

Objectives (20.01402.871) - KTI on Radionuclide Transport (05/12/00)

The purpose of the research discussed in this scientific notebook is to evaluate the available data from the geochemical literature, as well as geochemical, geological, and hydrologic data in the vicinity of Yucca Mountain to help evaluate the DOE safety case for radionuclide transport from the proposed repository. Uses of these data may include field, laboratory, and natural analog geochemical information related to retardation (sorption, precipitation, dissolution). Computer codes that may be used include the most recent versions of EPA geochemistry code MINTEQA2, the USGS hydrochemistry code PHREEQC, GIS software such as ArcView, and commercial software such as Microsoft Excel, TableCurve 2D&3D, SigmaPlot, and WordPerfect.

David R. Turner

CNWR/Principal Scientist

DRJ

6/12/00

DR

Work by OLI Systems, Inc. as subcontractor to CNWRA

Radionuclide Transport KTI:

In FY98 and FY99, OLI Systems, Inc. conducted for the CNWRA an extensive literature survey of the key geochemical parameters affecting radionuclide adsorption and constructed thermodynamic sorption models using a uniform, simplified surface complexation modeling approach. During FY98, a large amount of data on the radionuclide adsorption was collected from the open literature and general trends of the adsorption with various geochemical parameters, such as mineral surface area, solution pH, redox potential, radionuclide concentration, ionic strength, and carbonate concentration, were identified. Additional information on colloid transport of radionuclides was also provided.

During FY99, OLI staff developed the parameters necessary to produce internally consistent thermodynamic models to simulate the available sorption data for a number of cationic (Am, Pu, Np, U) and anionic (I, Tc, Se) radionuclides of concern in high-level waste performance assessment. OLI staff also conducted a review of ion exchange data with a focus on modeling ion exchange in multicomponent systems.

During FY00 OLI staff collaborated with CNWRA staff to complete two manuscripts summarizing the thermodynamic sorption modeling of cationic and anionic radionuclide sorption. These manuscripts will be submitted for publication in the open, peer-reviewed literature, and will serve to document sorption modeling research conducted by OLI on behalf of the CNWRA. The author-final manuscripts include a discussion of data sources, observed sorption behavior, modeling approach and parameterization, and modeling results. The manuscripts also contain a discussion of the implications of the modeling effort for high-level nuclear waste (HLW) performance assessment calculations.

Copies of the original articles/reports reviewed by OLI staff are maintained by D.R. Turner in four notebooks:

•OLI Colloids Literature (2 notebooks)

•OLI Sorption Literature (2 notebooks)

Copies of the original reports and electronic copies of the reports and data analysis submitted by OLI are maintained by D.R. Turner in a notebook entitled:

•OLI Reports 1998-1999 (1 notebook)

Electronic copies of the data and reports are also included at the end of this scientific notebook.

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DR

Neptunium(+5) Speciation Using PHREEQC Version 1.6

We have used PHREEQC, Version 1.6 (Parkhurst, 1995) to study Np(V) speciation and evaluate possible aqueous species that might influence Np(V) uptake by calcite. Equilibrium constants for Np species used in the calculations are:

Thermodynamic data used for PHREEQC, Version 1.6 Np(V) speciation calculations.

Aqueous Speciation Reactions:	Log K
$\text{NpO}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{OH}^0 + \text{H}^+$	-8.9
$\text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{CO}_3^-$	4.6
$\text{NpO}_2^+ + 2\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{3-}$	7.0
$\text{NpO}_2^+ + 3\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$	8.5
$\text{NpO}_2^+ + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}^0(\text{aq})$	-0.4

These data are based on the eq3/6 database (data0.com.r6, version 8). The calculated relative stabilities of Np(V) species as a function of pH in equilibrium with atmospheric PCO_2 conditions at 25 °C in a 1.17×10^{-7} m Np solution (0.1 molal NaCl matrix) are shown in Figure 1 The calcite saturation index (SI) is shown for comparison. At laboratory pH conditions (pH ~ 8.4), the solution is slightly supersaturated (SI > 0) with respect to calcite, with the degree of supersaturation increasing with increasing pH.

Under atmospheric PCO_2 conditions, Np hydrolysis is greatly reduced by carbonate complexation; $\text{NpO}_2\text{OH}^0(\text{aq})$ reaches a maximum near pH ~8.5 and decreases with further increases in pH. At pH ~ 8, NpO_2^+ is still the principal species, but at pH > 8.5, formation of the Np(V) carbonate species become progressively more important, and for pH ≥ 9.5, $\text{NpO}_2(\text{CO}_3)_3^{5-}$ is calculated to represent more than 90% of the aqueous Np. Under the experimental conditions ($\text{PCO}_2 = 10^{-3.5}$ atm; pH = 8.4; $\Sigma\text{Np(V)} = 1.2 \times 10^{-7}$ molal) examined, the solution was undersaturated with respect to the Np(V) solid phases $\text{NpO}_2\text{OH}(\text{am})$ and Np_2O_5 .

Under pH conditions where NpO_2^+ is the predominant aqueous species Np(V) can apparently fit into the calcite structure. Under the laboratory pH conditions investigated (pH ~ 8.4), the solution was supersaturated with respect to calcite (Figure 1), and NpO_2^+ remained the predominant species in solution (~50-60 percent). Under higher pH conditions where calcite supersaturation is greater, it is possible that Np uptake by calcite is reduced due to the predominance of aqueous Np(V)-carbonate complexes. Saturated zone groundwater in the vicinity of Yucca Mountain (Turner, 1998; Turner and Pabalan, 1997) ranges in pH from about 6.4 to a maximum of 9.6, suggesting that formation of aqueous Np(V)-carbonate complexes may reduce Np coprecipitation.

Changes in PCO_2 might also lead to an increase in carbonate complexation of Np(V), potentially reducing uptake of NpO_2^+ by calcite. For example, calculations fixing pH at 8.4 and varying PCO_2 show that for $\text{PCO}_2 \geq 10^{-3}$ atm, Np(V) speciation is dominated by carbonate complexes (Figure 2). For $\text{PCO}_2 \geq 10^{-2.5}$ atm, NpO_2^+ represents less than 10 percent total Np. This suggests that even though calcite supersaturation is increasing, the formation of aqueous Np(V) carbonate complexes may tend to reduce coprecipitation and keep Np in solution. This is potentially significant in the groundwaters around Yucca

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Mountain where PCO_2 typically exceed 10^{-3} atm. For example, calculated PCO_2 values are lognormally distributed, with a mean Log PCO_2 of about -2.5 (Turner, 1998).

Uptake of U(VI) by coprecipitation with calcite is minimal compared with Np(V)-calcite (Nugent and Reeder, 1999; Reeder et al., 2000). This is likely to be due to differences in the aqueous speciation of the two actinides. In contrast to Np(V), uncomplexed uranyl ion (UO_2^{+2}) is effectively zero under the pH conditions of our experiment (Figure 3). At pH > 6.5, U(VI) is complexed with aqueous carbonate, and at the pH ~ 8.4 (laboratory conditions), virtually all of the uranyl ion is present as $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$. The strength of the uranyl carbonate complexes is such that no free uranyl is available for incorporation into the calcite structure, limiting the opportunity for U(VI) uptake by coprecipitation with calcite.

Neptunium-calcite coprecipitation is only an effective mechanism for those groundwaters that are saturated/supersaturated with respect to calcite. Calcite is a common trace mineral in wells around Yucca Mountain (Bish et al., 1996), but groundwaters from tuff aquifers within a few kilometers of the proposed repository (e.g., well J-13) tend to be calcite-undersaturated (Kerrisk, 1987; Murphy, 1995). On a regional scale, however, and near the location of the hypothetical critical group at Lathrop Wells proposed in 10 CFR 63.115(b)(1) (Nuclear Regulatory Commission, 1999a), groundwater is slightly supersaturated with respect to calcite (Turner, 1998). Other potentially complicating groundwater chemistry includes Mg^{+2} , which acts as a poison on U(VI) uptake (Nugent and Reeder, 1999). It is reasonable to infer that Mg^{+2} , may also reduce Np(V) coprecipitation. Reported Mg concentration in the groundwaters around Yucca Mountain vary from about 0.1 to 150 mg/L (Perfect et al., 1995; Turner, 1998), with a mean of about 15 mg/L. The upper portion of this range is similar to the Mg^{+2} concentration (~120 mg/L) observed by Nugent and Reeder (1999) to reduce U(VI) uptake, suggesting that there may be sufficient magnesium in some Yucca Mountain waters to affect Np(V)-calcite coprecipitation. It is important to note, however, that the groundwaters within the flow paths around and south of Yucca Mountain to the critical group tend to exhibit much lower Mg-concentrations (1 to 2 mg/L) (Perfect et al., 1995). There are also still gaps in the geochemistry of the saturated zone flow path, although to some extent these may be filled by samples collected as part of the current Nye County EWDP (Nye County, 2000).

Input and Output Files (electronic) included in packet at the end of this scientific notebook

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DPS

PHREEQC Input File:

TITLE Test Example: Speciation of Np(V), $1.17e-7$ molal NpO₂⁺, \ $PCO_2=1e-3.5$; Speciation over pH range

SOLUTION 1

-units	mol/kgw		
pH	8.39		
pe	8.451		
temp	25.0		
Na	0.1015	charge	
Ca	0.0015		
Alkalinity	0.0015	as HCO ₃ ⁻	
Cl	0.103		
Np(+5)	0.000000117	as NpO ₂	

#Np(V) fixed as dominant redox state. pe adjusted to maintain Np(V).

PHASES 1

Fix H+
H+ = H+
log_k = 0.0

END

SELECTED_OUTPUT

-file npspec4.123
-molalities NpO₂⁺ NpO₂Cl NpO₂OH NpO₂CO₃⁻ NpO₂(CO₃)₂⁻³ NpO₂(CO₃)₃⁻⁵
-saturation_indices Calcite

Use Solution 1

EQUILIBRIUM_PHASES 1

Fix H+	-4.00	NaOH	10.0
CO ₂ (g)	-3.5		1.0

END

Use Solution 1

EQUILIBRIUM_PHASES 1

Fix H+	-4.25	NaOH	10.0
CO ₂ (g)	-3.5		1.0

END

... Increasing pH by 0.25 pH units

Use Solution 1

EQUILIBRIUM_PHASES 1

Fix H+	-10.75	NaOH	10.0
CO ₂ (g)	-3.5		1.0

END

Use Solution 1

EQUILIBRIUM_PHASES 1

Fix H+	-11.00	NaOH	10.0
CO ₂ (g)	-3.5		1.0

END

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REFERENCES:

Bish, D.L., J.W. Carey, B.A. Carlos, S.J. Chipera, G.D. Guthrie, Jr., S.S. Levy, D.T. Vaniman, G. WoldeGabriel. 1996. *Summary and Synthesis Report on Mineralogy and Petrology Studies for the Yucca Mountain Site Characterization Project, WBS Element 1.2.3.2.1.1 and 1.2.2.2.1.2*, Los Alamos, NM: Los Alamos National Laboratory.

Kerrisk, J.F. 1987. *Groundwater Chemistry at Yucca Mountain, Nevada, and Vicinity*, LA-10929-MS, Los Alamos, NM: Los Alamos National Laboratory.

Murphy, W.M. 1995. Contributions of thermodynamic and mass transport modeling to evaluation of groundwater flow and groundwater travel time at Yucca Mountain, Nevada. T. Murakami and R.C. Ewing, eds. *Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management - XVIII*. Pittsburgh, PA: MRS: 419-426.

Nugent, M. and R.J. Reeder. 1999. The effect of growth rate, (U/Ca)_{aq}, and Mg²⁺ on uranyl ion coprecipitation with calcite. *Proceedings of the 9th annual V. M. Goldschmidt Conference*, Cambridge, MA. p 213.

Nye County. 2000. *Nye County Nuclear Waste Repository Project Office: Early Warning Drilling Program*. Available at <http://www.nyecounty.com/ewdpmain.htm>.

Parkhurst, D.L. 1995. *User's Guide to PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations*. Water Resources Investigations Report 95-4227. Lakewood, CO: United States Geological Survey.

Perfect, D.L., C.C. Faunt, W.C. Steinkampf, A.K. Turner, *Hydrochemical Data Base for the Death Valley Region, California and Nevada*, USGS Open-File Report 94-305, Denver, CO: U.S. Geological Survey, 1995.

Reeder, R.J., Nugent, M., Lamble, G. M., Tait, C. D. and Morris, D. E. 2000. Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. *Environmental Science and Technology* 34: 638-644.

Turner, D.R.. 1998. *Radionuclide Sorption in Fractures at Yucca Mountain, Nevada: A Preliminary Demonstration of Approach for Performance Assessment*, Letter Report to U.S. Nuclear Regulatory Commission, San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

Turner, D.R. and R.T. Pabalan. 1999. Abstraction of mechanistic sorption model results for performance assessment calculations at Yucca Mountain, Nevada. *Waste Management* 19: 375-388.

U.S. Nuclear Regulatory Commission. 1999a. *NRC Disposal of High-Level Radioactive Wastes in a Proposed Geologic Repository at Yucca Mountain, Nevada*, Federal Register 64 (34): 8,640-8,679, Washington, DC: U.S. Government Printing Office.

Wanner H. and Forest I., eds. 1992. *Chemical Thermodynamics of Uranium*. North-Holland, Amsterdam.

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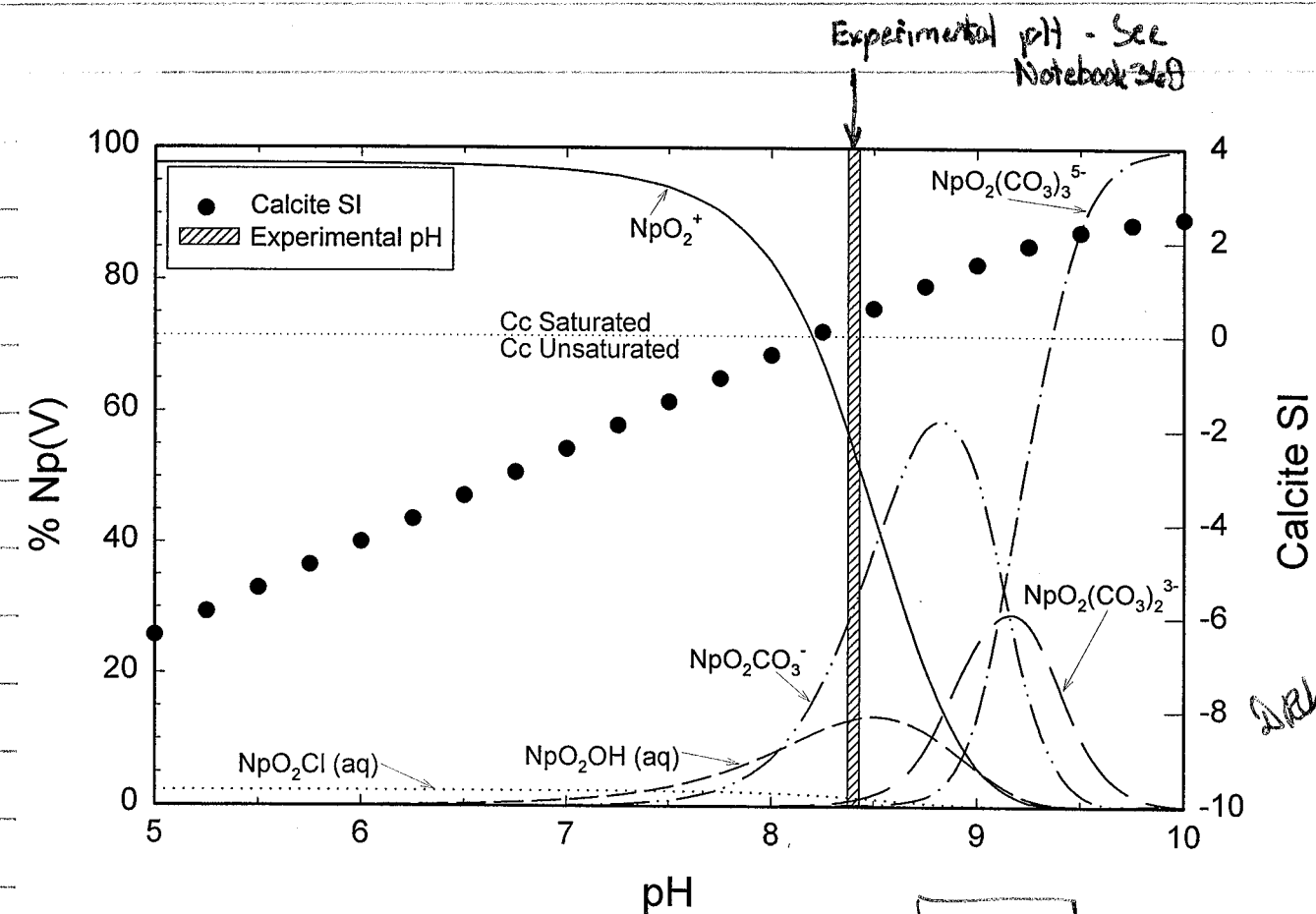


Figure 1

Variable pH

Atmospheric P_{CO_2} $10^{-3.5}$ atm

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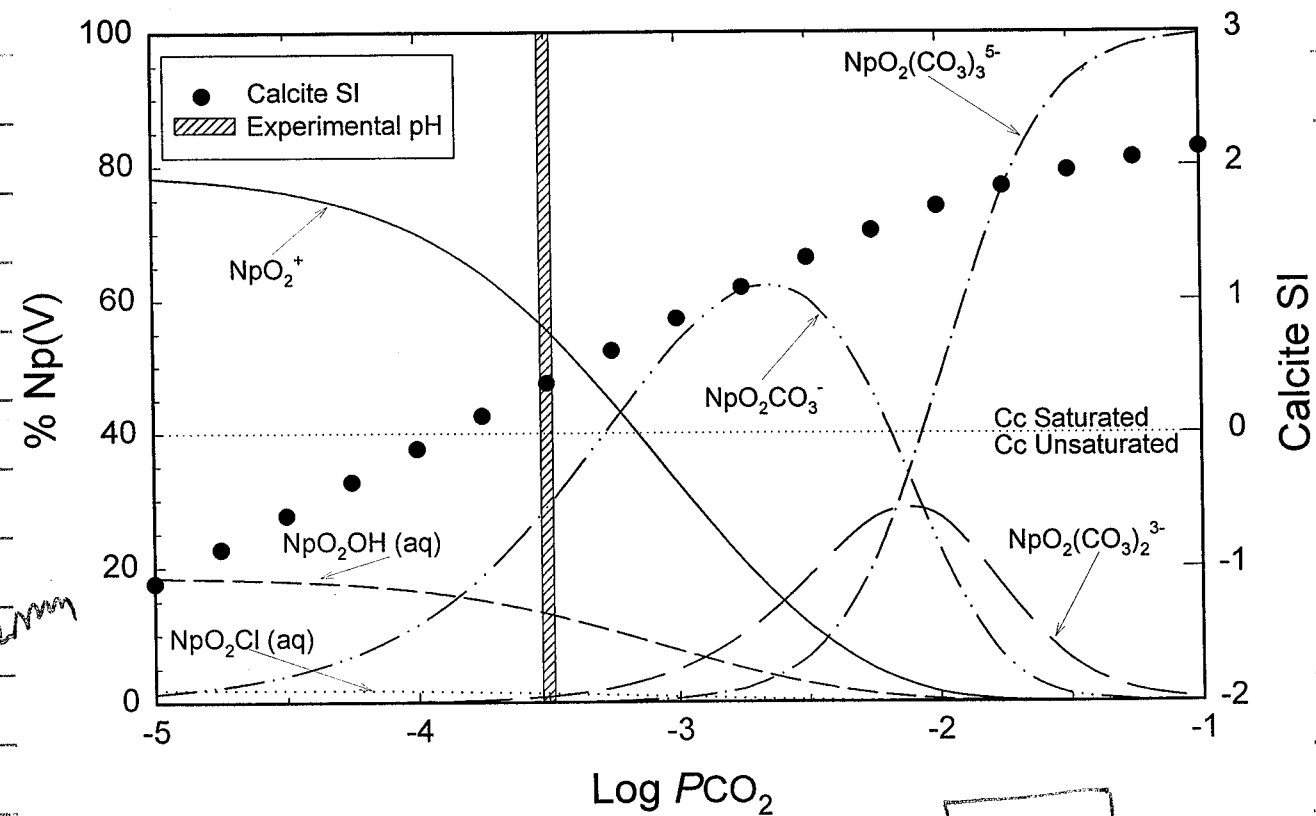


Figure 2

Variable P_{CO_2}
 $\text{pH} = 8.4$

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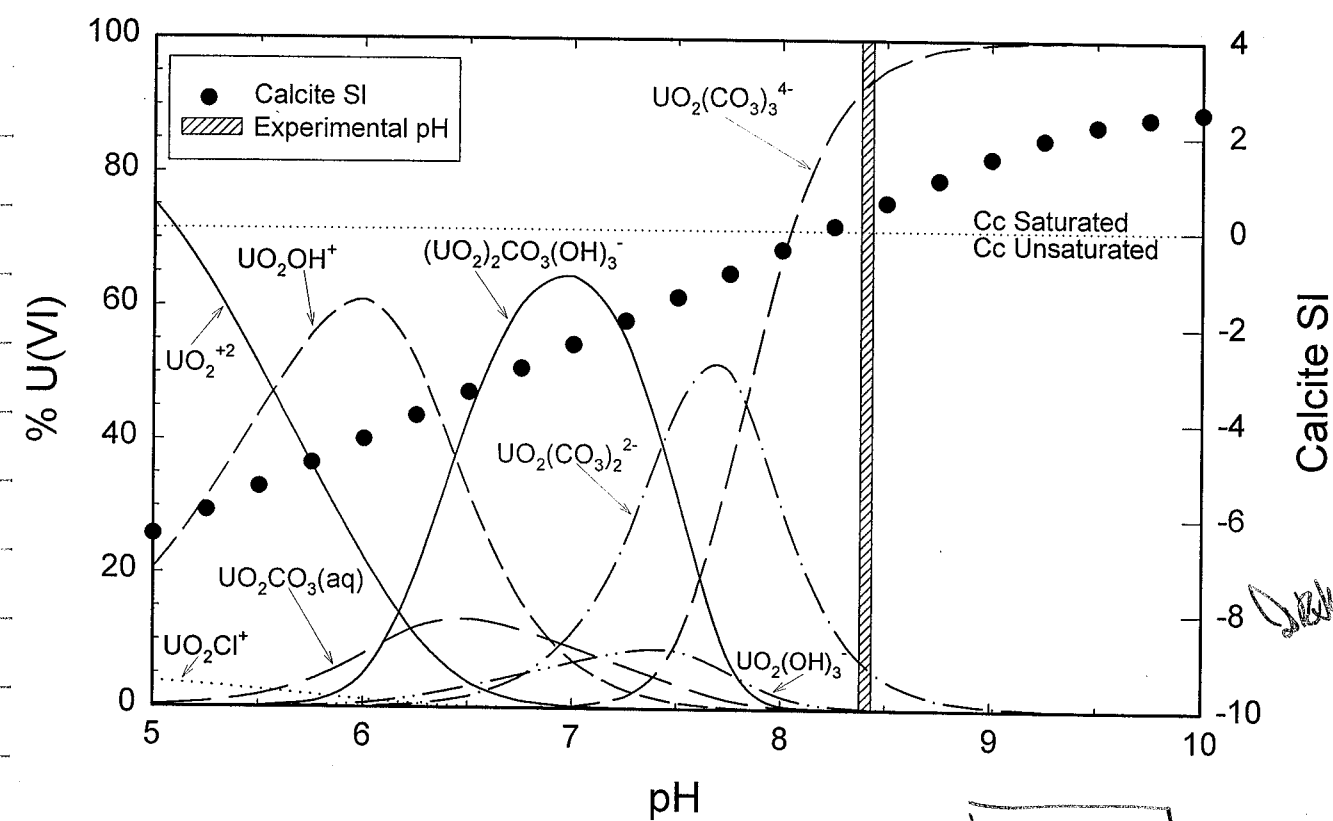


Figure 3

Atmospheric P_{CO_2}
 Variable pH

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	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1		sim	pH	pe	si_Calcite	m_NpO2+	%NpO2+	m_NpO2C	%NpO2C	m_NpO2O	%NpO2O	m_NpO2C	%NpO2C	m_NpO2C	%NpO2C	m_NpO2C	%NpO2C	Total
2		2	4.00	16.6064	-8.3971	1.14E-07	97.69	2.70E-09	2.31	1.10E-12	0.00	9.89E-17	0.00	4.54E-27	0.00	2.20E-37	0.00	1.17E-07
3	All Np-LogK from databas	3	4.25	16.3564	-7.8971	1.14E-07	97.69	2.70E-09	2.31	1.95E-12	0.00	3.13E-16	0.00	4.54E-26	0.00	6.97E-36	0.00	1.17E-07
4		4	4.50	16.1064	-7.3971	1.14E-07	97.69	2.70E-09	2.31	3.46E-12	0.00	9.89E-16	0.00	4.54E-25	0.00	2.20E-34	0.00	1.17E-07
5	O(2)/O(0) redox (atmosph	5	4.75	15.8564	-6.8971	1.14E-07	97.68	2.70E-09	2.31	6.16E-12	0.01	3.13E-15	0.00	4.54E-24	0.00	6.97E-33	0.00	1.17E-07
6	PCO2=1e-3.5	6	5.00	15.6064	-6.3971	1.14E-07	97.68	2.70E-09	2.31	1.10E-11	0.01	9.89E-15	0.00	4.54E-23	0.00	2.20E-31	0.00	1.17E-07
7	Variable pH	7	5.25	15.3564	-5.8971	1.14E-07	97.67	2.70E-09	2.31	1.95E-11	0.02	3.13E-14	0.00	4.54E-22	0.00	6.96E-30	0.00	1.17E-07
8		8	5.50	15.1064	-5.3971	1.14E-07	97.66	2.70E-09	2.31	3.46E-11	0.03	9.88E-14	0.00	4.54E-21	0.00	2.20E-28	0.00	1.17E-07
9		9	5.75	14.8564	-4.8971	1.14E-07	97.64	2.70E-09	2.31	6.16E-11	0.05	3.12E-13	0.00	4.53E-20	0.00	6.96E-27	0.00	1.17E-07
10		10	6.00	14.6064	-4.3971	1.14E-07	97.60	2.70E-09	2.31	1.09E-10	0.09	9.88E-13	0.00	4.53E-19	0.00	2.20E-25	0.00	1.17E-07
11		11	6.25	14.3564	-3.8971	1.14E-07	97.52	2.70E-09	2.31	1.94E-10	0.17	3.12E-12	0.00	4.53E-18	0.00	6.96E-24	0.00	1.17E-07
12		12	6.50	14.1064	-3.3972	1.14E-07	97.39	2.70E-09	2.30	3.45E-10	0.30	9.86E-12	0.01	4.52E-17	0.00	2.20E-22	0.00	1.17E-07
13		13	6.75	13.8564	-2.8972	1.14E-07	97.15	2.69E-09	2.30	6.12E-10	0.52	3.11E-11	0.03	4.51E-16	0.00	6.93E-21	0.00	1.17E-07
14		14	7.00	13.6064	-2.3973	1.13E-07	96.70	2.68E-09	2.29	1.08E-09	0.93	9.79E-11	0.08	4.49E-15	0.00	2.18E-19	0.00	1.17E-07
15		15	7.25	13.3564	-1.8974	1.12E-07	95.84	2.65E-09	2.27	1.91E-09	1.63	3.07E-10	0.26	4.45E-14	0.00	6.85E-18	0.00	1.17E-07
16		16	7.50	13.1064	-1.3977	1.10E-07	94.11	2.60E-09	2.23	3.34E-09	2.85	9.52E-10	0.81	4.38E-13	0.00	2.13E-16	0.00	1.17E-07
17		17	7.75	12.8565	-0.8982	1.06E-07	90.51	2.50E-09	2.14	5.70E-09	4.88	2.90E-09	2.48	4.21E-12	0.00	6.50E-15	0.00	1.17E-07
18		18	8.00	12.6065	-0.3993	9.69E-08	82.90	2.29E-09	1.96	9.28E-09	7.94	8.38E-09	7.17	3.86E-11	0.03	1.89E-13	0.00	1.17E-07
19		19	8.25	12.3565	0.0982	7.88E-08	67.96	1.86E-09	1.60	1.34E-08	11.57	2.16E-08	18.59	3.15E-10	0.27	4.92E-12	0.00	1.16E-07
20		20	8.50	12.1065	0.5922	4.73E-08	44.78	1.11E-09	1.06	1.43E-08	13.54	4.09E-08	38.73	1.90E-09	1.80	9.52E-11	0.09	1.06E-07
21		21	8.75	11.8566	1.0767	1.28E-08	20.96	2.99E-10	0.49	6.85E-09	11.26	3.49E-08	57.34	5.20E-09	8.55	8.44E-10	1.39	6.08E-08
22		22	9.00	11.6067	1.536	1.18E-09	5.85	2.74E-11	0.14	1.12E-09	5.57	1.02E-08	50.61	4.93E-09	24.53	2.67E-09	13.30	2.01E-08
23		23	9.25	11.3570	1.9346	6.48E-11	0.62	1.49E-12	0.01	1.09E-10	1.04	1.77E-09	16.99	2.89E-09	27.69	5.59E-09	53.64	1.04E-08
24		24	9.50	11.1078	2.2234	2.69E-12	0.02	5.92E-14	0.00	7.87E-12	0.06	2.32E-10	1.77	1.39E-09	10.61	1.15E-08	87.54	1.31E-08
25		25	9.75	10.8603	2.3894	6.33E-14	0.00	1.26E-15	0.00	3.13E-13	0.00	1.73E-11	0.06	4.78E-10	1.75	2.69E-08	98.19	2.74E-08
26		26	10.00	10.6261	2.5081	2.47E-16	0.00	3.68E-18	0.00	1.88E-15	0.00	2.10E-13	0.00	5.14E-11	0.07	7.26E-08	99.93	7.26E-08
27		27	10.25	10.3953	2.5809	2.93E-17	0.00	3.79E-19	0.00	3.64E-16	0.00	3.28E-14	0.00	1.80E-11	0.02	9.63E-08	99.98	9.63E-08
28		28	10.50	10.1456	2.5858	2.89E-17	0.00	3.73E-19	0.00	6.39E-16	0.00	3.30E-14	0.00	1.86E-11	0.02	1.04E-07	99.98	1.04E-07
29		29	10.75	9.8958	2.5885	2.87E-17	0.00	3.70E-19	0.00	1.13E-15	0.00	3.32E-14	0.00	1.91E-11	0.02	1.08E-07	99.98	1.08E-07
30		30	11.00	9.6459	2.5899	2.87E-17	0.00	3.69E-19	0.00	2.00E-15	0.00	3.33E-14	0.00	1.93E-11	0.02	1.11E-07	99.98	1.11E-07

PHREEQC, V.1.6 Output Np-speciation

Redox fixed by equilibrium w/ atmospheric oxygen (22% O₂)

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CJS

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	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
1		sim	pH	pe	si_Calcite	m_NpO2+	%NpO2+	m_NpO2Cl	%NpO2Cl	m_NpO2OH	%NpO2OH	m_NpO2CO	%NpO2CO	m_NpO2C	%NpO2C	m_NpO2(CO	%NpO2(CO	Total
2		2	4.00	13.4455	-8.3957	1.14E-07	97.69	2.70E-09	2.31	1.10E-12	0.00	9.92E-17	0.00	4.57E-27	0.00	2.22E-37	0.00	1.17E-07
3	All Np-LogK from databas	3	4.25	13.6295	-7.8957	1.14E-07	97.69	2.70E-09	2.31	1.95E-12	0.00	3.14E-16	0.00	4.57E-26	0.00	7.04E-36	0.00	1.17E-07
4		4	4.50	13.1905	-7.3957	1.14E-07	97.69	2.70E-09	2.31	3.47E-12	0.00	9.92E-16	0.00	4.57E-25	0.00	2.22E-34	0.00	1.17E-07
5	Set pe	5	4.75	12.5472	-6.8957	1.14E-07	97.68	2.70E-09	2.31	6.18E-12	0.01	3.14E-15	0.00	4.57E-24	0.00	7.04E-33	0.00	1.17E-07
6	PCO2=1e-3.5	6	5.00	13.0047	-6.3957	1.14E-07	97.68	2.70E-09	2.31	1.10E-11	0.01	9.92E-15	0.00	4.57E-23	0.00	2.22E-31	0.00	1.17E-07
7	Variable pH	7	5.25	12.4286	-5.8957	1.14E-07	97.67	2.70E-09	2.31	1.95E-11	0.02	3.14E-14	0.00	4.57E-22	0.00	7.03E-30	0.00	1.17E-07
8		8	5.50	11.9302	-5.3957	1.14E-07	97.66	2.70E-09	2.31	3.47E-11	0.03	9.92E-14	0.00	4.57E-21	0.00	2.22E-28	0.00	1.17E-07
9		9	5.75	11.908	-4.8957	1.14E-07	97.64	2.70E-09	2.31	6.18E-11	0.05	3.14E-13	0.00	4.56E-20	0.00	7.03E-27	0.00	1.17E-07
10		10	6.00	11.7289	-4.3957	1.14E-07	97.60	2.70E-09	2.31	1.10E-10	0.09	9.91E-13	0.00	4.56E-19	0.00	2.22E-25	0.00	1.17E-07
11		11	6.25	11.4103	-3.8957	1.14E-07	97.52	2.70E-09	2.31	1.95E-10	0.17	3.13E-12	0.00	4.56E-18	0.00	7.03E-24	0.00	1.17E-07
12		12	6.50	10.9919	-3.3957	1.14E-07	97.39	2.70E-09	2.30	3.46E-10	0.30	9.89E-12	0.01	4.55E-17	0.00	2.22E-22	0.00	1.17E-07
13		13	6.75	10.7833	-2.8958	1.14E-07	97.15	2.69E-09	2.30	6.15E-10	0.53	3.12E-11	0.03	4.54E-16	0.00	7.00E-21	0.00	1.17E-07
14		14	7.00	10.5369	-2.3958	1.13E-07	96.70	2.68E-09	2.29	1.09E-09	0.93	9.82E-11	0.08	4.52E-15	0.00	2.21E-19	0.00	1.17E-07
15		15	7.25	10.1462	-1.896	1.12E-07	95.83	2.65E-09	2.27	1.92E-09	1.64	3.08E-10	0.26	4.48E-14	0.00	6.92E-18	0.00	1.17E-07
16		16	7.50	9.96791	-1.3962	1.10E-07	94.10	2.60E-09	2.23	3.35E-09	2.86	9.56E-10	0.82	4.40E-13	0.00	2.15E-16	0.00	1.17E-07
17		17	7.75	9.79431	-0.8968	1.06E-07	90.48	2.50E-09	2.14	5.72E-09	4.89	2.91E-09	2.48	4.24E-12	0.00	6.56E-15	0.00	1.17E-07
18		18	8.00	9.62197	-0.3979	9.69E-08	82.86	2.29E-09	1.96	9.31E-09	7.96	8.41E-09	7.19	3.89E-11	0.03	1.91E-13	0.00	1.17E-07
19		19	8.25	9.39734	0.0996	7.94E-08	67.89	1.88E-09	1.60	1.36E-08	11.60	2.18E-08	18.63	3.20E-10	0.27	5.01E-12	0.00	1.17E-07
20		20	8.50	8.90992	0.5936	5.23E-08	44.69	1.23E-09	1.05	1.59E-08	13.56	4.54E-08	38.79	2.12E-09	1.81	1.06E-10	0.09	1.17E-07
21		21	8.75	8.28213	1.0781	2.44E-08	20.90	5.74E-10	0.49	1.32E-08	11.26	6.71E-08	57.36	1.00E-08	8.59	1.64E-09	1.40	1.17E-07
22		22	9.00	7.64583	1.5372	6.81E-09	5.82	1.59E-10	0.14	6.50E-09	5.56	5.91E-08	50.53	2.87E-08	24.58	1.56E-08	13.37	1.17E-07
23		23	9.25	6.9958	1.9356	7.20E-10	0.62	1.65E-11	0.01	1.21E-09	1.04	1.98E-08	16.91	3.23E-08	27.65	6.29E-08	53.78	1.17E-07
24		24	9.50	6.31035	2.224	2.37E-11	0.02	5.23E-13	0.00	6.97E-11	0.06	2.06E-09	1.76	1.24E-08	10.56	1.02E-07	87.60	1.17E-07
25		25	9.75	5.53778	2.3898	2.66E-13	0.00	5.28E-15	0.00	1.32E-12	0.00	7.27E-11	0.06	2.03E-09	1.73	1.15E-07	98.20	1.17E-07
26		26	10.00	5.30158	2.5087	3.85E-16	0.00	5.74E-18	0.00	2.94E-15	0.00	3.28E-13	0.00	8.11E-11	0.07	1.16E-07	99.93	1.16E-07
27		27	10.25	5.25096	2.5809	3.50E-17	0.00	4.52E-19	0.00	4.37E-16	0.00	3.91E-14	0.00	2.14E-11	0.02	1.15E-07	99.98	1.15E-07
28		28	10.50	4.97246	2.5858	3.20E-17	0.00	4.13E-19	0.00	7.10E-16	0.00	3.66E-14	0.00	2.07E-11	0.02	1.15E-07	99.98	1.15E-07
29		29	10.75	4.4302	2.5885	3.05E-17	0.00	3.93E-19	0.00	1.20E-15	0.00	3.52E-14	0.00	2.02E-11	0.02	1.15E-07	99.98	1.15E-07
30		30	11.00	4.92934	2.5899	2.96E-17	0.00	3.82E-19	0.00	2.08E-15	0.00	3.45E-14	0.00	2.00E-11	0.02	1.15E-07	99.98	1.15E-07

Redox fixed by Np(V) dominance
and Np redox. Used to generate Fig.1 (pg.7)

6/12/00
DRJ

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1		sim	pH	pe	Log PCO2	si_Calcite	m_NpO2+	%NpO2+	m_NpO2Cl	%NpO2Cl	m_NpO2OH	%NpO2OH	m_NpO2CO3	%NpO2CO3	m_NpO2(CO3)	%NpO2(CO3)	m_NpO2(CO3)	%NpO2(CO3)	Total
2		2	8.39	9.38697	-5.00	-1.1159	9.17E-08	78.36	2.17E-09	1.85	2.16E-08	18.49	1.52E-09	1.30	1.33E-12	0.00	1.24E-15	0.00	1.17E-07
3	All Np-LogK from database	3	8.39	9.38614	-4.75	-0.8661	9.08E-08	77.57	2.15E-09	1.83	2.14E-08	18.31	2.67E-09	2.28	4.17E-12	0.00	6.89E-15	0.00	1.17E-07
4		4	8.39	9.38451	-4.50	-0.6164	8.92E-08	76.22	2.11E-09	1.80	2.10E-08	17.98	4.66E-09	3.99	1.30E-11	0.01	3.81E-14	0.00	1.17E-07
5	Set pe	5	8.39	9.38073	-4.25	-0.367	8.65E-08	73.91	2.04E-09	1.75	2.04E-08	17.44	8.04E-09	6.87	3.97E-11	0.03	2.08E-13	0.00	1.17E-07
6	Fixed pH = 8.39	6	8.39	9.37091	-4.00	-0.118	8.20E-08	70.11	1.94E-09	1.66	1.93E-08	16.54	1.36E-08	11.59	1.19E-10	0.10	1.12E-12	0.00	1.17E-07
7	Variable CO2	7	8.39	9.33364	-3.75	0.1302	7.51E-08	64.18	1.77E-09	1.52	1.77E-08	15.13	2.21E-08	18.87	3.47E-10	0.30	5.79E-12	0.00	1.17E-07
8		8	8.39	9.16538	-3.50	0.3769	6.51E-08	55.64	1.54E-09	1.31	1.53E-08	13.11	3.40E-08	29.10	9.55E-10	0.82	2.87E-11	0.02	1.17E-07
9		9	8.39	8.81079	-3.25	0.6213	5.23E-08	44.68	1.23E-09	1.05	1.23E-08	10.52	4.86E-08	41.55	2.45E-09	2.09	1.33E-10	0.11	1.17E-07
10		10	8.39	8.42965	-3.00	0.8614	3.80E-08	32.50	8.91E-10	0.76	8.93E-09	7.64	6.29E-08	53.74	5.71E-09	4.88	5.68E-10	0.49	1.17E-07
11		11	8.39	8.04364	-2.75	1.0945	2.45E-08	20.94	5.70E-10	0.49	5.73E-09	4.90	7.20E-08	61.56	1.19E-08	10.21	2.23E-09	1.90	1.17E-07
12		12	8.39	7.64987	-2.50	1.316	1.35E-08	11.52	3.10E-10	0.26	3.13E-09	2.68	7.04E-08	60.20	2.17E-08	18.58	7.90E-09	6.76	1.17E-07
13		13	8.39	7.24335	-2.25	1.5199	5.79E-09	4.95	1.30E-10	0.11	1.33E-09	1.14	5.37E-08	45.97	3.19E-08	27.26	2.41E-08	20.58	1.17E-07
14		14	8.39	6.82156	-2.00	1.6992	1.63E-09	1.39	3.55E-11	0.03	3.69E-10	0.32	2.69E-08	23.01	3.22E-08	27.54	5.58E-08	47.71	1.17E-07
15		15	8.39	6.51545	-1.75	1.8485	2.57E-10	0.22	5.30E-12	0.00	5.67E-11	0.05	7.53E-09	6.44	1.95E-08	16.71	8.96E-08	76.58	1.17E-07
16		16	8.39	6.78043	-1.50	1.9864	2.33E-11	0.02	4.44E-13	0.00	4.93E-12	0.00	1.21E-09	1.03	7.44E-09	6.36	1.08E-07	92.58	1.17E-07
17		17	8.39	7.2388	-1.25	2.058	1.38E-12	0.00	2.37E-14	0.00	2.78E-13	0.00	1.27E-10	0.11	2.04E-09	1.75	1.15E-07	98.14	1.17E-07
18		18	8.39	7.7481	-1.00	2.1326	6.14E-14	0.00	9.28E-16	0.00	1.15E-14	0.00	9.93E-12	0.01	4.53E-10	0.39	1.16E-07	99.60	1.17E-07
19		19	8.39	8.01645	-0.75	2.1674	1.21E-14	0.00	1.70E-16	0.00	2.17E-15	0.00	2.58E-12	0.00	2.02E-10	0.17	1.16E-07	99.82	1.16E-07
20		20	8.39	8.0166	-0.50	2.1674	1.21E-14	0.00	1.70E-16	0.00	2.17E-15	0.00	2.58E-12	0.00	2.02E-10	0.17	1.16E-07	99.82	1.16E-07

Constant pH = 8.4

Variable Pco2

Used for Figure 2 (pg.8)

6/12/00
DJS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG
1		sim	pH	pe	si, Calcite	m_UO2+2	%UO2+2	m_UO2C1+	%UO2C1+	m_UO2C2	%UO2C2	m_UO2OH	%UO2OH	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)	m_UO2(OH)	%UO2(OH)
2	LogK(UO2(OH)2=13.0	2	4.00	8.56516	-8.3957	1.09E-07	92.80	5.44E-09	4.65	1.69E-11	0.01	2.97E-09	2.54	3.72E-13	0.00	2.90E-15	0.00	1.00E-24	0.00	6.97E-13	0.00	1.73E-18	0.00	3.62E-12	0.00	4.81E-18	0.00	1.06E-25	0.00	5.01E-18	0.00	1.17E-07	1.00E+02
3	U-LogK from database	3	4.25	8.55547	-7.8957	1.06E-07	90.89	5.33E-09	4.56	1.63E-11	0.01	5.17E-09	4.42	1.15E-12	0.00	1.60E-14	0.00	9.81E-24	0.00	2.73E-12	0.00	2.91E-17	0.00	1.18E-11	0.01	4.72E-17	0.00	3.27E-24	0.00	8.56E-17	0.00	1.17E-07	1.00E+02
4		4	4.50	8.54613	-7.3957	1.03E-07	87.94	5.15E-09	4.40	1.60E-11	0.01	8.89E-09	7.60	3.52E-12	0.00	8.69E-14	0.00	9.48E-23	0.00	8.05E-12	0.01	4.66E-16	0.00	3.62E-11	0.03	4.56E-16	0.00	9.98E-23	0.00	1.42E-15	0.00	1.17E-07	1.00E+02
5	pe adjusted for U(VI)	5	4.75	8.52149	-6.8957	9.70E-08	82.95	4.86E-09	4.15	1.51E-11	0.01	1.49E-08	12.75	1.05E-11	0.01	4.61E-13	0.00	8.94E-22	0.00	2.27E-11	0.04	6.96E-15	0.00	1.08E-10	0.09	4.30E-15	0.00	2.98E-21	0.00	2.25E-14	0.00	1.17E-07	1.00E+02
6		6	5.00	8.48498	-6.3957	8.81E-08	75.25	4.41E-09	3.77	1.37E-11	0.01	2.41E-08	20.57	3.02E-11	0.03	2.35E-12	0.00	8.11E-21	0.00	5.90E-11	0.10	9.24E-14	0.00	3.10E-10	0.28	3.90E-14	0.00	8.54E-20	0.00	3.29E-13	0.00	1.17E-07	1.00E+02
7		7	5.25	8.41035	-5.8957	7.54E-08	64.42	3.77E-08	3.22	1.17E-11	0.01	3.66E-08	31.31	8.16E-11	0.07	1.13E-11	0.01	6.95E-20	0.00	1.37E-10	0.23	1.03E-12	0.00	8.39E-10	0.72	3.34E-13	0.00	2.31E-18	0.00	4.23E-12	0.01	1.17E-07	1.00E+02
8		8	5.50	8.3052	-5.3957	5.95E-08	50.89	2.98E-09	2.55	9.24E-12	0.01	5.15E-08	43.98	2.04E-10	0.17	5.03E-11	0.04	5.49E-19	0.00	2.70E-10	0.46	9.04E-12	0.02	2.09E-09	1.79	2.84E-12	0.00	5.78E-17	0.00	4.76E-11	0.08	1.17E-07	1.00E+02
9		9	5.75	8.16253	-4.8957	4.24E-08	36.24	2.12E-09	1.81	6.58E-12	0.01	6.52E-08	55.70	4.59E-10	0.39	2.01E-10	0.17	3.91E-18	0.00	4.33E-10	0.74	5.80E-11	0.15	4.72E-09	4.03	1.88E-11	0.02	1.30E-15	0.00	4.28E-10	0.73	1.17E-07	1.00E+02
10		10	6.00	7.95523	-4.3957	2.61E-08	22.28	1.30E-09	1.12	4.05E-12	0.00	7.12E-08	60.88	8.93E-10	0.76	6.96E-10	0.59	2.40E-17	0.00	5.17E-10	0.88	2.40E-10	0.61	9.17E-09	7.84	1.18E-10	0.10	2.53E-14	0.00	2.88E-09	4.93	1.17E-07	1.00E+02
11		11	6.25	7.63208	-3.8957	1.25E-08	10.66	6.24E-10	0.53	1.94E-12	0.00	6.08E-08	51.81	1.35E-09	1.15	1.87E-09	1.60	1.15E-16	0.00	3.74E-10	0.64	4.67E-10	1.20	1.39E-08	11.86	5.53E-10	0.47	3.83E-13	0.00	1.17E-08	20.08	1.17E-07	1.00E+02
12		12	6.50	7.1741	-3.3957	4.36E-09	3.72	2.18E-10	0.19	6.76E-13	0.00	3.77E-08	32.19	1.49E-09	1.28	3.68E-09	3.14	4.02E-18	0.00	1.44E-10	0.25	3.54E-10	0.91	1.53E-08	13.10	1.83E-09	1.65	4.23E-12	0.00	2.55E-08	43.57	1.17E-07	1.00E+02
13		13	6.75	6.62122	-2.8958	1.22E-09	1.04	6.08E-11	0.05	1.89E-13	0.00	1.87E-08	15.96	1.32E-09	1.13	5.77E-09	4.93	1.12E-15	0.00	3.55E-11	0.06	1.37E-10	0.35	1.35E-08	11.55	5.39E-09	4.61	3.73E-11	0.03	3.53E-08	60.29	1.17E-07	1.00E+02
14		14	7.00	6.00872	-2.3958	2.98E-10	0.25	1.49E-11	0.01	4.63E-14	0.00	8.15E-09	6.96	1.02E-09	0.87	7.96E-09	6.80	2.75E-15	0.00	6.76E-12	0.01	3.58E-11	0.09	1.05E-08	8.96	1.32E-08	11.30	2.89E-10	0.25	3.77E-08	64.49	1.17E-07	1.00E+02
15		15	7.25	5.35767	-1.896	6.55E-11	0.06	3.26E-12	0.00	1.02E-14	0.00	3.18E-09	2.72	7.10E-10	0.61	8.84E-09	8.41	6.04E-15	0.00	1.03E-12	0.00	6.77E-12	0.02	7.29E-09	6.23	2.91E-08	24.84	2.01E-09	1.72	3.24E-08	55.40	1.17E-07	1.00E+02
16		16	7.50	4.62498	-1.3962	1.19E-11	0.01	5.92E-13	0.00	1.83E-15	0.00	1.02E-06	0.87	4.05E-10	0.35	9.98E-09	8.53	1.06E-14	0.00	1.06E-13	0.00	7.06E-15	0.00	4.16E-09	3.55	5.24E-08	44.81	1.15E-08	9.63	1.89E-08	32.05	1.17E-07	1.00E+02
17		17	7.75	3.77748	-0.8968	1.34E-12	0.00	6.68E-14	0.00	2.07E-16	0.00	2.05E-10	0.18	1.44E-10	0.12	6.33E-09	5.41	1.23E-14	0.00	4.28E-15	0.00	1.81E-14	0.00	1.48E-09	1.27	5.92E-08	50.60	4.11E-08	35.15	4.25E-09	7.26	1.17E-07	1.00E+02
18		18	8.00	2.95704	-0.3979	8.03E-14	0.00	4.01E-15	0.00	1.24E-17	0.00	2.19E-11	0.02	2.74E-11	0.02	2.14E-09	1.83	7.40E-15	0.00	4.89E-17	0.00	6.96E-17	0.00	2.82E-10	0.24	3.56E-08	30.42	7.84E-08	67.01	2.73E-10	0.47	1.17E-07	1.00E+02
19		19	8.25	2.24164	0.0998	3.28E-15	0.00	1.64E-16	0.00	5.06E-19	0.00	1.59E-12	0.00	3.54E-12	0.00	4.91E-10	0.42	3.02E-15	0.00	2.58E-19	0.00	8.42E-20	0.00	3.94E-11	0.03	1.45E-08	12.44	1.02E-07	87.10	8.08E-12	0.01	1.17E-07	1.00E+02
20		20	8.50	1.55588	0.5936	1.13E-16	0.00	5.61E-18	0.00	1.73E-20	0.00	8.69E-14	0.00	8.84E-13	0.00	9.47E-11	0.08	1.04E-15	0.00	9.61E-22	0.00	6.02E-23	0.00	3.94E-12	0.00	5.00E-09	4.27	1.12E-07	95.64	1.69E-13	0.00	1.17E-07	1.00E+02
21		21	8.75	0.880675	1.0781	3.61E-18	0.00	1.78E-19	0.00	5.48E-22	0.00	5.48E-15	0.00	3.85E-14	0.00	1.69E-11	0.01	3.32E-16	0.00	3.08E-24	0.00	3.44E-26	0.00	3.96E-13	0.00	1.60E-09	1.37	1.15E-07	98.62	3.03E-15	0.00	1.17E-07	1.00E+02
22		22	9.00	0.210877	1.5372	1.11E-19	0.00	5.38E-21	0.00	1.64E-23	0.00	2.95E-16	0.00	3.88E-15	0.00	2.89E-12	0.00	1.02E-16	0.00	9.03E-27	0.00	1.69E-29	0.00	3.78E-14	0.00	4.90E-10	0.42	1.17E-07	99.58	4.94E-17	0.00	1.17E-07	1.00E+02
23		23	9.25	-0.457927	1.9356	3.20E-21	0.00	1.51E-22	0.00	4.53E-25	0.00	1.48E-17	0.00	3.27E-16	0.00	4.59E-13	0.00	2.94E-17	0.00	2.31E-29	0.00	6.70E-33	0.00	3.36E-15	0.00	1.42E-10	0.12	1.17E-07	99.88	6.97E-19	0.00	1.17E-07	1.00E+02
24		24	9.50	-1.15983	2.224	8.11E-23	0.00	3.54E-24	0.00	1.02E-26	0.00	6.27E-19	0.00	2.42E-17	0.00	6.17E-14	0.00	7.44E-18	0.00	4.32E-32	0.00	1.57E-36	0.00	2.49E-16	0.00	3.59E-11	0.03	1.17E-07	99.97	6.95E-21	0.00	1.17E-07	1.00E+02
25		25	9.75	-1.95948	2.3688	1.45E-24	0.00	5.15E-26	0.00	1.34E-28	0.00	1.88E-20	0.00	1.12E-18	0.00	5.32E-15	0.00	1.31E-18	0.00	3.51E-35	0.00	0.00E+00	0.00	1.16E-17	0.00	6.37E-12	0.01	1.17E-07	99.99	2.78E-23	0.00	1.17E-07	1.00E+02
26		26	10.00	-2.92525	2.5387	9.87E-27	0.00	2.04E-28	0.00	3.98E-31	0.00	1.16E-22	0.00	1.40E-20	0.00	1.32E-16	0.00	8.48E-20	0.00	2.62E-39	0.00	0.00E+00	0.00	1.46E-19	0.00	4.22E-13	0.00	1.16E-07	100.00	6.72E-27	0.00	1.16E-07	1.00E+02
27		27	10.25	-2.95307	2.5809	1.97E-27	0.00	3.10E-29	0.00	5.25E-32	0.00	2.72E-23	0.00	6.53E-21	0.00	1.15E-16	0.00	1.57E-19	0.00	2.55E-40	0.00	0.00E+00	0.00	2.94E-20	0.00	1.45E-13	0.00	1.15E-07	100.00	1.53E-27	0.00	1.15E-07	1.00E+02
28		28	10.50	-3.13182	2.5658	1.83E-27	0.00	2.86E-29	0.00	4.83E-32	0.00	4.46E-23	0.00	1.90E-20	0.00	5.98E-16	0.00	1.45E-18	0.00	6.89E-40	0.00	0.00E+00	0.00	2.77E-20	0.00	1.40E-13	0.00	1.15E-07	100.00	7.50E-27	0.00	1.15E-07	1.00E+02
29		29	10.75	-3.03856	2.5685	1.75E-27	0.00	2.73E-29	0.00	4.61E-32	0.00	7.56E-23	0.00	5.78E-20	0.00	3.22E-15	0.00	1.39E-17	0.00	1.99E-39	0.00	0.00E+00	0.00	2.68E-20	0.00	1.38E-13	0.00	1.15E-07	100.00	3.90E-26	0.00	1.15E-07	1.00E+02
30		30	11.00	7.25877	2.5989	1.71E-27	0.00	2.66E-29	0.00	4.49E-32	0.00	1.31E-22	0.00	1.78E-19	0.00	1.76E-14	0.00	1.36E-16	0.00	6.00E-39	0.00	0.00E+00	0.00	2.63E-20	0.00	1.36E-13	0.00	1.15E-07	100.00	2.10E-25	0.00	1.15E-07	1.00E+02

U(VI) speciation

Fixed as U(VI), Uranium redox controls pe

Atmospheric Pco2 (10^{-3.5} atm)

Variable pH

Used for Fig 3 (pg. 9)

Note: All PHREEQC Input/Output and Excel files in pocket at the end of this notebook

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REVISION OF THE NUMERICAL OPTIMIZATION CODE, FITEQL V2.0
— Supplement to the Final Report on "Thermodynamic Modeling of Radionuclide Sorption"

6/12/00
JRL

Peiming Wang
OLI Systems, Inc.
108 American Road
Morris Plains, NJ 07950

December 7, 1999

The general non-linear least-square optimization program, FITEQL version 2.0 (Westall, 1982b), which was used in the thermodynamic modeling of radionuclide sorption (Wang and Anderko, 1999) for the determination of optimal values of surface complexation constants (or binding constants), has been revised to incorporate the activity coefficient model based on the B-dot equation of Helgeson (1969) for aqueous speciation calculations.

Details of the B-dot model and its advantages over the Davies equation, which was used by Westall (1982a, 1982b) in the FITEQL v2.0 code for the ionic strength correction, were discussed by Helgeson (1969) and Wang and Anderko (1999).

The B-dot activity coefficient model can be represented by the following equations:

$$\log \gamma_i = z_i^2 \log \gamma_0$$

$$\log \gamma_0 = -\frac{A_\gamma \sqrt{I}}{1 + a B_\gamma \sqrt{I}} + \frac{\dot{B}}{z_i^2} I$$

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Simplifications have been made in the revision of the FITEQL code: (1) the solute hard core diameter (a_i) is assigned a fixed value of 4.0 Å, a reasonable value that has been used in the formulation for the water activity that is quasi-consistent with the B-dot equation (Wolery, 1992a, 1992b); (2) a constant value of 0.015 has been assigned to \dot{B}/z_i^2 at 25°C. The two assignments allow the values of $\log \gamma_i$ to agree within 0.003 with those calculated using the original B-dot equation for most aqueous ions with $|z_i| = 1-3$ considered in this study at $I=0.1$ and 25°C, a condition that is typically used in radionuclide adsorption measurements. At the typical ionic strengths found in most sorption experiments (i.e., $I \leq 0.1$ M) and in waters used for the high-level waste performance assessment ($10^{-3} \sim 10^{-2}$ M), the difference in binding constants obtained using activity coefficients calculated with the modified model and with the original B-dot model is expected to be negligible. This has been tested by comparisons of $\log K_c$ values determined

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using the following two approaches: (1) $\log K_c$ from the revised FITEQL program using the modified B-dot model for ionic strength correction; (2) $\log K_c$ values manually corrected to $I=0$ from those determined at the ionic strength of interest. The correction in the latter case was made using activity coefficients calculated from the original B-dot equation. The differences in $\log K_c$ thus obtained were of the order of 10^{-2} , which is about the same order of magnitude as the standard deviations for the estimated binding constants in the tested cases.

The revision of the FITEQL (v2.0) code included changes made to a subroutine, *ACT0*, and two entries, *ACTZ* and *ACTX*, in the FORTRAN program. In *ACT0*, the values of the constants in activity coefficient model, A_γ , B_γ , \dot{B}/z_i^2 , and a_i are assigned (see lines 14155-14170); in *ACTZ*, a component of the Jacobian matrix for chemical equilibrium is assigned with respect to the ionic strength. Changes were made to lines 14238 and 14240 for the expression in $d\gamma_0/dI$ (compared to line 14240 in the original code). The expression for $\log \gamma_0$ is changed in *ACTX* (line 14340). The codes before and after the revision are listed in the attachment (only the affected portion of the code is shown). The lines where changes were made have been marked with asterisks. These lines are located toward the end of the FITEQL v2.0 code. Definitions for the program variables have been described by Westall (1982a), and those related to the activity coefficient can be found in Westall (1982b).

OK/mm

References

Helgeson H. C. (1969) Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures. *Am. J. Sci.* **267**, 729-804.

Wang P. and Anderko A. (1999) Thermodynamic Modeling of Radionuclide Sorption. Final Report to Center for Nuclear Waste Regulatory Analyses. OLI Systems, Inc. Morris Plains, NJ 07950

Westall J. C. (1982a) *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data, Version 1.2*. Department of Chemistry, Oregon State University, Report 82-01.

Westall J. C. (1982b) *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants from Experimental Data, Version 2.0*. Department of Chemistry, Oregon State University, Report 82-02.

Wolery T. J. (1992a) *EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide, Version 7.0*. Lawrence Livermore National Laboratory.

Wolery T. J. (1992b) *EQ3NR, A Computer Program for Geochemical Modeling of Aqueous-Speciation-Solubility Calculations: Theoretical Manual, User's Guide, and Related Documentation, Version 7.0*. Lawrence Livermore National Laboratory.

6/12/00
DBI

Portion of the FITEQL Code Prior to the Revision

Subroutine ACT0

Common/parm/itmax, iter, eps, nes, nec, ksr, kact, ktst

Common/var/gx(10), x(10), t(10), to(10), y(10), yabs(10), z(10,10),

1c(50), gc(50), gk(50), a(50,10), b(50,10), idx(10), idy(50), name(10)

Common/n/nt, ntx, nx, nuk, nut, nux, ndap

C

coefa=-0.509

coefc=0.3

kf=iadx(170)

tf=t(kf)

goto 200

entry actz

xf=x(kf)

tf=t(kf)

sqrtf=sqrt(tf)

dxdt=xf*alog(10.)*coefa*(1./(2.*sqrtf*(1+sqrtf)**2)-coefc)

do 100 j=1, nec

100 z(j,kf)=z(j,kf)*dxdt

zkfzkf=z(kf,kf)

z(kf,kf)=z(kf,kf)-1.

return

entry actx

if(kf.gt.nt) return

yf=y(kf)

tf=tf-yf

if(tf.lt.0.0) tf=(tf+yf)/10.

200 sqrtf=sqrt(tf)

gx(kf)=coefa*(sqrtf/(1.+sqrtf)-coefc*tf)

x(kf)=10.**gx(kf)

t(kf)=tf

return

end

00014110

00014120

00014130

00014140

00014145

00014150

00014160

00014170

00014180

00014190

00014200

00014230

00014232

00014234

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DBI

Portion of the FITEQL Code After the Revision

Subroutine ACT0

Common/parm/itmax, iter, eps, nes, nec, ksr, kact, ktst

Common/var/gx(10), x(10), t(10), to(10), y(10), yabs(10), z(10,10),

1c(50), gc(50), gk(50), a(50,10), b(50,10), idx(10), idy(50), name(10)

Common/n/nt, ntx, nx, nuk, nut, nux, ndap

C

coefa=-0.5114

coefb=0.3288

coefc=0.015

azero=4.0

kf=iadx(170)

tf=t(kf)

goto 200

entry actz

xf=x(kf)

tf=t(kf)

sqrtf=sqrt(tf)

dxdt=coefa/(2.*sqrtf*(1.+azero*coefb*sqrtf)**2)+coefc

dxdt=xf*alog(10.)*dxdt

do 100 j=1, nec

100 z(j,kf)=z(j,kf)*dxdt

zkfzkf=z(kf,kf)

z(kf,kf)=z(kf,kf)-1.

return

entry actx

if(kf.gt.nt) return

yf=y(kf)

tf=tf-yf

if(tf.lt.0.0) tf=(tf+yf)/10.

200 sqrtf=sqrt(tf)

gx(kf)=coefa*sqrtf/(1.+azero*coefb*sqrtf)+coefc*tf

x(kf)=10.**gx(kf)

t(kf)=tf

return

end

00014110

00014120

00014130

00014140

00014145

00014150

00014155*

00014160*

00014165*

00014170*

00014180

00014190

00014200

00014230

00014232

00014234

00014236

00014238*

00014240*

00014242

00014244

00014246

00014248

00014250

00014280

00014290

00014300

00014310

00014320

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00014340*

00014350

00014360

00014370

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Electronic copy of entire source code (revised) for FITEQL
is include in packet at end of this Scientific Notebook

6/12/00
DRA

Adding Tc data from the NEA Tc Database (Sandino and Ostholts, 1999)

The technetium data from the NEA Tc Database were added to the PHREEQC, Version 1.6 thermodynamic database. The reactions and Log K values (25 °C) are given here. An EXCEL (Microsoft Office 97) spreadsheet was used to calculate Log K from the Gibbs free energies reported in Sandino and Ostholts (1999) as a cross-check. Agreement is good, typically within rounding errors. The complete electronic file (PHREEQC.DAT) is enclosed in the envelope at the end of this scientific notebook.

1st Page of PHREEQC.DAT

```
SOLUTION_MASTER_SPECIES
#
# Database MINRAD95.DAT
# Modified by D.Turner 4/99 to include radionuclide data
# from EQ3/6 Data0.com.r16(26jun92 release). Consistent
# with CNWRA MINTEQA2 database (12/96).
#
# Modified by D. Turner 4/00 to include Tc-data from the
# NEA Thermodynamic Database project website:
# www.nea.fr/html/dbtb/tdbdata/TCDATA.DAT and
# www.nea.fr/html/dbtb/tdbdata/TCREAC.DAT
# Commented out the following Aqueous Species:
# Tc+3, TcO4-3, (TcO)2(OH)4(aq), H2TcO4(aq), HTcO4-,
# HTcO4(aq)
# Commented out the following Solids:
# Tc(metal), TcOH, Tc(OH)2, Tc(OH)3, TcS2, TcS3, Tc2S7,
# TcO2·2H2O, TcO3, Tc3O4, Tc4O7, NaTcO4
#####
#           essential definitions           #
#####
#
#element species           alk           gfw_formula           element_gfw
#
Alkalinity           CO3-2           1.0           61.0173           61.0173
E           e-           0.0           0.0           0.0
H           H+           -1.0           1.008           1.008
H(0)           H2           0.0           1.008
H(+1)           H+           -1.0           1.008
O           H2O           0.0           16.00           16.00
O(-2)           H2O           0.0           16.00           16.00
O(0)           O2           0.0           16.00           16.00
#####
Ag           Ag+           0.0           107.868           107.868
Al           Al+3           0.0           26.9815           26.9815
Am           Am+3           0.0           243.0614           243.0614
Am(+3)           Am+3           0.0           243.0614
Am(+4)           Am+4           0.0           243.0614
Am(+5)           AmO2+           0.0           243.0614
Am(+6)           AmO2+2           0.0           243.0614
As           H3AsO4           -1.0           74.9216           74.9216
As(+3)           H3AsO3           0.0           74.9216
As(+5)           H3AsO4           -1.0           74.9216
B           H3BO3           0.0           10.81           10.81
Ba           Ba+2           0.0           137.34           137.34
Be           Be+2           0.0           9.0122           9.0122
Br           Br-           0.0           79.904           79.904
C           CO3-2           2.0           61.0173           12.011
```

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C(+4)	CO3-2	2.0	61.0173	
#C(-4)	CH4	0.0	16.042	
Ca	Ca+2	0.0	40.08	40.08
Cd	Cd+2	0.0	112.399	112.399
Cl	Cl-	0.0	35.453	35.453
Co	Co+2	0.0	58.9332	58.9332
Co(+2)	Co+2	0.0	58.9332	
Co(+3)	Co+3	0.0	58.9332	
Cr	CrO4-2	0.0	51.996	51.996
Cr(+2)	Cr+2	0.0	51.996	
Cr(+3)	Cr(OH)2+	0.0	51.996	
Cr(+6)	CrO4-2	0.0	51.996	
Cs	Cs+	0.0	132.9054	132.9054
Cu	Cu+2	0.0	63.546	63.546
Cu(+1)	Cu+	0.0	63.546	
Cu(+2)	Cu+2	0.0	63.546	
Eu	Eu+3	0.0	151.965	151.965
Eu(+2)	Eu+2	0.0	151.965	
Eu(+3)	Eu+3	0.0	151.635	
F	F-	0.0	18.9984	18.9984
Fe	Fe+3	0.0	55.847	55.847
Fe(+2)	Fe+2	0.0	55.847	
Fe(+3)	Fe+3	-2.0	55.847	
Hg	Hg(OH)2	0.0	200.59	200.59
Hg(+2)	Hg(OH)2	0.0	200.59	
Hg(+1)	Hg2+2	0.0	200.59	
Hg(+0)	Hg	0.0	200.59	
I	I-	0.0	126.904	126.904
K	K+	0.0	39.102	39.102
Li	Li+	0.0	6.939	6.939
Mg	Mg+2	0.0	24.312	24.312
Mn	Mn+3	0.0	54.938	54.938
Mn(+2)	Mn+2	0.0	54.938	
Mn(+3)	Mn+3	0.0	54.938	
Mn(+6)	MnO4-2	0.0	54.938	
Mn(+7)	MnO4-	0.0	54.938	
N	NO3-	0.0	14.0067	14.0067
#N(0)	N2	0.0	14.0067	
N(-3)	NH4+	0.0	14.0067	
N(+3)	NO2-	0.0	14.0067	
N(+5)	NO3-	0.0	14.0067	
Na	Na+	0.0	22.9898	22.9898
Ni	Ni+2	0.0	58.71	58.71
Np	NpO2+	0.0	243.0614	243.0614
Np(+3)	Np+3	0.0	243.0614	
Np(+4)	Np+4	0.0	243.0614	
Np(+5)	NpO2+	0.0	243.0614	
Np(+6)	NpO2+2	0.0	243.0614	
P	PO4-3	2.0	30.9738	30.9738
Pb	Pb+2	0.0	207.19	207.19
Pu	Pu+4	0.0	244.0000	244.0000
Pu(+3)	Pu+3	0.0	244.0000	
Pu(+4)	Pu+4	0.0	244.0000	
Pu(+5)	PuO2+	0.0	244.0000	
Pu(+6)	PuO2+2	0.0	244.0000	
Ra	Ra+2	0.0	226.025	226.025
Rb	Rb+	0.0	85.4699	85.4699
Ru	RuO4-2	0.0	101.0700	101.0700
Ru(+2)	Ru+2	0.0	101.0700	
Ru(+3)	Ru+3	0.0	101.0700	
Ru(+4)	Ru(OH)2+2	0.0	101.0700	
Ru(+6)	RuO4-2	0.0	101.0700	
Ru(+7)	RuO4-	0.0	101.0700	
S	SO4-2	0.0	96.0616	32.064
S(-2)	HS-	1.0	32.064	
S(+6)	SO4-2	0.0	96.0616	

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DPA (8/29/00)

Sb	Sb(OH) 6-	6.0	172.772	172.772
Sb(+3)	Sb(OH) 3	3.0	172.772	
Sb(+5)	Sb(OH) 6-	0.0	172.772	
Se	SeO4-2	0.0	78.96	78.96
Se(-2)	HSe-	0.0	78.96	
Se(+4)	SeO3-2	0.0	78.96	
Se(+6)	SeO4-2	0.0	78.96	
Si	H4SiO4	0.0	96.1155	28.0843
Sn	Sn+4	0.0	118.710	118.710
Sn(+2)	Sn+2	0.0	118.710	
Sn(+4)	Sn+4	0.0	118.710	
Sr	Sr+2	0.0	87.62	87.62
Tc	TcO4-	0.0	98.0000	98.0000
#Tc(+3)	Tc+3	0.0	98.0000	
Tc(+4)	TcO+2	0.0	98.0000	
#Tc(+5)	TcO4-3	0.0	98.0000	
Tc(+6)	TcO4-2	0.0	98.0000	
Tc(+7)	TcO4-	0.0	98.0000	
Th	Th+4	0.0	232.0381	232.0381
Tl	Tl(OH) 3	0.0	204.37	204.37
Tl(+1)	Tl+	0.0	204.37	
Tl(+3)	Tl(OH) 3	0.0	204.37	
U	UO2+2	0.0	238.0290	238.0290
U(+3)	U+3	0.0	238.0290	
U(+4)	U+4	0.0	238.0290	
U(+5)	UO2+	0.0	238.0290	
U(+6)	UO2+2	0.0	238.0290	
V	VO2+	0.0	50.94	50.94
V(+2)	V+2	0.0	50.94	
V(+3)	V+3	0.0	50.94	
V(+4)	VO+2	0.0	50.94	
V(+5)	VO2+	0.0	50.94	
Zn	Zn+2	0.0	65.37	65.37
Zr	Zr+4	0.0	91.224	91.224

REFERENCES:

Sandino, M.C.A. and E. Ostholts. 1999. *Chemical Thermodynamics Volume 3: Chemical Thermodynamics of Technetium*. Nuclear Energy Agency/Organisation for Economic Cooperation and Development. Amsterdam: Elsevier.

6/12/00
DPA

Aqueous		log K
Tc(IV) ✓ 1)	$TcO^{+2} + H_2O = TcO(OH)^+ + H^+$	-1.50
✓ 2)	$TcO^{+2} + 2H_2O = TcO(OH)_2^0 + 2H^+$	-4.00
✓ 3)	$TcO^{+2} + 3H_2O = TcO(OH)_3^- + 3H^+$	-14.90
✓ 4)	$TcO^{+2} + CO_3^{-2} + H_2O = TcCO_3(OH)_2^0$	15.24
✓ 5)	$TcO^{+2} + CO_3^{-2} + 2H_2O = TcCO_3(OH)_3^- + H^+$	6.46
Solids		
Tc(IV) ✓ 1)	$Tc(s) + H_2O = TcO^{+2} + 2H^+ + 4e^-$	-21.09
✓ 2)	$TcO_2(s) + 2H^+ = TcO^{+2} + H_2O$	-8.39
✓ 3)	$TcO_2 \cdot 1.6H_2O(s) + 2H^+ = TcO^{+2} + 2.6H_2O$	-4.40
Tc(VII) ✓ 1)	$NH_4TcO_4(s) = TcO_4^- + NH_4^+$	-0.91
✓ 2)	$TlTcO_4(s) = TcO_4^- + Tl^+$	-5.32
✓ 3)	$AgTcO_4(s) = TcO_4^- + Ag^+$	-3.27
✓ 4)	$NaTcO_4 \cdot 4H_2O(s) = TcO_4^- + Na^+ + 4H_2O$	0.79
✓ 5)	$CsTcO_4(s) = TcO_4^- + Cs^+$	-3.65
✓ 6)	$Tc_2O_7 + H_2O = 2TcO_4^- + 2H^+$	+15.30
✓ 7)	$Tc_2O_7 \cdot H_2O = 2TcO_4^- + 2H^+$	+14.11
Redox		
✓ 1)	$TcO_4^- + e^- = TcO_4^{2-}$	-10.80
✓ 2)	$TcO_4^- + 6H^+ + 3e^- = TcO^{+2} + 3H_2O$	33.429
✓ 3)	$TcO_4^- + 2e^- = TcO_4^{3-}$	20.30

Cation Check:
Check Pu^{4+} (Wang et al., 2000a)

Prepared for submission to *Geochimica et Cosmochimica Acta*

Thermodynamic Modeling of the Adsorption of Radionuclides on Selected Minerals. I: Cations

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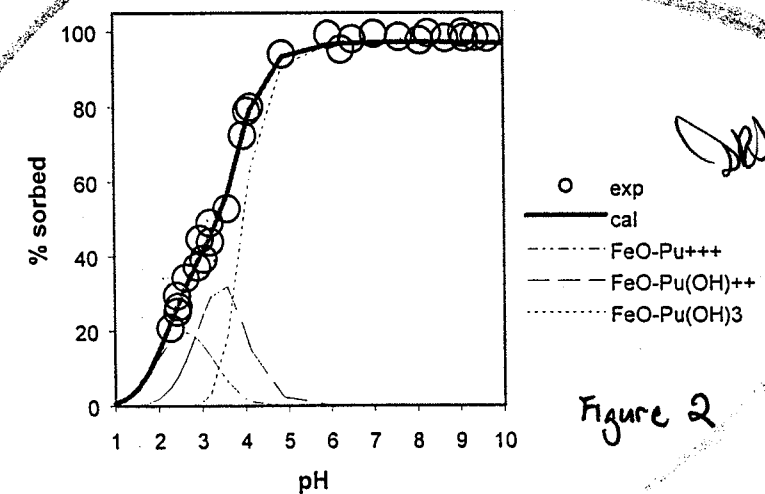


Figure 2. Sorption of Pu(IV) on goethite. Experimental data are from Sanchez et al. (1985) ($A_{sp}=45$ m²/g; $m/V=0.633$ g/L; $[Pu(IV)]_{total}=1.1 \times 10^{-4}$ M; $I=0.1$ M NaNO₃) and the solid line is calculated using the parameters listed in Tables 1 and 3. The surface complexes included in the model are $\equiv FeO-Pu^{+3}$, $\equiv FeO-PuOH^{+2}$, and $\equiv FeO-Pu(OH)_3^0$. The dashed lines represent contributions from the formation of various surface complexes to the total amount of adsorption.

DRJ

Table 1. Aqueous Reactions Associated with Pu(IV), Pu(V), Am(III), Np(V) and Their Equilibrium Constants at 25°C^a 01402.871.050

DRJmm

Aqueous Reactions	log K (I=0)	I=0.1
$\text{Pu}^{4+} + \text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$	-0.50	-1.17
$\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{Pu}(\text{OH})_2^{2+} + 2\text{H}^+$	-2.32	-3.42
$\text{Pu}^{4+} + 3\text{H}_2\text{O} = \text{Pu}(\text{OH})_3^+ + 3\text{H}^+$	-5.28	-6.60
$\text{Pu}^{4+} + 4\text{H}_2\text{O} = \text{Pu}(\text{OH})_4^0 + 4\text{H}^+$	-9.52	-10.84

Parameters used in Fig. 2

Table 3. Summary of Parameters Used for the Determination of Binding Constants for the Sorption of Pu on Various Minerals^a

Radionuclide/Solid	A _{sp} , m ² /g	m/V, g/L	C _{NH} , M	I, M	P _{CO2} , atm	log K ₁ ^b	log K ₂ ^b	log K ₃ ^c	log K ₄ ^c	log K ₅ ^c	log K ₆ ^c	log K ₇ ^c	ref.
Pu(IV)/Goethite(α-FeOOH)	45	0.633	1.0x10 ⁻¹¹	0.1 (NaNO ₃)	None	7.35	-9.17	-	14.33 (0.06)	8.79 (0.08)	-	-3.92 (0.14)	24
Pu(IV)/α-Al ₂ O ₃	0.51	10	6.0x10 ⁻¹⁰	0.01 (NaClO ₄)	None	8.33	-9.73	-	-	11.43 (0.06)	4.18 (0.31)	-3.69 (0.29)	29
Pu(IV)/Quartz(SiO ₂)	2.8	10	1.8x10 ⁻¹¹	0.005 (art. g.w.) ^d 2x10 ⁻³ M ^e	-	-7.20	-	-	-	-4.21 (0.23)	-	-	28
Pu(V)/Goethite(α-FeOOH)	45	0.633	1.0x10 ⁻¹¹	0.1 (NaNO ₃)	None	7.35	-9.17	5.14 (0.03)	-2.95 (0.08)	-11.35 (0.31)	-	-	24
Pu(V)/γ-Al ₂ O ₃	130	0.2	2.0x10 ⁻¹⁰	0.1 (NaClO ₄)	None	6.85	-9.05	-	-	-11.02 (0.09)	-	-	26

DRJmm

^a A site density of 2.31 sites/nm² (from Dzombak and Morel, 1990) was assigned to all minerals.

^b Acidity constants from Turner and Sassman (1996).

^c Binding constants K₁ through K₅ correspond to the following surface reactions (M²⁺ = Pu⁴⁺ for Pu(IV) and M²⁺ = PuO₂⁺ for Pu(V)):

$\text{≡XOH}^0 + \text{M}^{2+} = \text{≡XOH-M}^{2+} \quad (K_1)$ $\text{≡XOH}^0 + \text{M}^{2+} = \text{≡XO-M}^{2+1} + \text{H}^+ \quad (K_2)$ $\text{≡XOH}^0 + \text{M}^{2+} + \text{H}_2\text{O} = \text{≡XO-MOH}^{2+2} + 2\text{H}^+ \quad (K_3)$ $\text{≡XOH}^0 + \text{M}^{2+} + 2\text{H}_2\text{O} = \text{≡XO-M}(\text{OH})_2^{2+3} + 3\text{H}^+ \quad (K_4)$ $\text{≡XOH}^0 + \text{M}^{2+} + 3\text{H}_2\text{O} = \text{≡XO-M}(\text{OH})_3^{2+4} + 4\text{H}^+ \quad (K_5)$

^d Ionic strength was calculated based on the ionic composition of the artificial ground water given by the authors.

^e Total carbonate concentration.

DRJ

8/29/00

Summary of FITEQL input

DRJmm

From Table 3 on pg 28 of this notebook

log K (I=0)

14.33

8.79

-3.92

DRJmm

After Dzombak & Morel (1990)

log K (I=0.1)

12.68

7.25

-5.24

DRJ

8/29/00

log T_{XOH} = -3.96

DRJ

8/29/00

A_{SP} = 45 m²/g

m/V = 0.633 g/L

C_{NO3} = 10⁻¹¹ M

I = 0.1 M NaNO₃

log K₊ = 7.35 (I=0) 7.24 (I=0.1)

log K₋ = -9.17 -9.06

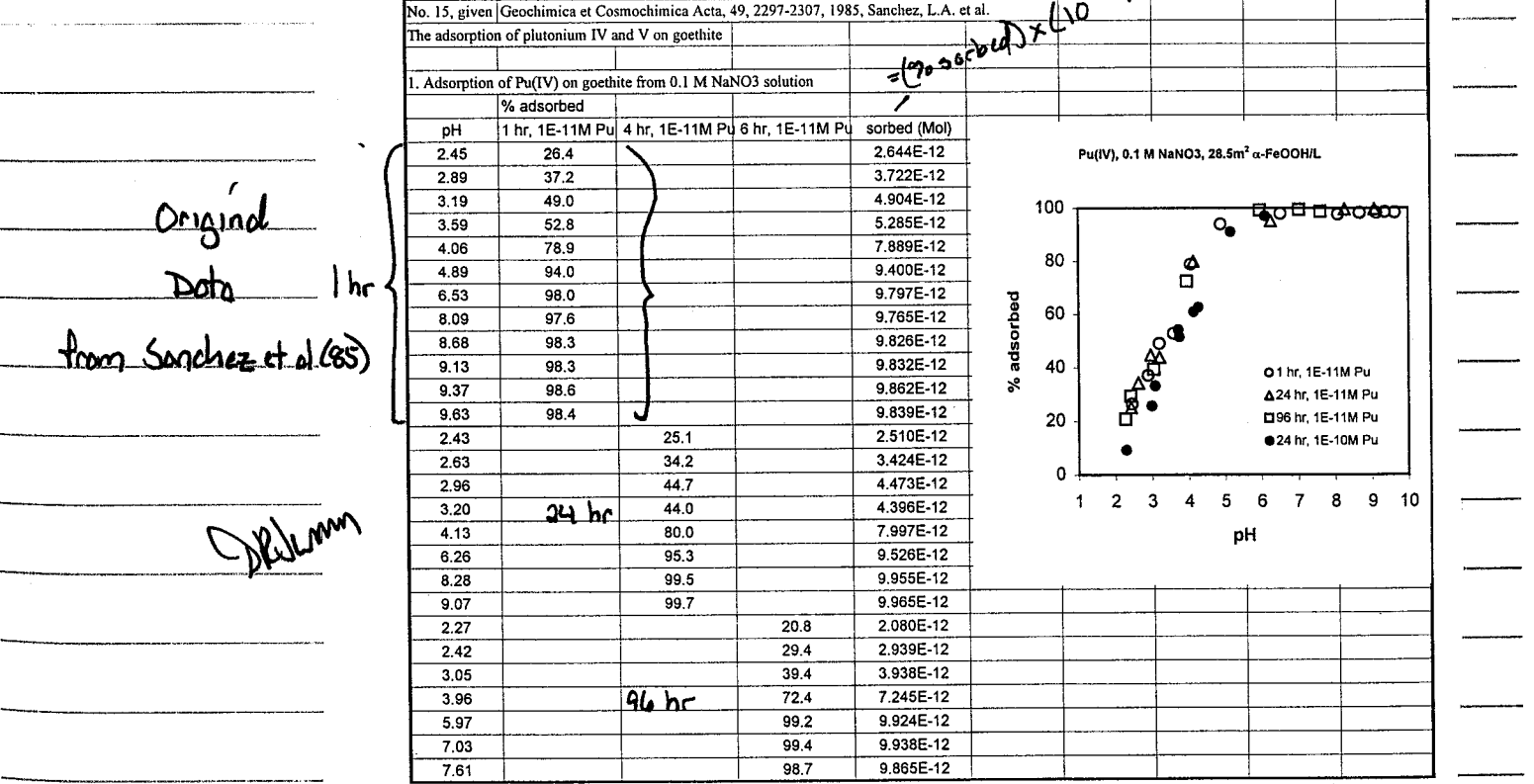
log K₂ XOH + Pu⁴⁺ = XOPu³⁺ + H⁺

log K₃ XOH + Pu⁴⁺ + H₂O = XOPuOH²⁺ + 2H⁺

log K₅ XOH + Pu⁴⁺ + 3H₂O = XOPu(OH)₃⁰ + 4H⁺

From Table 3

01402.871.050



8/29/00

Parameter Optimization using

8/29/00

DRJ

FITEQL, Vers. 2.0

DRJ

32-bit Power for Lahey Computer Systems
Phar Lap's 386|DOS-Extender(tm) Version 4.1L
Copyright (C) 1986-92 Phar Lap Software, Inc.
Available Memory = 15356 Kb

FITEQL, Ver. 2.0
Output

INPUT DATA FOR VERIFICATION

HEMICAL EQUILIBRIUM PROBLEM

ID	X	LOGX	T	GROUP	NAME
1	1.10E-04	-3.96	1.09E-04	I: T	XOH
160	1.00E-02	-2.00	0.00E+00	I: T	PSIO
41	1.00E-11	-11.00	1.00E-11	I: T	Pu+4
42	1.00E+00	0.00	0.00E+00	II: T,X	Puad
50	1.00E+00	0.00	0.00E+00	III:X	H+
3	1.00E-01	-1.00	0.00E+00	III:X	NA+
5	1.00E-01	-1.00	0.00E+00	III:X	NO3-

ATRIX A

ID	LOGK	1	160	41	42	50	3	5
50	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
41	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
4101	-1.17	0.00	0.00	1.00	0.00	-1.00	0.00	0.00
4102	-3.42	0.00	0.00	1.00	0.00	-2.00	0.00	0.00
4103	-6.60	0.00	0.00	1.00	0.00	-3.00	0.00	0.00
4104	-10.84	0.00	0.00	1.00	0.00	-4.00	0.00	0.00
100	-13.78	0.00	0.00	0.00	0.00	-1.00	0.00	0.00
1050	7.24	1.00	1.00	0.00	0.00	1.00	0.00	0.00
1100	-9.06	1.00	-1.00	0.00	0.00	-1.00	0.00	0.00
1	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
4201	12.68	1.00	3.00	1.00	1.00	-1.00	0.00	0.00
4202	7.25	1.00	2.00	1.00	1.00	-2.00	0.00	0.00
4203	-5.24	1.00	0.00	1.00	1.00	-4.00	0.00	0.00

ATRIX B

ID	LOGK	1	160	41	42	50	3	5
50	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
41	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
4101	-1.17	0.00	0.00	1.00	0.00	-1.00	0.00	0.00
4102	-3.42	0.00	0.00	1.00	0.00	-2.00	0.00	0.00
4103	-6.60	0.00	0.00	1.00	0.00	-3.00	0.00	0.00
4104	-10.84	0.00	0.00	1.00	0.00	-4.00	0.00	0.00
100	-13.78	0.00	0.00	0.00	0.00	-1.00	0.00	0.00
1050	7.24	1.00	1.00	0.00	0.00	1.00	0.00	0.00
1100	-9.06	1.00	-1.00	0.00	0.00	-1.00	0.00	0.00
1	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
4201	12.68	1.00	3.00	1.00	1.00	-1.00	0.00	0.00
4202	7.25	1.00	2.00	1.00	1.00	-2.00	0.00	0.00
4203	-5.24	1.00	0.00	1.00	1.00	-4.00	0.00	0.00

OUY-CHAPMAN MODEL

S M**2/G = 45.0 A G/L = 0.633

ELECTROLYTE CONCENTRATION MOL/L = 0.100000 ELECTROLYTE VALENCE = 1.

ARAMETERS FOR OPTIMIZATION:

LOG K FOR SPECIES: 4201 4202 4203

INPUT DATA FOR VERIFICATION

ERIAL DATA AND ERROR ESTIMATES

Sorption
Runs to
be optimized
Echoed Input

FITEQL, Ver. 2.0
Input
Chemical
Equilibrium
Model

Sorption
Rxn

TOTAL CONCENTRATION FOR COMPONENT:

1	42
2	2.640E-12
3	3.720E-12
4	4.900E-12
5	5.290E-12
6	7.890E-12
7	9.400E-12
8	9.800E-12
9	9.770E-12
10	9.830E-12
11	9.830E-12
12	9.860E-12
13	9.840E-12
14	2.510E-12
15	3.420E-12
16	4.470E-12
17	4.400E-12
18	8.000E-12
19	9.530E-12
20	9.960E-12
21	9.970E-12
22	2.080E-12
23	2.940E-12
24	3.940E-12
25	7.250E-12
26	9.920E-12
27	9.940E-12
	9.870E-12

OG FREE CONCENTRATION FOR COMPONENT:

1	50
2	-2.34
3	-2.78
4	-3.08
5	-3.48
6	-3.95
7	-4.78
8	-6.42
9	-7.98
10	-8.57
11	-9.02
12	-9.26
13	-9.52
14	-2.32
15	-2.52
16	-2.85
17	-3.09
18	-4.02
19	-6.15
20	-8.17
21	-8.96
22	-2.16
23	-2.31
24	-2.94
25	-3.85
26	-5.86
27	-6.92
	-7.50

TANDARD DEVIATION OF TOTAL CONCENTRATION:

COMPONENT 42 RELATIVE 0.1000 ABSOLUTE 2.000E-13
VALUES OF ADJUSTABLE PARAMETERS AT EACH ITERATION: LOG K, T, LOG X

I	V(Y): SOS/DF	4201	4202	4203
---	--------------	------	------	------

FITEQL, Ver. 2.0
Output (cont'd)

Sorption
Data
Input

Echoed Input

8/29/00
DR

0	1.268E+01	7.250E+00	-5.240E+00	2.120E-01
1	1.274E+01	7.259E+00	-5.110E+00	9.400E-02
2	1.275E+01	7.258E+00	-5.091E+00	9.334E-02
3	1.275E+01	7.259E+00	-5.091E+00	9.334E-02
4	1.275E+01	7.259E+00	-5.091E+00	9.334E-02

} Output

*** OPTIMIZATION PROCEDURE CONVERGED

4	1.275E+01	7.259E+00	-5.091E+00	9.334E-02	Final Values
---	-----------	-----------	------------	-----------	--------------

↑
log k₂ ↑
log k₃ ↑
log k₅

log k₂ = 12.75 + 1.65 = 14.40 vs. 14.33
(I=0.1) (I=0)

log k₃ = 7.24 + 1.54 = 8.80 vs. 8.79
(I=0.1) (I=0)

log k₅ = -5.091 + 1.32 = -3.77 vs. -3.42
(I=0.1) (I=0)

Table 3
values

DR

Very good agreement

FITEQL Output

= 4201 + 4202 + 4203
= $\left(\frac{\text{srb}(\text{Mol})}{10^{-11}}\right) + 100$

pH		4201	4202	4203	srb(Mol)	srb(%)
2.45	1	2.13E-12	5.97E-13	1.98E-15	2.73E-12	27.3
2.89	2	2.17E-12	1.65E-12	4.01E-14	3.86E-12	38.6
3.19	3	1.73E-12	2.55E-12	2.35E-13	4.51E-12	45.1
3.59	4	8.99E-13	3.12E-12	1.58E-12	5.60E-12	56.0
4.06	5	2.07E-13	1.80E-12	5.69E-12	7.70E-12	77.0
4.89	6	6.85E-15	2.17E-13	9.23E-12	9.45E-12	94.5
6.53	7	4.90E-17	8.22E-15	9.77E-12	9.78E-12	97.8
8.09	8	3.04E-18	1.29E-15	9.80E-12	9.80E-12	98.0
8.68	9	1.32E-18	7.38E-16	9.80E-12	9.80E-12	98.0
9.13	10	6.47E-19	4.60E-16	9.80E-12	9.80E-12	98.0
9.37	11	4.23E-19	3.46E-16	9.79E-12	9.79E-12	97.9
9.63	12	2.55E-19	2.47E-16	9.79E-12	9.79E-12	97.9
2.43	13	2.11E-12	5.64E-13	1.71E-15	2.67E-12	26.7
2.63	14	2.26E-12	9.54E-13	7.17E-15	3.22E-12	32.2
2.96	15	2.09E-12	1.86E-12	6.18E-14	4.01E-12	40.1
3.20	16	1.71E-12	2.58E-12	2.48E-13	4.53E-12	45.3
4.13	17	1.57E-13	1.54E-12	6.29E-12	7.98E-12	79.8
6.26	18	9.41E-17	1.27E-14	9.75E-12	9.76E-12	97.6
8.28	19	2.33E-18	1.08E-15	9.80E-12	9.80E-12	98.0
9.07	20	7.16E-19	4.92E-16	9.80E-12	9.80E-12	98.0
2.27	21	1.87E-12	3.47E-13	5.05E-16	2.21E-12	22.1
2.42	22	2.10E-12	5.48E-13	1.59E-15	2.65E-12	26.5
3.05	23	1.97E-12	2.14E-12	1.06E-13	4.21E-12	42.1
3.96	24	3.02E-13	2.18E-12	4.77E-12	7.24E-12	72.4
5.97	25	2.02E-16	2.11E-14	9.72E-12	9.74E-12	97.4
7.03	26	1.70E-17	4.06E-15	9.79E-12	9.79E-12	97.9
7.61	27	6.18E-18	2.07E-15	9.80E-12	9.80E-12	98.0

Compare
% sorbed
to Fig. 2
(pg. 27 of
this notebook)
Good agreement.
Also matches
original data
(Pg. 29 this
notebook)
well.

QA Check - Anion Sorption (Selenite, SeO₃²⁻)

8/29/00

Prepared for submission to *Geochimica et Cosmochimica Acta*

DR

Thermodynamic Modeling of the Adsorption of Radionuclides on Selected Minerals. II: Anions

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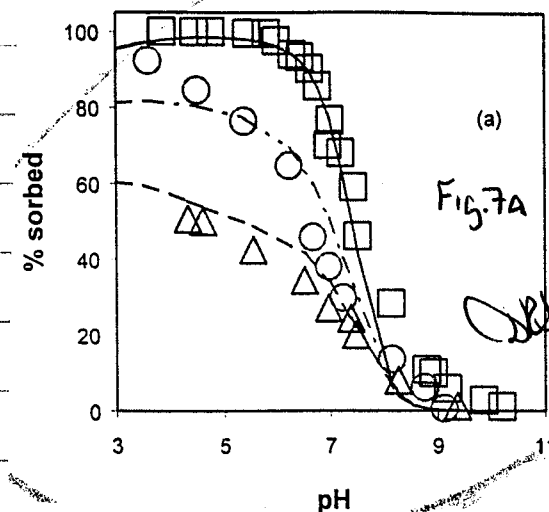


Figure 7. Sorption of selenite on goethite. The lines are calculated using parameters listed in Tables 1

and 3. Surface complexes included in the model are $\equiv\text{FeOH}_2\text{-HSeO}_3^0$ and $\equiv\text{FeOH-HSeO}_3^-$. Experimental

data are from Balistrieri and Chao (1987) ($A_{sp}=49 \text{ m}^2/\text{g}$; $I=0.1 \text{ M KCl}$). (a) $m/V=0.03 \text{ g/L}$, $[\text{SeO}_3^{2-}]_{\text{total}} =$

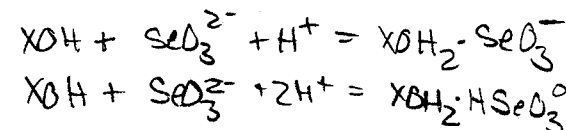
$6.5 \times 10^{-7} \text{ M}$ (solid line); \circ , $[\text{SeO}_3^{2-}]_{\text{total}} = 2.83 \times 10^{-6} \text{ M}$ (dash-dot line); Δ , $[\text{SeO}_3^{2-}]_{\text{total}} = 5.34 \times 10^{-6} \text{ M}$

(dashed line). (b) $[\text{SeO}_3^{2-}]_{\text{total}} = 6.5 \times 10^{-7} \text{ M}$; \square , $m/V=0.03 \text{ g/L}$ (solid line); \circ , $m/V=0.006 \text{ g/L}$ (dashed line);

Δ , $m/V=0.003 \text{ g/L}$ (dotted line).

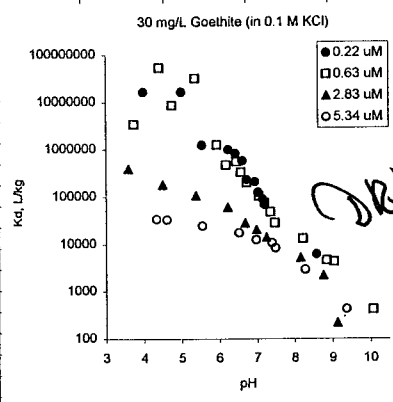
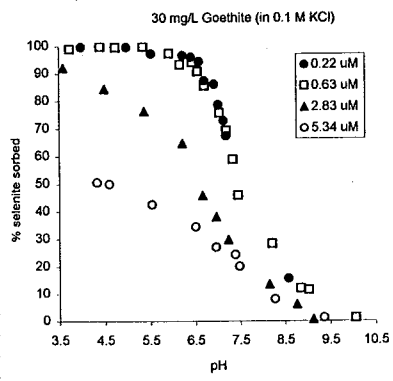
$A=49 \text{ m}^2/\text{g}$
 $m/V=0.03$

$\log k^+ = 7.35$
 $\log k^- = -9.17$



log k⁺
12.99
18.83

SELENIUM ADSORPTION BY GOETHITE									
Adsorption of selenite (SeO ₃ ²⁻) on goethite in 0.1 M KCl as a function of total selenite concentration and the equilibrium pH									
pH	% selenite sorbed				Kd, L/kg				
	0.22 uM	0.63 uM	2.83 uM	5.34 uM	0.22 uM	0.63 uM	2.83 uM	5.34 uM	
3.99	99.80				1.66E+07				
4.99	99.80				1.66E+07				
5.54	97.43				1.26E+06				
6.24	96.78				1.00E+06				
6.42	96.16				8.34E+05				
6.60	94.61				5.85E+05				
6.72	87.53				2.34E+05				
6.93	86.29				2.10E+05				
7.02	78.90				1.25E+05				
7.14	73.05				9.03E+04				
7.20	67.51				6.93E+04				
8.58	15.75				6.23E+03				
3.74		99.04				3.45E+06			
4.41		99.94				5.36E+07			
4.75		99.62				8.64E+06			
5.36		99.90				3.21E+07			
5.93		97.41				1.25E+06			
6.17		93.40				4.72E+05			
6.45		94.31				5.52E+05			
6.57		90.92				3.34E+05			
6.72		85.68				1.89E+05			
7.05		75.82				1.05E+05			
7.20		69.35				7.54E+04			
7.35		58.89				4.77E+04			
7.46		45.95				2.83E+04			
8.22		28.39				1.32E+04			
8.85		12.05				4.57E+03			
9.03		11.43				4.30E+03			
10.06		1.23				4.14E+02			
3.59			92.28				3.99E+05		
4.50			84.55				1.82E+05		
5.38			76.51				1.09E+05		
6.22			64.78				6.13E+04		
6.67			45.99				2.84E+04		
6.97			38.29				2.07E+04		
7.24			29.97				1.43E+04		
8.15			13.62				5.26E+03		
8.75			6.21				2.21E+03		
9.12			0.65				2.19E+02		
4.33				60.71				3.43E+04	
4.60				60.08				3.34E+04	
5.54				42.66				2.48E+04	
6.51				34.61				1.76E+04	
6.97				27.21				1.25E+04	
7.39				24.42				1.08E+04	
7.48				20.11				8.39E+03	
8.27				8.08				2.93E+03	
9.36				1.26				4.25E+02	



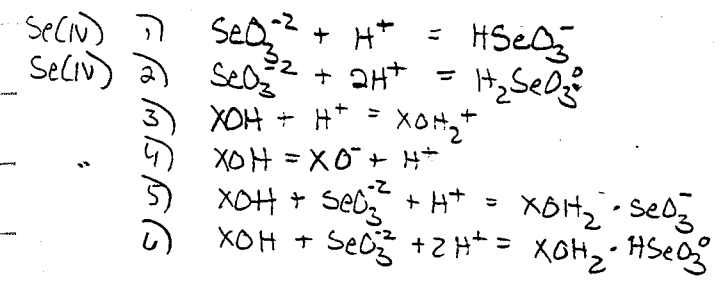
8/29/00
DRJ

pH	M _{sorbed}	% sorbed
3.59	2.612x10 ⁻⁶	92.28
4.50	2.393x10 ⁻⁶	84.55
5.38	2.165x10 ⁻⁶	76.51
6.22	1.833x10 ⁻⁶	64.78
6.67	1.302x10 ⁻⁶	45.99
6.97	1.084x10 ⁻⁶	38.29
7.24	9.48x10 ⁻⁷	29.97
8.15	3.85x10 ⁻⁷	13.62
8.75	1.76x10 ⁻⁷	6.21
9.12	1.84x10 ⁻⁸	0.65

SeO₃²⁻ Ballotrieri
+ Chao (1987)

Figure 7a

$M_T = 2.83 \times 10^{-6} \text{ M}$
 $m/v = 0.03 \text{ g/L}$
 $A_{sp} = 49 \text{ m}^2/\text{g}$



7.29 } Table 1
9.86 }

7.35 } Table 3
-9.17 }

12.99 } Table 3
18.83 } estimated Wang et al.
(0.1402.871.060)

$M_T = 2.83 \times 10^{-6} \text{ SeO}_3^{2-}$

$m/v = 0.03 \text{ g/L}$

$A = 49 \text{ m}^2/\text{g}$

$T_{\text{XOH}} = \frac{(2.31 \times 49 \times 0.03) \times (1 \times 10^5)}{6.023 \times 10^{23}}$

$\log = -5.548$

$5.638 \times 10^{-6} \text{ M}$

$\log = -5.249$

$I = 0.1 \text{ M KCl}$

Summary of FITEQL Input Data

DRJ

8/29/00

8/29/00
DRJ

8/29/00
DBJ

32-bit Power for Lahey Computer Systems
Phar Lap's 386|DOS-Extender(tm) Version 4.1L
Copyright (C) 1986-92 Phar Lap Software, Inc.
Available Memory = 15356 Kb

INPUT DATA FOR VERIFICATION

CHEMICAL EQUILIBRIUM PROBLEM

ID	X	LOGX	T	GROUP	NAME
1	5.62E-06	-5.25	5.64E-06	I: T	XOH
160	1.00E-02	-2.00	0.00E+00	I: T	PSIO
41	2.82E-06	-5.55	2.83E-06	I: T	SeO3
42	1.00E+00	0.00	0.00E+00	II: T,X	Sead
50	1.00E+00	0.00	0.00E+00	III:X	H+
3	1.00E-01	-1.00	0.00E+00	III:X	K+
5	1.00E-01	-1.00	0.00E+00	III:X	Cl-

MATRIX A

ID	LOGK	1	160	41	42	50	3	5
1	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
41	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
4101	6.85	0.00	0.00	1.00	0.00	1.00	0.00	0.00
4102	9.20	0.00	0.00	1.00	0.00	2.00	0.00	0.00
100	-13.78	0.00	0.00	0.00	0.00	-1.00	0.00	0.00
1050	7.24	1.00	1.00	0.00	0.00	1.00	0.00	0.00
1100	-9.06	1.00	-1.00	0.00	0.00	-1.00	0.00	0.00
4201	12.99	1.00	-1.00	1.00	1.00	1.00	0.00	0.00
4202	18.83	1.00	0.00	1.00	1.00	2.00	0.00	0.00

MATRIX B

ID	LOGK	1	160	41	42	50	3	5
1	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
41	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
4101	6.85	0.00	0.00	1.00	0.00	1.00	0.00	0.00
4102	9.20	0.00	0.00	1.00	0.00	2.00	0.00	0.00
100	-13.78	0.00	0.00	0.00	0.00	-1.00	0.00	0.00
1050	7.24	1.00	1.00	0.00	0.00	1.00	0.00	0.00
1100	-9.06	1.00	-1.00	0.00	0.00	-1.00	0.00	0.00
4201	12.99	1.00	-1.00	1.00	1.00	1.00	0.00	0.00
4202	18.83	1.00	0.00	1.00	1.00	2.00	0.00	0.00

GOUY-CHAPMAN MODEL

S M**2/G = 49.0 A G/L = 0.030

ELECTROLYTE CONCENTRATION MOL/L = 0.100000 ELECTROLYTE VALENCE = 1.

Input Data
Equilibrium Model

DBJmm

Echoed
Input

DBJmm 8/29/00

8/29/00
DBJ

PARAMETERS FOR OPTIMIZATION:

LOG K FOR SPECIES: 4201 4202
INPUT DATA FOR VERIFICATION

SERIAL DATA AND ERROR ESTIMATES

TOTAL CONCENTRATION FOR COMPONENT:

	42
1	2.610E-06
2	2.390E-06
3	2.170E-06
4	1.830E-06
5	1.300E-06
6	1.080E-06
7	8.480E-07
8	3.850E-07
9	1.760E-07
10	1.840E-08

Mass SeO_3^{-2} sorbed

Input values

Echoed
Input

LOG FREE CONCENTRATION FOR COMPONENT:

	50
1	-3.48
2	-4.39
3	-5.27
4	-6.11
5	-6.56
6	-6.86
7	-7.13
8	-8.04
9	-8.64
10	-9.01

pH corrected for mass-based
(I=0.1 M, Davies Equation)

DBJmm

STANDARD DEVIATION OF TOTAL CONCENTRATION:

COMPONENT 42 RELATIVE 0.1000 ABSOLUTE 1.800E-09
VALUES OF ADJUSTABLE PARAMETERS AT EACH ITERATION: LOG K, T, LOG X

I	V(Y): SOS/DF	4201	4202
0		1.299E+01	1.883E+01
1		1.268E+01	1.783E+01
2		1.247E+01	1.817E+01
3		1.240E+01	1.801E+01
4		1.235E+01	1.815E+01
5		1.233E+01	1.806E+01
6		1.232E+01	1.814E+01
7		1.232E+01	1.809E+01
8		1.231E+01	1.813E+01
9		1.231E+01	1.810E+01
10		1.231E+01	1.812E+01
11		1.231E+01	1.810E+01
12		1.231E+01	1.812E+01
13		1.231E+01	1.811E+01
14		1.231E+01	1.812E+01
15		1.231E+01	1.811E+01
16		1.231E+01	1.811E+01
17		1.231E+01	1.811E+01

Parameter Optimization

Output
Fitting Log k
for Rms 4201
+
4202
(sorption)

8/29/00
DKJ

18	1.231E+01	1.811E+01	1.650E+01
19	1.231E+01	1.811E+01	1.650E+01
20	1.231E+01	1.811E+01	1.650E+01
21	1.231E+01	1.811E+01	1.650E+01
22	1.231E+01	1.811E+01	1.650E+01
23	1.231E+01	1.811E+01	1.650E+01
24	1.231E+01	1.811E+01	1.650E+01
25	1.231E+01	1.811E+01	1.650E+01
26	1.231E+01	1.811E+01	1.650E+01
27	1.231E+01	1.811E+01	1.650E+01
28	1.231E+01	1.811E+01	1.650E+01
29	1.231E+01	1.811E+01	1.650E+01
30	1.231E+01	1.811E+01	1.650E+01
31	1.231E+01	1.811E+01	1.650E+01
32	1.231E+01	1.811E+01	1.650E+01
33	1.231E+01	1.811E+01	1.650E+01
34	1.231E+01	1.811E+01	1.650E+01

More Output

DKJmm

**** OPTIMIZATION PROCEDURE CONVERGED

34 1.231E+01 1.811E+01 1.650E+01 ← Final Values

$\log K_2 \log K_3$ $\log K_2 + \log K_3$

mass based $\log k$ Excellent Comparison

$\log K_2$ $12.31 + 0.55 = 12.86$ vs. 12.99 in 01402.871.060 (Table 3)

$\log K_3$ $18.11 + 0.66 = 18.77$ vs. 18.83 in 01402.871.060 (Table 3)

Output from FITEQL $\text{Srb1} + \text{Srb2}$ % srbed

DESCRIPTOF	CHEMICAL	EQUILIBRIUM		(MOL/L)
	Srb 1	Srb 2	Se(srb,tot)	%sorbed
pH	xoh2seo3	xoh2hseo3		
3.59	6.77E-07	1.60E-06	2.28E-06	80.40989
4.50	1.40E-06	8.43E-07	2.24E-06	79.13781
5.38	1.81E-06	3.52E-07	2.16E-06	76.34629
6.22	1.81E-06	1.31E-07	1.94E-06	68.70318
6.67	1.63E-06	6.85E-08	1.70E-06	60.08799
6.97	1.42E-06	4.00E-08	1.46E-06	51.51767
7.24	1.16E-06	2.21E-08	1.18E-06	41.66502
8.15	2.08E-07	1.15E-09	2.09E-07	7.40106
8.75	2.33E-08	8.42E-11	2.34E-08	0.826648
9.12	5.25E-09	1.54E-11	5.26E-09	0.186021

$$= \frac{(2.28 \times 10^{-6})}{(2.83 \times 10^{-6})} \times 100$$

Compare w/ Figure 7(a) (Pg. 33 of this notebook) DKJmm

$6.77 \times 10^{-7} + 1.60 \times 10^{-6} = 2.28 \times 10^{-6}$

8/29/00
DKJ

REFERENCES:

Balistreri L.S. and Chao T.T. (1987) Selenium adsorption by goethite, *Soil Sci. Soc. Am. J.* **51**, 1145-1151.

Dzombak D.A. and Morel, F.M.M. (1990) *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons.

Sanchez A.L., Murray J.W., and Sibley T.H. (1985) The adsorption of plutonium IV and V on goethite. *Geochim. Cosmochim. Acta* **49**, 2297-2307.

Turner D.R. and Sassman S.A. (1996) Approaches to sorption modeling for high-level waste performance assessment. *J. Contam. Hydrol.* **21**, 311-332.

DKJmm

J.R. Johnson
8/29/00

Developing sorption coefficient statistics UZ matrix for input into TPA.

As described previously, one goal of this work has been to develop information that can be used to incorporate, at least indirectly, the effects of chemistry on radionuclide sorption coefficients. Based on the method outlined in Pabalan et al. (1998), Bertetti et al. (1998), and Turner (1998), we have used the Diffuse-Layer Model (DLM) to model sorption for the range in UZ porewater chemistries represented by the data of Yang et al. (1996, 1998).

Assumptions include:

- Sorption behavior as a function of pH and carbonate concentration is similar for aluminosilicate minerals when expressed in terms of K_D/A' , where A' is the effective surface area (BET surface area in the case of nonporous minerals, 10 % of BET in the case of sheet minerals such as montmorillonite, gibbsite, and kaolinite). Also implicit in this assumption is that aluminosilicate minerals will dominate sorption in the tuff units at YM.
- The effect outlined above has been demonstrated for U(VI) and Np(V) (Pabalan et al., 1998 and Bertetti et al., 1998). It is assumed that it is also true for other actinides such as Am(III), Pu(V), and Th(IV).
- The mean pore size in the matrix at YM is $0.1\ \mu\text{m}$ (Travis and Nuttall, 1987), which is assumed to be true for all hydrostratigraphic units used in TPA.
- The water chemistries of Yang et al. (1996, 1998) represent the likely range in UZ porewater chemistry at YM.
- As appropriate, mean values from tpa.inp for solubility limits, density, and porosity are used in DLM simulations.

The steps involved in this modeling exercise are:

- Identify sorption experiments that can be used to calibrate the DLM parameters.

We used the following sorption experiments for Am(III), Th(IV), and Pu(V) sorption on γ -alumina (Righetto et al., 1988; 1991); Np(V) and U(VI) sorption on montmorillonite (Turner et al., 1998a; Pabalan and Turner, 1997). DLM parameters were determined assuming $A' = 10\%$ of BET measured area for both γ -alumina (BET=130 m²/g; $A'=13.0\text{ m}^2/\text{g}$) and montmorillonite (BET=97 m²/g; $A'=9.7\text{ m}^2/\text{g}$).

- Determine the DLM parameters for these experiments.

The DLM parameters in Turner et al. (1998a) and Pabalan and Turner (1997) were used for Np(V)- and U(VI)-montmorillonite. The computer code FITEQL, Version 2.0 was used to determine DLM parameters for Am(III)-, Pu(V)-, and Th(IV)- γ -alumina. Turner (1995) used FITEQL with the BET surface area for γ -alumina (130 m²/g), to determine that the surface species $>\text{AlOAm}^{+2}$, $>\text{AlOPuO}_2^0$, and $>\text{AlOTh}^{+3}$ were adequate to fit the data. We reinterpreted the data using $A' = 13.0\text{ m}^2/\text{g}$ and the updated CNWRA radionuclide database [updated Am(III) data to the NEA database and PuO₂+ data to the EQ3/6 database (data0.com.r2, 02aug95)] to derive new binding constants:

Radionuclide-Mineral	Surface Complex	Binding constant	Reference
Np(V)-montmorillonite	$>\text{AlO}^-$	-9.73	Turner et al. (1998a)
	$>\text{AlOH}_2^+$	8.33	Turner et al. (1998a)
	$>\text{SiO}^-$	-7.20	Turner et al. (1998a)
	$>\text{AlO-NpO}_2(\text{OH})^-$	-13.79	Turner et al. (1998a)
U(VI)-montmorillonite	$>\text{SiOH-NpO}_2^+$	4.05	Turner et al. (1998a)
	$>\text{AlO}^-$	-9.73	Pabalan and Turner (1997)
	$>\text{AlOH}_2^+$	8.33	Pabalan and Turner (1997)
	$>\text{SiO}^-$	-7.20	Pabalan and Turner (1997)
Am(III)- γ alumina	$>\text{AlO-}\text{UO}_2^+$	2.70	Pabalan and Turner (1997)
	$>\text{SiO-}\text{UO}_2^+$	2.60	Pabalan and Turner (1997)
	$>\text{AlO-(UO}_2)_3(\text{OH})_5^0$	-14.95	Pabalan and Turner (1997)
	$>\text{SiO-(UO}_2)_3(\text{OH})_5^0$	-15.29	Pabalan and Turner (1997)
Pu(V)- γ alumina	$>\text{AlO}^-$	-9.73 -9.05	Turner and Sassman (1996)
	$>\text{AlOH}_2^+$	8.33 6.85	Turner and Sassman (1996)
	$>\text{AlO-Am}^{2+}$	4.66	This study [modified Turner(1995)]
Th(IV)- γ alumina	$>\text{AlO}^-$	-9.73 -9.05	Turner and Sassman (1996)
	$>\text{AlOH}_2^+$	8.33 6.85	Turner and Sassman (1996)
	$>\text{AlO-PuO}_2^0$	-2.18	This study [modified Turner(1995)]
	$>\text{AlO}^-$	-9.73 -9.05	Turner and Sassman (1996)
	$>\text{AlOH}_2^+$	8.33 6.85	Turner and Sassman (1996)
	$>\text{AlO-Th}^{3+}$	15.3	This study [modified Turner(1995)]

The models for U(VI) and Np(V)-montmorillonite have been demonstrated in Pabalan and Turner (1997) and Turner et al. (1998a), respectively. The DLM for Am(III)-, Pu(V)-, and Th(IV)- γ -alumina are shown here.

↑↑
Note: The original alumina protonation constants ($K_1 = -9.73$; $K_2 = 8.33$) were entered as γ -alumina. These are actually α -alumina from Turner & Sassman (1996). The correct values were used in the calculations (see input files in pp.43-46)
JES 2/8/01

Am(III)-Alumina Sorption

The graph shows the percentage of Am(III) sorbed by alumina as a function of pH. The x-axis represents pH from 4 to 12, and the y-axis represents % sorbed from 0.00 to 100.00. The data points are as follows:

pH	% sorbed
4.5	0.00
5.0	0.00
5.5	10.00
6.0	30.00
6.5	55.00
7.0	75.00
7.5	95.00
8.0	98.00
8.5	99.00
9.0	100.00
10.0	100.00
11.0	100.00
12.0	100.00

Pu(V)-Alumina Sorption

pH	% sorbed
4.0	0.00
5.0	0.00
6.0	2.00
7.0	52.00
7.5	72.00
8.0	85.00
9.0	98.00
9.5	98.00
10.0	100.00
10.5	100.00
11.0	100.00
12.0	100.00

Th(IV)-Alumina Sorption

The graph plots the percentage of Th(IV) sorbed against the pH of the solution. The data points (open circles) and the fitted curve (solid line) show a sharp increase in sorption between pH 2 and 4, reaching a plateau near 100% sorption from pH 4 to 7, and then a decrease at higher pH values.

pH	% sorbed
1.1	10.0
1.4	8.0
1.6	18.0
1.9	10.0
2.1	30.0
2.4	48.0
2.6	48.0
2.9	78.0
3.1	65.0
3.6	92.0

/ADS1PSIO
-check table on pg. 41 (corrected 2/8/01)

DR 2/8/2001

2/6/01
2R

Np(V)-montmorillonite

UE-25UZ-N2(15.8) ;SampID=UE-25UZ-N2 ;ArcID=2
UTM=4079446.0 North; 549859.0 East; Date=18-Aug-89
25.00 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 9.70 0.000 0.000 81
330 0.000E-01 -7.70 y /H+1
150 0.140E+02 -3.46 y /Ca+2
460 0.230E+01 -4.02 y /Mg+2
500 0.510E+02 -2.65 y /Na+1
180 0.100E+02 -3.55 y /Cl-1
732 0.290E+02 -3.52 y /SO4-2
140 0.114E+03 -2.74 y /CO3-2
770 0.113E+02 -3.73 y /H4SiO4
552 2.690E-01 -6.00 y /npO2+
813 0.000E-01 0.00 y /ADS1PSIo
811 1.687E-05 -4.77 y /ADS1TYP1
812 2.033E-05 -4.69 y /ADS1TYP2

2 4
5523300 -10.0000 10.5015 /npO2(oh)
5521400 4.6000 12.7951 /npO2(co3)-1
5521401 7.0000 7.1390 /npO2(co3)2-3
5521402 8.5000 6.2630 /npO2(co3)3-5
3 1
330 7.7000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 6
5523301 npO2(oh)2- 0.0000 -22.4000 0.000 0.000-1.00 4.00 0.00 0.0000
0.00 3 -2.000 330 1.000 552 2.000 2 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113300 >AlO- 0.0000 -9.7300 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 8.3300 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8115520 >AlONpO2OH- 0.0000 -13.7900 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 5 1.000 811 1.000 552 1.000 2 -2.000 330 -1.000 813 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8123300 >SiO- 0.0000 -7.2000 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 812 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8125520 >SiOHnpO2+ 0.0000 4.0500 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 812 1.000 552 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

2R

2/6/01
2R

Pu(V)-gamma alumina

UE-25UZ-N2(15.8) ;SampID=UE-25UZ-N2 ;ArcID=2
UTM=4079446.0 North; 549859.0 East; Date=18-Aug-89
25.00 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 13.00 0.000 0.000 81
330 0.000E-01 -7.70 y /H+1
642 1.200E-01 -6.36 y /PuO2+1
150 0.140E+02 -3.46 y /Ca+2
460 0.230E+01 -4.02 y /Mg+2
500 0.510E+02 -2.65 y /Na+1
180 0.100E+02 -3.55 y /Cl-1
732 0.290E+02 -3.52 y /SO4-2
140 0.114E+03 -2.74 y /CO3-2
770 0.113E+02 -3.73 y /H4SiO4
813 0.000E-01 0.00 y /ADS1PSIo
811 4.986E-05 -4.30 y /ADS1TYP1

3 1
330 7.7000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 3
8113300 >AlO- 0.0000 -9.0500 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 6.8500 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8116420 >AlOPuO2 0.0000 -2.1800 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 642 -1.000 330 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

2R

Th(IV)-gamma alumina

UE-25UZ-N2(15.8) ;SampID=UE-25UZ-N2 ;ArcID=2
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25.00 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 13.00 0.000 0.000 81
330 0.000E-01 -7.70 y /H+1
866 2.300E-01 -6.01 y /Th+4
150 0.140E+02 -3.46 y /Ca+2
460 0.230E+01 -4.02 y /Mg+2
500 0.510E+02 -2.65 y /Na+1
180 0.100E+02 -3.55 y /Cl-1
732 0.290E+02 -3.52 y /SO4-2
140 0.114E+03 -2.74 y /CO3-2
770 0.113E+02 -3.73 y /H4SiO4
813 1.000E-07 -7.00 y /ADS1PSIo
811 4.986E-05 -4.30 y /ADS1TYP1

3 1
330 7.7000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 3
8113300 >AlO- 0.0000 -9.0500 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 6.8500 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118660 >AlOTh+3 0.0000 15.3000 0.000 0.000 3.00 0.00 0.00 0.0000
0.00 4 1.000 811 1.000 866 -1.000 330 3.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

2R

U(VI)-montmorillonite

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4 1 7
1.000E+00 9.70 0.000 0.000 81
330 0.000E-01 -7.70 y /H+1
893 2.700E-01 -6.00 y /uo2+2
150 0.140E+02 -3.46 y /Ca+2
460 0.230E+01 -4.02 y /Mg+2
500 0.510E+02 -2.65 y /Na+1
180 0.100E+02 -3.55 y /Cl-1
732 0.290E+02 -3.52 y /SO4-2
140 0.114E+03 -2.74 y /CO3-2
770 0.113E+02 -3.73 y /H4SiO4
813 0.000E-01 0.00 y /ADS1PSIO
811 1.687E-05 -5.57 y /ADS1TYP1
812 2.033E-05 -5.23 y /ADS1TYP2

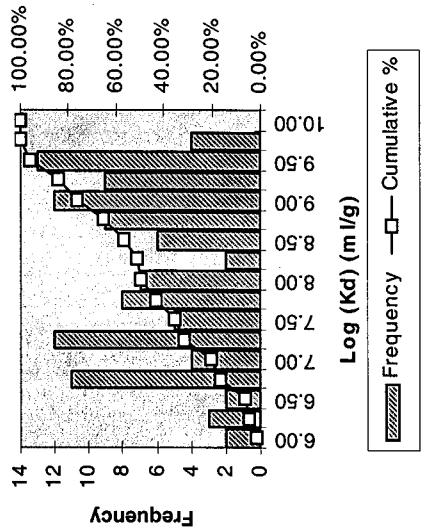
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8933301 -13.0000 18.0940 /uo2 (oh) 2
3 1
330 7.7000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIO

2 5
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0.00 3 1.000 812 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8128930 >SiOUO2+ 0.0000 2.6000 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 4 1.000 812 1.000 893 -1.000 330 1.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113300 >AlO- 0.0000 -9.7300 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
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0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118930 >AlOUO2+ 0.0000 2.7000 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 4 1.000 811 1.000 893 -1.000 330 1.000 813 0.000 0 0.000 0
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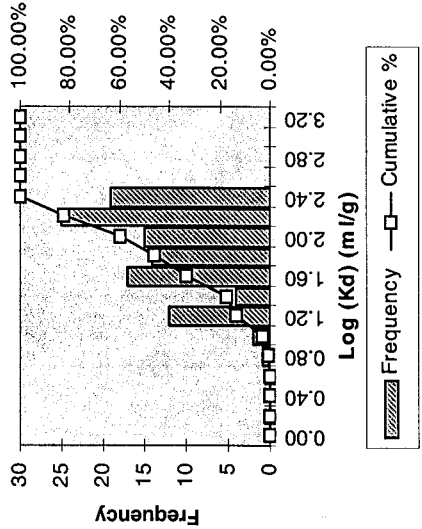
Running these MINTEQA2 models allows generation of sorption coefficients for the observed ranges in water chemistry for the five radionuclide-mineral systems considered here. Normalized to effective surface area K_A of the minerals used in the calibration experiments, and assuming that the pH- and PCO_2 -dependent sorption behavior is similar for aluminosilicates, these sorption coefficient distributions can be recast in terms of K_D for each of the hydrostratigraphic units used in TPA.

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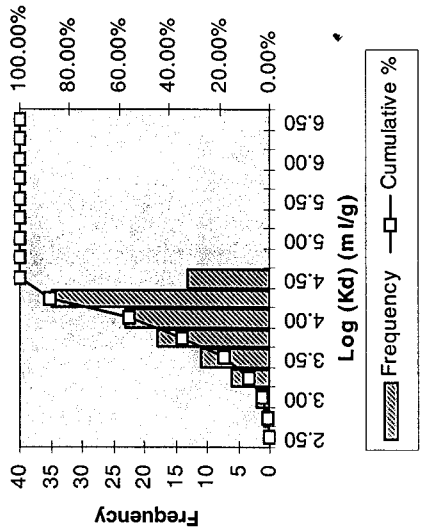
Am(III)-alumina



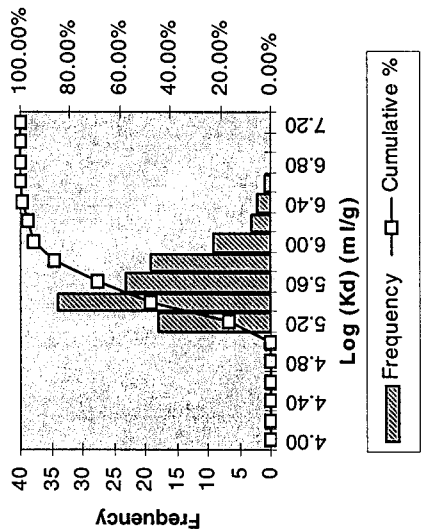
Np(V)-montmorillonite



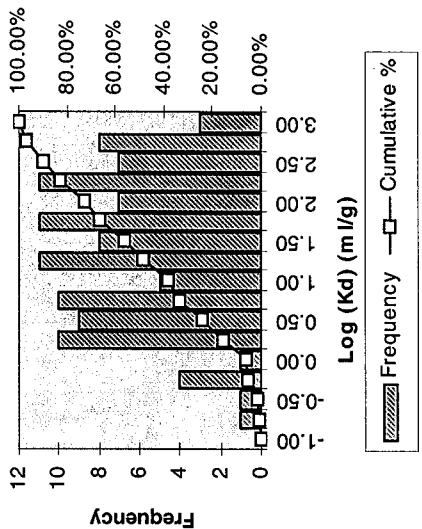
Pu(V)-alumina



Th(IV)-alumina



U(VI)-montmorillonite



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The log K_A distributions and descriptive statistics calculated using Microsoft Excel 97 are given here:

Descriptive Statistics

log K_A (mL/m ²)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Mean	6.908	0.798	2.734	4.367	0.312
Median	6.960	0.871	2.787	4.331	0.315
Mode	#N/A	1.251	#N/A	#N/A	#N/A
Standard Deviation	1.0822	0.4018	0.3923	0.2892	0.9439
Sample Variance	1.1711	0.1614	0.1539	0.0836	0.8910
Kurtosis	-1.1282	-0.6234	0.1294	0.8502	-0.9137
Skewness	-0.2397	-0.6203	-0.8435	0.8975	-0.0948
Range	4.420	1.651	1.785	1.470	3.852
Minimum	4.171	-0.308	1.451	3.914	-1.795
Maximum	8.591	1.343	3.236	5.385	2.057
Sum	752.9	87.0	298.0	476.0	34.0
Count	109	109	109	109	109

The final step in using this information in TPA is to apply this distribution to each hydrostratigraphic unit and transform the K_A into K_D (in mL/g). Assuming that aluminosilicates will dominate sorption in these units, it follows that the chemical dependent sorption behavior, and therefore these distributions, should hold for each unit. The key parameter for each transform to K_A will therefore be the surface area. Arthur (1996) presents a relationship among porosity, dry density, and pore radius such that:

$$\text{Specific Surface Area} = \frac{3\phi_r}{\rho_r r}$$

where ϕ_r is porosity of the rock, ρ_r is density of the rock in g/m³, and r is the radius of the pore in meters. For the YM region, parameter values were taken from the input file for TPA 3.1.4. The value for the pore radius was set at 0.05 μ m based on work by Travis and Nuttall (1987) that suggests that more than 50 percent (median value) of the pores are less than 0.1 μ m in diameter. Parameter values and calculated surface area is presented here. It is interesting to note that the calculated surface areas agree very well with measured surface areas (2.6 to 10 m²/g) reported for total surface areas of tuff samples in Triay et al. (1996):

Unit	ϕ_r	ρ_r	r	Surface area (m ² /g)
TSw	0.12	2.46E+3	5.0E-08	2.9
CHnv	0.33	2.26E+3	5.0E-08	8.8
CHnz	0.32	2.40E+3	5.0E-08	8.0
PPw	0.28	2.54E+3	5.0E-08	6.6
UCF	0.28	2.42E+3	5.0E-08	6.9
BFw	0.12	2.57E+3	5.0E-08	2.8
UFZ	0.12	2.63E+3	5.0E-08	2.7

By using the relationship $K_A \cdot (A) = K_D$, sorption coefficients are determined for each radionuclide (5 total) for each of seven hydrostratigraphic units (in m³/g = 1000 mL/g):

Log KD(m3/kg)	Am(III)-TSw	Am(III)-CHnv	Am(III)-CHnz	Am(III)-PPw	Am(III)-UCF	Am(III)-BFw	Am(III)-UFZ
Mean	4.370	4.852	4.811	4.727	4.747	4.355	4.339
Median	4.423	4.905	4.864	4.780	4.799	4.408	4.392
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	1.0822	1.0822	1.0822	1.0822	1.0822	1.0822	1.0822
Sample Variance	1.1711	1.1711	1.1711	1.1711	1.1711	1.1711	1.1711
Kurtosis	-1.1282	-1.1282	-1.1282	-1.1282	-1.1282	-1.1282	-1.1282
Skewness	-0.2397	-0.2397	-0.2397	-0.2397	-0.2397	-0.2397	-0.2397
Range	4.420	4.420	4.420	4.420	4.420	4.420	4.420
Minimum	1.633	2.116	2.074	1.991	2.010	1.618	1.602
Maximum	6.054	6.536	6.494	6.411	6.430	6.038	6.023
Sum	476.3	528.9	524.4	515.3	517.4	474.7	473.0
Count	109	109	109	109	109	109	109

Log KD(m3/kg)	Np(V)-TSw	Np(V)-CHnv	Np(V)-CHnz	Np(V)-PPw	Np(V)-UCF	Np(V)-BFw	Np(V)-UFZ
Mean	-1.739	-1.257	-1.298	-1.382	-1.363	-1.754	-1.770
Median	-1.666	-1.184	-1.226	-1.309	-1.290	-1.682	-1.697
Mode	-1.287	-0.805	-0.846	-0.930	-0.910	-1.302	-1.318
Standard Deviation	0.4018	0.4018	0.4018	0.4018	0.4018	0.4018	0.4018
Sample Variance	0.1614	0.1614	0.1614	0.1614	0.1614	0.1614	0.1614
Kurtosis	-0.6234	-0.6234	-0.6234	-0.6234	-0.6234	-0.6234	-0.6234
Skewness	-0.6203	-0.6203	-0.6203	-0.6203	-0.6203	-0.6203	-0.6203
Range	1.651	1.651	1.651	1.651	1.651	1.651	1.651
Minimum	-2.846	-2.364	-2.405	-2.489	-2.469	-2.861	-2.877
Maximum	-1.195	-0.713	-0.754	-0.838	-0.818	-1.210	-1.226
Sum	-189.6	-137.0	-141.5	-150.6	-148.5	-191.2	-193.0
Count	109	109	109	109	109	109	109

Log KD(m3/kg)	Pu(V)-TSw	Pu(V)-CHnv	Pu(V)-CHnz	Pu(V)-PPw	Pu(V)-UCF	Pu(V)-BFw	Pu(V)-UFZ
Mean	0.196	0.678	0.637	0.553	0.572	0.181	0.165
Median	0.249	0.731	0.690	0.606	0.626	0.234	0.218
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.3923	0.3923	0.3923	0.3923	0.3923	0.3923	0.3923
Sample Variance	0.1539	0.1539	0.1539	0.1539	0.1539	0.1539	0.1539
Kurtosis	0.1294	0.1294	0.1294	0.1294	0.1294	0.1294	0.1294
Skewness	-0.8435	-0.8435	-0.8435	-0.8435	-0.8435	-0.8435	-0.8435
Range	1.785	1.785	1.785	1.785	1.785	1.785	1.785
Minimum	-1.087	-0.605	-0.646	-0.730	-0.710	-1.102	-1.118
Maximum	0.698	1.180	1.139	1.055	1.075	0.683	0.667
Sum	21.4	73.9	69.4	60.3	62.4	19.7	18.0
Count	109	109	109	109	109	109	109

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Log KD(m3/kg)	Th(IV)-TSw	Th(IV)-CHnv	Th(IV)-CHnz	Th(IV)-PPw	Th(IV)-UCF	Th(IV)-BFw	Th(IV)-UFZ
Mean	1.829	2.311	2.270	2.186	2.206	1.814	1.798
Median	1.793	2.275	2.234	2.150	2.170	1.778	1.762
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.2892	0.2892	0.2892	0.2892	0.2892	0.2892	0.2892
Sample Variance	0.0836	0.0836	0.0836	0.0836	0.0836	0.0836	0.0836
Kurtosis	0.8502	0.8502	0.8502	0.8502	0.8502	0.8502	0.8502
Skewness	0.8975	0.8975	0.8975	0.8975	0.8975	0.8975	0.8975
Range	1.470	1.470	1.470	1.470	1.470	1.470	1.470
Minimum	1.377	1.859	1.817	1.734	1.753	1.361	1.346
Maximum	2.847	3.329	3.288	3.204	3.223	2.832	2.816
Sum	199.4	251.9	247.4	238.3	240.4	197.7	196.0
Count	109	109	109	109	109	109	109

See Table

Log KD(m3/kg)	U(VI)-TSw	U(VI)-CHnv	U(VI)-CHnz	U(VI)-PPw	U(VI)-UCF	U(VI)-BFw	U(VI)-UFZ
Mean	-2.225	-1.743	-1.785	-1.868	-1.849	-2.241	-2.256
Median	-2.223	-1.741	-1.782	-1.866	-1.846	-2.238	-2.254
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.9439	0.9439	0.9439	0.9439	0.9439	0.9439	0.9439
Sample Variance	0.8910	0.8910	0.8910	0.8910	0.8910	0.8910	0.8910
Kurtosis	-0.9137	-0.9137	-0.9137	-0.9137	-0.9137	-0.9137	-0.9137
Skewness	-0.0948	-0.0948	-0.0948	-0.0948	-0.0948	-0.0948	-0.0948
Range	3.852	3.852	3.852	3.852	3.852	3.852	3.852
Minimum	-4.333	-3.850	-3.892	-3.975	-3.956	-4.348	-4.364
Maximum	-0.480	0.002	-0.040	-0.123	-0.104	-0.496	-0.511
Sum	-242.6	-190.0	-194.5	-203.6	-201.5	-244.2	-246.0
Count	109	109	109	109	109	109	109

See Table

It is important to note that for a given radionuclide, the method used here results in the same distribution for each hydrostratigraphic unit, since K_D is determined by multiplying K_A by a unit-specific constant (A^*). It is also possible to use this information to develop correlation coefficients between each of the radionuclides. Using the data analysis tools in Microsoft Excel 97, the following correlation coefficients are developed for K_A (and therefore K_D):

K_A (mL/m ²)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.9056426	1			
Pu(V)	0.9025125	0.9628663	1		
Th(IV)	-0.0349612	-0.0448095	-0.0682032	1	
U(VI)	0.3419898	0.4073383	0.4786748	-0.0173596	1

For log K_A (and log K_D), the correlation coefficients are different:

log K_A (mL/m ²)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.8373419	1			
Pu(V)	0.9640062	0.8813727	1		
Th(IV)	0.1119944	0.2598956	0.1087378	1	
U(VI)	0.3455182	0.6096958	0.4893751	0.1648243	1

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These K_D distributions and correlation coefficients were passed to the PA element for incorporation in TPA ~~2.1.4~~.

4.0.
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Key Geochemical Parameters Controlling Actinide Sorption by Surface Complexation

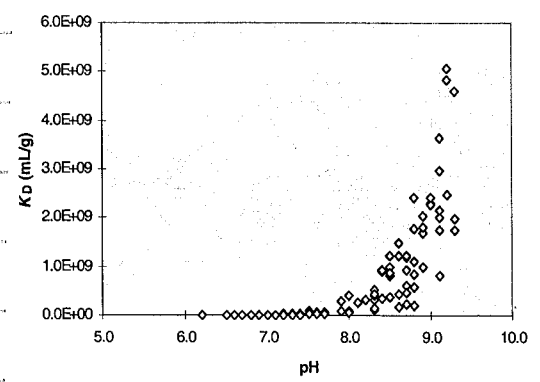
One of the advantages of this approach is the ability to examine the role of measurable geochemical parameters on sorption behavior. As outlined in Bertetti et al. (1998) and Pabalan et al. (1998), two key parameters controlling sorption behavior are pH and PCO₂. For the water analyses reported by Yang et al. (1996, 1998), the calculated sorption parameters are plotted against measured pH and calculated Log PCO₂. In most cases, this shows the expected trends (increasing sorption with increasing pH and decreasing Log PCO₂). One contradiction to these general trends is Th(IV). Upon examination, this appears to be due to the increasing strength of the Th(OH)₄ aqueous species with increasing pH. Because of its strong tendency to hydrolyze, thorium is strongly sorbed at the lower end of the pH range (~6) of the Yang et al. data. As pH increases to the higher values (up to pH~9), Th(OH)₄(aq) becomes the dominant aqueous species. Th(OH)₄(aq) successfully competes against the surface for available Th(IV), keeping thorium in the aqueous phase and reducing K_d. The different behavior as a response to PCO₂ is due to the lack of aqueous Th-carbonate species in the EQ3 (and MINTEQA2) data base in contrast to Am(III), Np(V), Pu(V), and U(VI) which all have at least one aqueous actinide-carbonate species in the database. Without aqueous Th(IV)-carbonate species, the effect of PCO₂ on sorption behavior is not direct competition of the solid surface and CO₃ for available thorium as it is for the other actinides considered here. Instead, the relationship is indirect; higher pH (where sorption is lower due to Th(OH)₄(aq) formation) corresponds to lower calculated PCO₂, giving the observed reduction in sorption with increasing PCO₂.

See Table

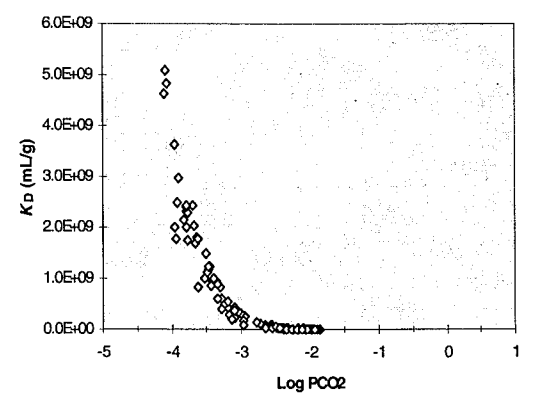
U(VI) also exhibits an apparent decrease in sorption with increasing pH, but this is for a different reason than that suggested for Th(IV). In the case of U(VI), hydrolysis occurs at a higher pH than for Th(IV), and the strong uranyl-carbonate species typically lead to a desorption edge in the pH range of 6.5 to about 8 in the presence of even small amounts of carbonate (Pabalan et al., 1998). The pH range reported in the Yang data (6.2 to 9.3) spans this pH range, giving the decrease in calculated sorption with increasing pH.

2/6/01
DB

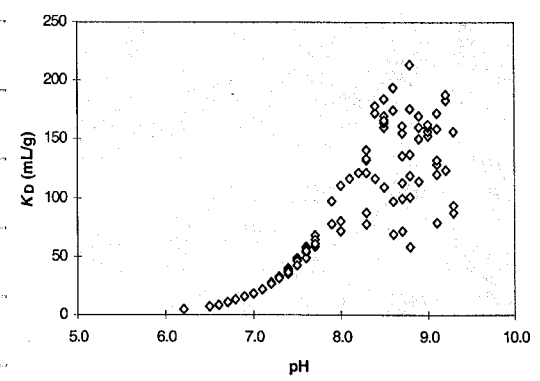
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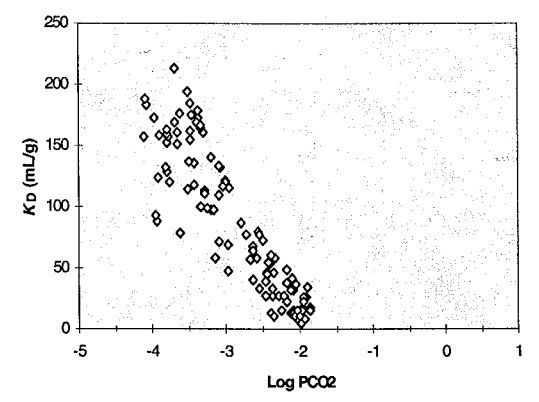
Am(III)-alumina



Np(V)-montmorillonite

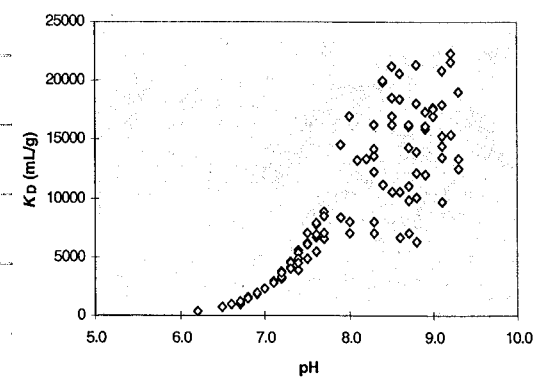


Np(V)-montmorillonite

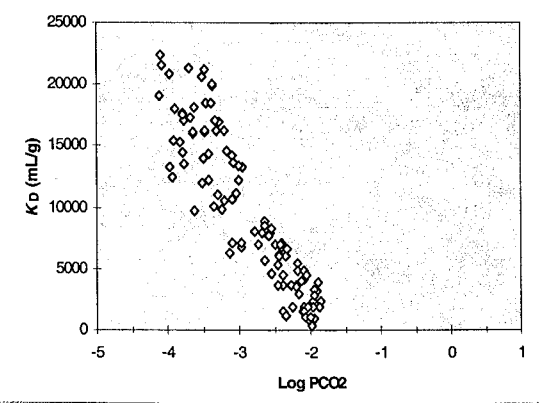


aluminum

Pu(V)-alumina



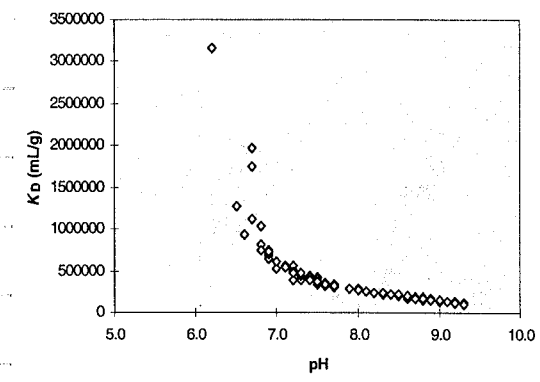
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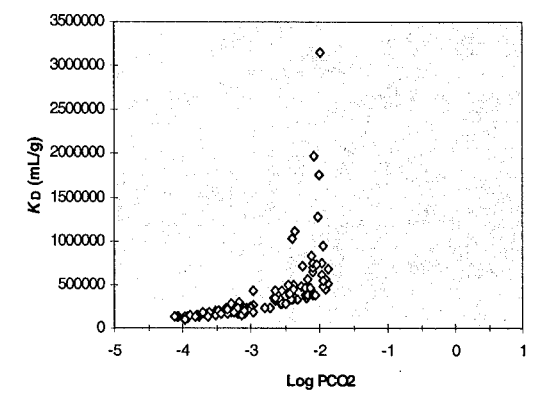
alumina DB 2/6/01

2/6/01
DB

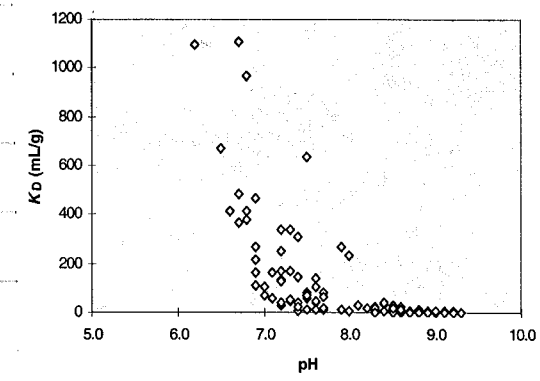
Th(IV)-alumina



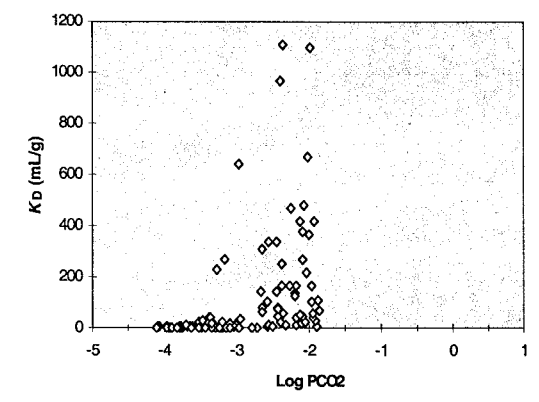
Th(IV)-alumina



U(VI)-montmorillonite



U(VI)-montmorillonite



aluminum

Arthur, R.C. 1996. *SITE-94: Adaptation of Mechanistic Sorption Models for Performance Assessment Calculations*. SKI Report 96:34. Stockholm, Sweden: Swedish Nuclear Power Inspectorate.

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. 1998. Studies of neptunium^v sorption on quartz, clinoptilolite, montmorillonite, and α -alumina. E.A. Jenne, ed. *Adsorption of Metals by Geomedia*. New York, NY: Academic Press, Inc.: 131-148.

Pabalan, R.T., and D.R. Turner. 1997. Uranium(6+) sorption on montmorillonite: Experimental and surface complexation modeling study. *Aqueous Geochemistry* 2: 203-226.

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. 1998. Uranium^{VI} sorption onto selected mineral surfaces. E.A. Jenne, ed. *Adsorption of Metals by Geomedia*. New York, NY: Academic Press, Inc.: 99-130.

Righetto, L., G. Bidoglio, B. Marcandalli, and I.R. Bellobono. 1988, Surface interactions of actinides with alumina colloids. *Radiochimica Acta* 44/45:73-75.

Righetto, L., G. Bidoglio, G. Azimonti, and I.R. Bellobono. 1991. Competitive actinide interactions in colloidal humic acid-mineral oxide systems. *Environmental Science and Technology* 25: 1913-1919.

Travis, B.J., and H.E. Nuttall. 1987. *Two-Dimensional Numerical Simulation of Geochemical Transport in Yucca Mountain*. LA-10532-MS. Los Alamos, NM: Los Alamos National Laboratory.

Triay, I.R., A. Meijer, J.L. Conca, K.S. Kung, R.S. Rundberg, and E.A. Strietelmeier. 1996a. *Summary and Synthesis Report on Radionuclide Retardation for the Yucca Mountain Site Characterization Project*. Milestone 3784. Los Alamos, NM: Chemical Science and Technology Division, Los Alamos National Laboratory.

Turner, D.R. 1995. *A Uniform Approach to Surface Complexation Modeling of Radionuclide Sorption*. CNWRA 95-001 San Antonio, TX: CNWRA.

Turner, D.R. 1998. *Radionuclide Sorption in Fractures at Yucca Mountain, Nevada: A Preliminary Demonstration of an Approach for Performance Assessment*. CNWRA Letter Report. San Antonio, TX: CNWRA.

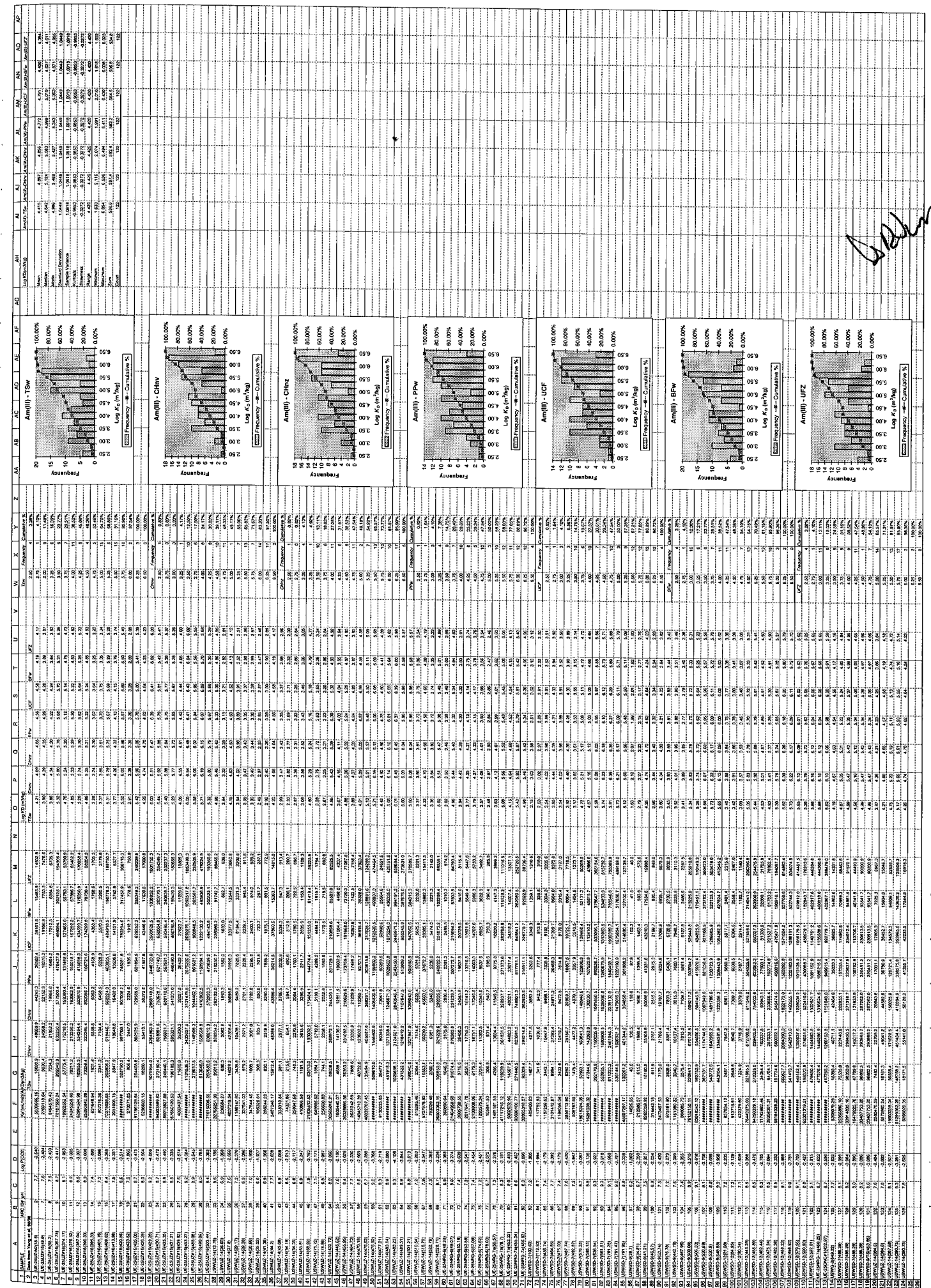
Turner, D.R. and S.A. Sassman. 1996. Approaches to sorption modeling for high-level waste performance assessment. *Journal of Contaminant Hydrology* 21: 311-332.

Turner, D.R., R.T. Pabalan, and F.P. Bertetti. 1998a. Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modeling study. *Clays and Clay Minerals* (in press).

Turner, D.R., G.W. Wittmeyer, and F.P. Bertetti. 1998b. *Radionuclide Sorption in the Alluvium at Yucca Mountain Nevada: A Preliminary Demonstration of Approach for Performance Assessment*. CNWRA Letter Report. San Antonio, TX: CNWRA.

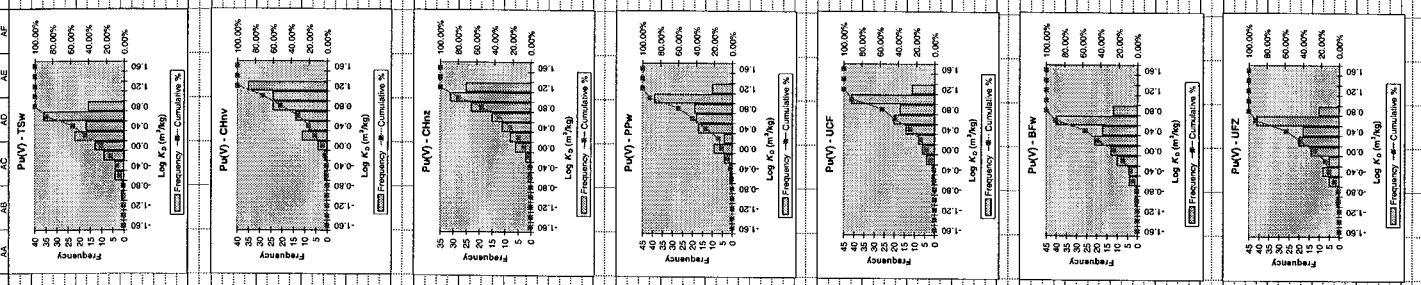
Yang, I.C., G.W. Rattray, P. Yu., *Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada*, Water Resources Investigations Report 96-4058, Denver, CO: U.S. Geological Survey 1996a.

Yang, I.C., P, Yu, G.W. Rattray, J.S. Ferarese, J.N. Ryan, *Hydrochemical Investigations in Characterizing the Unsaturated Zone at Yucca Mountain, Nevada*, Water-Resources Investigations Report 98-4132, Denver, CO: U.S. Geological Survey, 1998.



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Parameter	Indo-Indo	Indo-Pakistani	Pakistani-Pakistani	Indo-Pakistani	Indo-Pakistani
Mean	1.67	2.36	2.32	2.35	1.91
SD	0.75	0.75	0.75	0.75	0.75
Median	1.50	2.34	2.30	2.31	1.81
Mode	1.50	2.34	2.30	2.31	1.81
Range	0.75	0.75	0.75	0.75	0.75
Skewness	0.23	0.23	0.23	0.23	0.23
Kurtosis	1.51	1.51	1.51	1.51	1.51
Alpha	0.65	0.65	0.65	0.65	0.65
Gamma	0.65	0.65	0.65	0.65	0.65
Delta	1.37	1.69	1.47	1.52	1.36
Epsilon	2.37	2.39	2.38	2.38	2.35
Zeta	2.32	2.37	2.36	2.36	2.31
Eta	0.75	0.75	0.75	0.75	0.75

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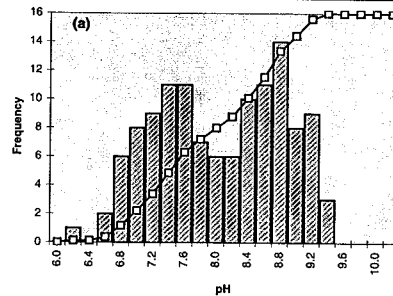
Log KD(m3/kg)	Am(III)-TSw	Am(III)-CHnv	Am(III)-CHnz	Am(III)-PPw	Am(III)-UCF	Am(III)-BFW	Am(III)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	4.41483226	4.89691693	4.85552425	4.7719782	4.79128335	4.39959229	4.38379803
Standard Deviation	1.04490848	1.04490848	1.04490848	1.04490848	1.04490848	1.04490848	1.04490848
Minimum	1.63343799	2.11552266	2.07412998	1.99058392	2.00988908	1.61819802	1.60240375
Maximum	6.0536685	6.53575318	6.49436049	6.41081444	6.43011959	6.03842854	6.02263427
Log KD(m3/kg)	Np(V)-TSw	Np(V)-CHnv	Np(V)-CHnz	Np(V)-PPw	Np(V)-UCF	Np(V)-BFW	Np(V)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	-1.70904563	-1.22696095	-1.26835364	-1.35189969	-1.33259453	-1.72428559	-1.74007986
Standard Deviation	0.39403512	0.39403512	0.39403512	0.39403512	0.39403512	0.39403512	0.39403512
Minimum	-2.84576083	-2.36367615	-2.40506884	-2.48861489	-2.46930974	-2.86100079	-2.87679506
Maximum	-1.17124607	-0.6891614	-0.73055408	-0.81410013	-0.79479498	-1.18648604	-1.20228031
Log KD(m3/kg)	Pu(V)-TSw	Pu(V)-CHnv	Pu(V)-CHnz	Pu(V)-PPw	Pu(V)-UCF	Pu(V)-BFW	Pu(V)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	0.22515816	0.70724283	0.66585015	0.5823041	0.60160925	0.20991819	0.19412393
Standard Deviation	0.38335569	0.38335569	0.38335569	0.38335569	0.38335569	0.38335569	0.38335569
Minimum	-1.08693915	-0.60485448	-0.64624716	-0.72979321	-0.71048806	-1.10217912	-1.11797338
Maximum	0.69821899	1.18030367	1.13891098	1.05536493	1.07467009	0.68297903	0.66718476
Log KD(m3/kg)	Th(IV)-TSw	Th(IV)-CHnv	Th(IV)-CHnz	Th(IV)-PPw	Th(IV)-UCF	Th(IV)-BFW	Th(IV)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	1.82664912	2.3087338	2.26734111	2.18379506	2.20310022	1.81140916	1.79561489
Standard Deviation	0.27521161	0.27521161	0.27521161	0.27521161	0.27521161	0.27521161	0.27521161
Minimum	1.37671623	1.85880091	1.81740822	1.73386217	1.75316733	1.36147627	1.345682
Maximum	2.84703245	3.32911712	3.28772443	3.20417838	3.22348354	2.83179248	2.81599821
Log KD(m3/kg)	U(VI)-TSw	U(VI)-CHnv	U(VI)-CHnz	U(VI)-PPw	U(VI)-UCF	U(VI)-BFW	U(VI)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	-2.19656129	-1.71447662	-1.7558693	-1.83941535	-1.8201102	-2.21180126	-2.22759552
Standard Deviation	0.89718222	0.89718222	0.89718222	0.89718222	0.89718222	0.89718222	0.89718222
Minimum	-4.3325192	-3.85043453	-3.89182721	-3.97537326	-3.95606811	-4.34775917	-4.36355344
Maximum	-0.48032055	0.00176412	-0.03962856	-0.12317461	-0.10386946	-0.49556052	-0.51135478

SITENUMBER	SAMPLE	ARCID	UTM(north)	UTM(east)	Date	Temp	Sp.Cond	Labph	Ca	Mg	Na	K	Cl	SO4	HCO3	CO3	PO4	NO3	F	SiO2	Al
Data from Yang et al. 1998																					
Original reported on CD2/HCO3-																					
UE-25U216(45.9)	UE-25U216	7	407898.0	549484.0	02-Dec-92	-9999.0	425.0	7.7	40.0	2.3	51.0	-9999.0	10.0	29.0	112.0	0.0	-9999.0	-9999.0	-9999.0	18.0	-9999.0
UE-25U216(49.9)	UE-25U216	8	407898.0	549484.0	16-Nov-92	-9999.0	430.0	7.8	42.5	13.4	21.5	-9999.0	32.4	72.3	114.7	45.0	-9999.0	23.1	-9999.0	77.5	0.5
UE-25U216(55.2)	UE-25U216	9	407898.0	549484.0	27-Sep-94	-9999.0	710.0	8.7	88.9	13.7	83.8	-9999.0	82.0	38.0	120.0	0.0	-9999.0	33.0	-9999.0	83.0	0.1
UE-25U216(374.17)	UE-25U216	10	407898.0	549484.0	09-Aug-93	-9999.0	430.0	8.1	26.5	8.2	47.9	-9999.0	24.0	28.0	196.0	0.0	-9999.0	17.0	-9999.0	57.1	0.0
UE-25U216(378.52)	UE-25U216	11	407898.0	549484.0	11-Aug-93	-9999.0	480.0	8.2	33.5	7.9	51.3	-9999.0	52.0	29.0	154.0	0.0	-9999.0	23.0	-9999.0	62.2	0.3
UE-25U216(387.04)	UE-25U216	12	407898.0	549484.0	04-Aug-93	-9999.0	430.0	8.5	14.1	2.4	67.3	-9999.0	27.0	14.0	139.0	13.0	-9999.0	26.0	-9999.0	52.9	0.0
UE-25U216(390.33)	UE-25U216	13	407898.0	549484.0	02-Sep-93	-9999.0	530.0	8.3	20.5	3.7	92.0	-9999.0	28.0	19.0	192.0	0.0	-9999.0	19.0	-9999.0	57.1	0.0
UE-25U216(395.33)	UE-25U216	14	407898.0	549484.0	23-Sep-93	-9999.0	830.0	7.4	32.4	19.7	98.2	-9999.0	50.0	18.0	324.0	12.0	-9999.0	19.0	-9999.0	48.7	0.0
UE-25U216(401.76)	UE-25U216	15	407898.0	549484.0	09-Sep-93	-9999.0	420.0	7.3	20.6	5.1	60.1	-9999.0	32.0	18.0	171.0	0.0	-9999.0	20.0	-9999.0	131.6	1.1
UE-25U216(409.62)	UE-25U216	16	407898.0	549484.0	01-Jul-93	-9999.0	530.0	8.4	17.0	2.4	99.0	-9999.0	58.0	23.0	47.8	58.8	-9999.0	18.0	-9999.0	62.1	1.7
UE-25U216(413.98)	UE-25U216	17	407898.0	549484.0	06-May-93	-9999.0	550.0	7.5	3.4	0.3	76.7	-9999.0	22.8	18.7	140.3	0.0	-9999.0	16.1	-9999.0	47.9	1.1
UE-25U216(420.56)	UE-25U216	18	407898.0	549484.0	29-Jun-93	-9999.0	490.0	8.6	4.4	0.6	95.0	-9999.0	21.0	25.0	72.0	46.8	-9999.0	18.0	-9999.0	66.3	2.8
UE-25U216(423.52)	UE-25U216	19	407898.0	549484.0	18-May-93	-9999.0	530.0	7.0	3.6	0.9	114.8	-9999.0	23.5	23.8	122.0	36.0	-9999.0	18.5	-9999.0	62.5	2.0
UE-25U216(426.08)	UE-25U216	21	407898.0	549484.0	07-Jul-93	-9999.0	550.0	8.7	5.0	0.5	124.0	-9999.0	45.0	45.0	131.8	35.4	-9999.0	25.0	-9999.0	73.2	4.7
UE-25U216(428.29)	UE-25U216	22	407898.0	549484.0	05-Apr-94	-9999.0	710.0	8.0	5.0	0.4	145.0	-9999.0	14.0	20.0	237.0	31.0	-9999.0	16.0	-9999.0	123.0	7.8
UE-25U216(429.28)	UE-25U216	23	407898.0	549484.0	28-Jul-93	-9999.0	580.0	9.2	3.3	0.3	104.0	-9999.0	20.0	16.0	72.0	70.8	-9999.0	14.0	-9999.0	68.6	3.4
UE-25U216(430.71)	UE-25U216	24	407898.0	549484.0	16-Sep-93	-9999.0	450.0	8.7	1.2	0.1	101.0	-9999.0	28.0	30.0	165.0	0.0	-9999.0	24.0	-9999.0	75.9	1.0
UE-25U216(435.35)	UE-25U216	25	407898.0	549484.0	14-Sep-93	-9999.0	570.0	8.8	1.9	0.1	134.0	-9999.0	23.0	23.0	160.0	43.0	-9999.0	19.0	-9999.0	80.5	3.4
UE-25U216(437.21)	UE-25U216	26	407898.0	549484.0	13-Jul-93	-9999.0	550.0	8.5	3.2	0.6	113.0	-9999.0	23.0	19.0	72.0	70.8	-9999.0	16.0	-9999.0	109.1	6.1
UE-25U216(439.83)	UE-25U216	27	407898.0	549484.0	17-Jun-93	-9999.0	550.0	7.8	1.7	0.8	79.9	-9999.0	18.9	13.7	18.3	87.6	-9999.0	11.3	-9999.0	68.9	1.2
UE-25U216(453.27)	UE-25U216	28	407898.0	549484.0	21-Sep-93	-9999.0	380.0	9.2	6.3	0.8	79.5	-9999.0	38.0	11.0	137.0	0.0	-9999.0	6.0	-9999.0	233.3	26.2
UE-25U216(488.08)	UE-25U216	29	407898.0	549484.0	30-Dec-93	-9999.0	570.0	8.9	10.0	0.3	100.0	-9999.0	53.0	27.0	181.0	0.0	-9999.0	13.0	-9999.0	36.0	0.7
UE-25U216(490.09)	UE-25U216	30	407898.0	549484.0	24-Jan-94	-9999.0	680.0	9.0	25.0	0.3	108.0	-9999.0	71.0	33.0	170.0	0.0	-9999.0	10.0	-9999.0	34.0	1.0
UE-25U216(503.44)	UE-25U216	32	407898.0	549484.0	15-Mar-94	-9999.0	420.0	8.4	17.3	0.3	66.0	-9999.0	27.0	20.0	87.0	19.0	-9999.0	6.0	-9999.0	47.4	0.7
USWUZ-14(13.78)	USWUZ-14	33	4080262.0	548033.0	19-Sep-94	-9999.0	1320.0	8.6	19.8	6.1	249.3	-9999.0	245.0	33.0	245.0	18.0	-9999.0	35.0	-9999.0	59.5	1.0
USWUZ-14(25.03)	USWUZ-14	34	4080262.0	548033.0	24-Mar-94	-9999.0	830.0	6.9	49.9	13.2	43.5	-9999.0	80.0	66.0	131.0	0.0	-9999.0	22.0	-9999.0	89.8	0.3
USWUZ-14(27.8)	USWUZ-14	35	4080262.0	548033.0	17-Mar-94	-9999.0	530.0	7.6	40.7	10.1	37.1	-9999.0	47.0	81.0	87.0	0.0	-9999.0	28.0	-9999.0	80.6	0.0
USWUZ-14(29.17)	USWUZ-14	36	4080262.0	548033.0	21-Apr-94	-9999.0	600.0	7.2	53.3	13.2	38.1	-9999.0	79.0	83.0	73.0	0.0	-9999.0	29.0	-9999.0	81.5	0.0
USWUZ-14(29.39)	USWUZ-14	37	4080262.0	548033.0	03-May-94	-9999.0	550.0	6.9	46.9	12.7	33.6	-9999.0	59.0	75.0	78.0	0.0	-9999.0	28.0	-9999.0	79.6	0.0
USWUZ-14(30.86)	USWUZ-14	38	4080262.0	548033.0	22-Mar-94	-9999.0	600.0	7.0	51.1	13.8	41.3	-9999.0	44.0	83.0	128.0	0.0	-9999.0	23.0	-9999.0	91.8	0.0
USWUZ-14(35.02)	USWUZ-14	39	4080262.0	548033.0	01-Sep-94	-9999.0	540.0	8.6	48.0	10.5	35.9	-9999.0	61.0	90.0	67.0	0.0	-9999.0	25.0	-9999.0	93.9	0.0
USWUZ-14(41.35)	USWUZ-14	40	4080262.0	548033.0	12-Apr-94	-9999.0	590.0	7.9	65.5	14.3	56.2	-9999.0	73.0	96.0	105.0	0.0	-9999.0	23.0	-9999.0	92.0	0.0
USWUZ-14(44.2)	USWUZ-14	41	4080262.0	548033.0	11-Aug-94	-9999.0	650.0	7.7	65.5	12.0	48.2	-9999.0	77.0	102.0	118.0	0.0	-9999.0	22.0	-9999.0	91.5	0.0
USWUZ-14(45.08)	USWUZ-14	42	4080262.0	548033.0	14-Apr-94	-9999.0	640.0	6.9	54.8	11.5	51.8	-9999.0	77.0	102.0	118.0	0.0	-9999.0	22.0	-9999.0	77.5	0.0
USWUZ-14(54.19)	USWUZ-14	43	4080262.0	548033.0	12-Sep-94	-9999.0	730.0	6.5	67.8	11.3	48.7	-9999.0	100.0	130.0	62.0	0.0	-9999.0	21.0	-9999.0	93.1	0.0
USWUZ-14(54.35)	USWUZ-14	44	4080262.0	548033.0	19-Apr-94	-9999.0	740.0	6.8	64.0	10.6	49.1	-9999.0	97.0	120.0	62.0	0.0	-9999.0	23.0	-9999.0	77.5	0.0
USWUZ-14(55.81)	USWUZ-14	45	4080262.0	548033.0	21-Apr-94	-9999.0	710.0	6.9	65.5	10.7	38.4	-9999.0	85.0	130.0	55.0	0.0	-9999.0	14.0	-9999.0	91.2	0.0
USWUZ-14(58.82)	USWUZ-14	46	4080262.0	548033.0	31-Oct-94	-9999.0	640.0	7.9	58.8	10.4	48.4	-9999.0	93.0	116.0	55.0	0.0	-9999.0	10.0	-9999.0	97.8	0.0
USWUZ-14(71.72)	USWUZ-14	47	4080262.0	548033.0	02-Mar-94	-9999.0	630.0	7.1	67.0	10.5	28.0	-9999.0	84.0	94.0	96.0	-9999.0	-9999.0	15.0	-9999.0	63.0	0.0
USWUZ-14(74.89)	USWUZ-14	49	4080262.0	548033.0	07-Feb-94	-9999.0	580.0	6.8	65.0	12.0	9.0	-9999.0	77.0	79.0	66.0	-9999.0	-9999.0	12.0	-9999.0	48.0	0.0
USWUZ-14(43.72)	USWUZ-14	54	4080262.0	548033.0	22-Dec-94	-9999.0	410.0	8.3	20.0	0.6	68.0	-9999.0	24.0	21.0	166.0	0.0	-9999.0	6.0	-9999.0	80.0	1.4
USWUZ-14(44.62)	USWUZ-14	55	4080262.0	548033.0	04-Apr-95	-9999.0	570.0	7.8	9.2	0.1	128.0	-9999.0	24.2	37.3	265.0	0.0	-9999.0	6.2	-9999.0	68.7	1.2
USWUZ-14(45.85)	USWUZ-14	56	4080262.0	548033.0	11-Apr-95	-9999.0	500.0	8.4	2.1	0.0	122.0	-9999.0	28.0	14.3	228.0	0.0	-9999.0	10.8	-9999.0	58.7	0.3
USWUZ-14(46.73)	USWUZ-14	57	4080262.0	548033.0	14-Apr-95	-9999.0	580.0	7.7	1.1	0.1	137.0	-9999.0	28.2	22.3	232.0	0.0	-9999.0	12.5	-9999.0	54.8	1.1
USWUZ-14(47.18)	USWUZ-14	58	4080262.0	548033.0	25-Jul-94	-9999.0	780.0	8.6	3.8	0.5	207.0	-9999.0	20.0	28.0	384.0	46.0	-9999.0	4.0	-9999.0	143.0	13.8
USWUZ-14(47.82)	USWUZ-14	59	4080262.0	548033.0	30-Aug-94	-9999.0	680.0	8.7	1.2	0.2	155.0	-9999.0	16.0	14.0	160.0	97.0	-9999.0	4.0	-9999.0	72.0	13.9
USWUZ-14(47.92)	USWUZ-14	60	4080262.0	548033.0	23-Aug-94	-9999.0	590.0	9.0	1.3	0.2	128.0	-9999.0	16.0	17.0	61.0	113.0	-9999.0	4.0	-9999.0	140.4	8.4
USWUZ-14(47.77)	USWUZ-14	61	4080262.0	548033.0	17-Aug-94	-9999.0	690.0	8.3	1.7	0.5	169.0	-9999.0	23.0	30.0	376.0	0.0	-9999.0	1.0	-9999.0	54.0	15.5
USWUZ-14(48.34)	USWUZ-14	62	4080262.0	548033.0	14-Sep-94	-9999.0	480.0	8.8	0.9	0.3	106.8	-9999.0	14.0	10.0	88.0	67.0	-9999.0	7.0	-9999.0	74.5	0.0
USWUZ-14(49.23)	USWUZ-14	63	4080262.0	548033.0	03-Oct-94	-9999.0	400.0	9.3	1.2	0.5	85.0	-9999.0	11.0	9.0	148.0	18.0	-9999.0	6.0	-9999.0	75.0	16.3
USWUZ-14(49.51)	USWUZ-14	64	4080262.0	548033.0	07-Oct-94	-9999.0	470.0	8.9	1.0	0.3	87.8	-9999.0	18.0	9.0	178.0	0.0	-9999.0	6.0	-9999.0	67.2	6.0
USWUZ-14(50.21)	USWUZ-14	65	4080262.0	548033.0	19-Jan-95	-9999.0	420.0	8.8	2.2	0.7	110.0	-9999.0	14.0	9.0	74.0	78.0	-9999.0	0.0	-9999.0	74.0	30.9
USWUZ-14(50.54)	USWUZ-14	66	4080262.0	548033.0	24-Oct-94	-9999.0	-9999.0	7.2	1.8	0.6	58.0	-9999.0	10.0	9.0	104.0	0.0	-9999.0	4.0	-9999.0	64.8	18.0
USWUZ-14(51.79)	USWUZ-14	67																			

Histogram (Meas. UZ Yang9)

2/8/01
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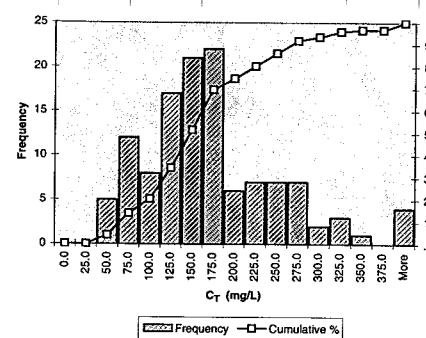
Bin	Frequency	Cumulative
6.0	0	.00%
6.2	1	.82%
6.4	0	.82%
6.6	2	2.46%
6.8	6	7.38%
7.0	8	13.93%
7.2	9	21.31%
7.4	11	30.33%
7.6	11	39.34%
7.8	7	45.08%
8.0	6	50.00%
8.2	6	54.92%
8.4	10	63.11%
8.6	11	72.13%
8.8	14	83.61%
9.0	8	90.16%
9.2	9	97.54%
9.4	3	100.00%
9.6	0	100.00%
9.8	0	100.00%
10.0	0	100.00%
More	0	100.00%



pH	
Mean	8.00
Median	8.05
Mode	8.7
Standard	0.7914
Sample Vt	0.6263
Kurtosis	-1.1411
Skewness	-0.1389
Range	3.1
Minimum	6.2
Maximum	9.3
Sum	976.0
Count	122

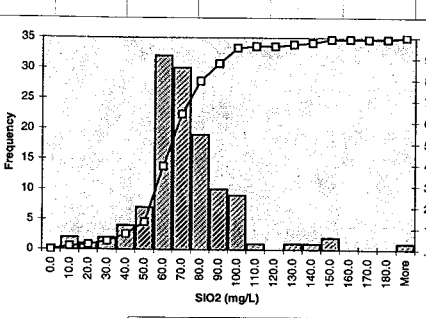
Original
Yang et al. data

Bin	Frequency	Cumulative
0.0	0	.00%
25.0	0	.00%
50.0	5	4.10%
75.0	12	13.93%
100.0	8	20.49%
125.0	17	34.43%
150.0	21	51.64%
175.0	22	69.67%
200.0	6	74.59%
225.0	7	80.33%
250.0	7	86.07%
275.0	2	93.44%
300.0	3	95.90%
325.0	1	96.72%
350.0	0	96.72%
375.0	0	96.72%
More	4	100.00%



C _t (total)	
Mean	161.45
Median	149.40
Mode	128.0
Standard	83.2395
Sample Vt	6928.8189
Kurtosis	1.9449
Skewness	1.1708
Range	442.0
Minimum	31.0
Maximum	473.0
Sum	18696.6
Count	122

Bin	Frequency	Cumulative
0.0	0	.00%
10.0	2	1.64%
20.0	1	2.46%
30.0	2	4.10%
40.0	4	7.38%
50.0	7	13.11%
60.0	32	39.34%
70.0	30	63.93%
80.0	19	79.51%
90.0	10	87.70%
100.0	9	95.08%
110.0	1	95.90%
120.0	0	95.90%
130.0	1	96.72%
140.0	1	97.54%
150.0	2	99.18%
160.0	0	99.18%
170.0	0	99.18%
180.0	0	99.18%
More	1	100.00%



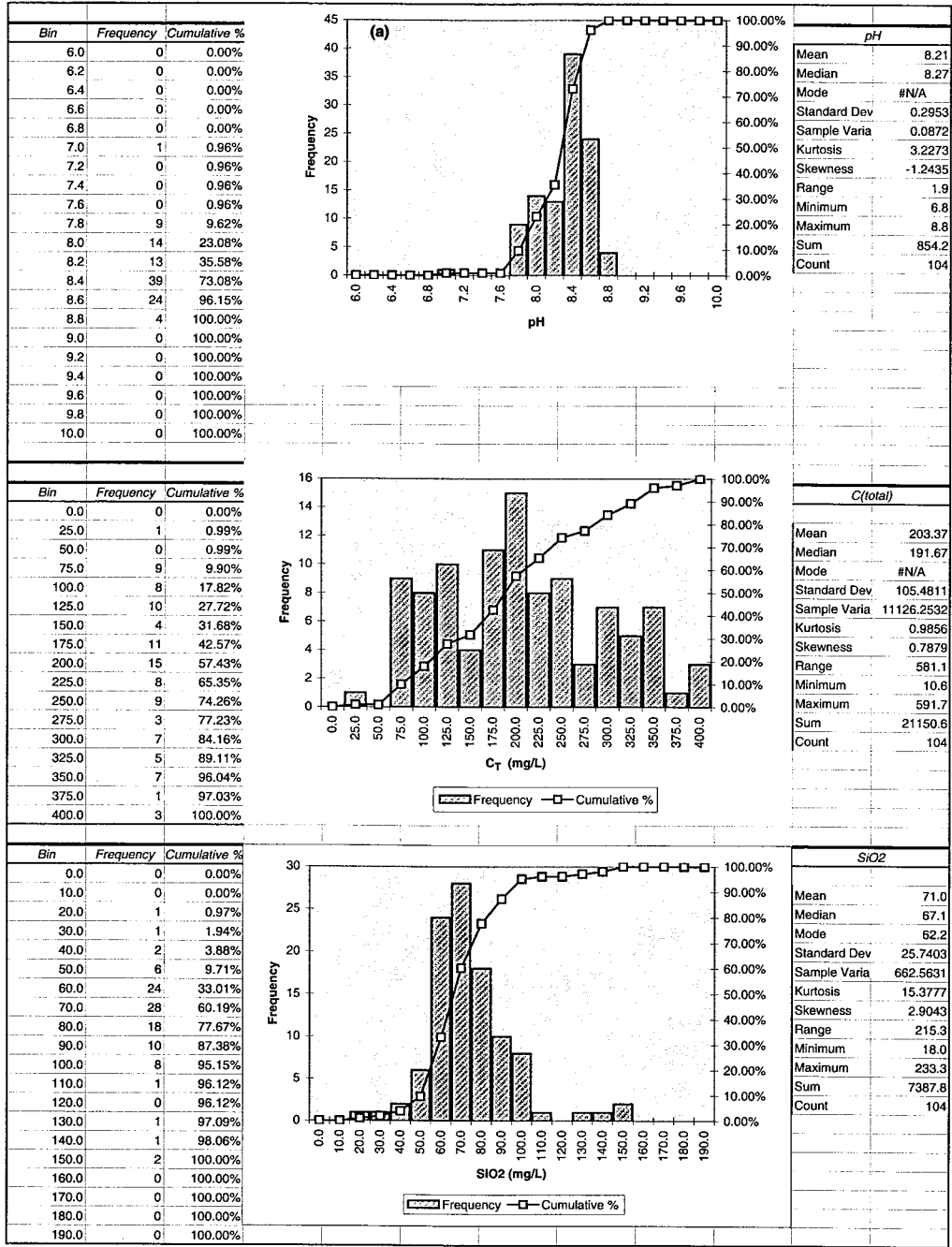
SiO2	
Mean	67.7
Median	64.5
Mode	55.0
Standard	26.2227
Sample Vt	687.6286
Kurtosis	13.2782
Skewness	2.3786
Range	225.6
Minimum	7.7
Maximum	233.3
Sum	8258.3
Count	122

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SITENUMBER	SAMPLE	ARCHID	UTM(east)	UTM(north)	Date	Temp	Sp. Conc.	Lab pH	Ca	Mg	Na	K	Cl	SO4	HCO3	CO3	PO4	NO3	F	SiO2	Al
Data from Yang et al. 1999																					
UE-250Z16(49.9)	UE-250Z16	7	407898.0	549484.0	20-Dec-92	20.3	425.0	7.96	42.5	13.4	21.5	99998.0	32.4	72.3	0.0	103.0	99998.0	23.1	99998.0	77.5	0.5
UE-250Z16(55.2)	UE-250Z16	8	407898.0	549484.0	10-Nov-92	20.4	430.0	8.11	55.0	11.0	20.0	99998.0	38.0	38.0	0.0	147.5	99998.0	33.0	99998.0	83.0	0.1
UE-250Z16(57.74)	UE-250Z16	9	407898.0	549484.0	27-Sep-94	25.9	710.0	8.23	28.9	13.7	83.8	99998.0	82.0	28.0	0.0	178.2	99998.0	17.0	99998.0	57.1	0.0
UE-250Z16(57.74)	UE-250Z16	10	407898.0	549484.0	09-Aug-93	28.1	430.0	8.18	28.5	6.2	47.9	99998.0	24.0	26.0	0.0	158.6	99998.0	23.0	99998.0	62.2	0.3
UE-250Z16(57.75)	UE-250Z16	11	407898.0	549484.0	11-Aug-93	28.1	480.0	8.14	33.5	7.9	51.3	99998.0	52.0	29.0	0.0	143.9	99998.0	28.0	99998.0	52.9	0.0
UE-250Z16(587.04)	UE-250Z16	12	407898.0	549484.0	04-Aug-93	28.3	430.0	8.22	14.1	2.4	67.5	99998.0	27.0	14.0	0.0	168.4	99998.0	18.0	99998.0	57.1	0.0
UE-250Z16(590.33)	UE-250Z16	13	407898.0	549484.0	02-Sep-93	28.4	530.0	8.37	20.5	3.7	92.0	99998.0	28.0	19.0	0.0	242.8	99998.0	18.0	99998.0	71.8	1.5
UE-250Z16(595.33)	UE-250Z16	14	407898.0	549484.0	23-Sep-93	26.4	930.0	8.49	32.4	19.7	98.2	99998.0	50.0	18.0	0.0	333.6	99998.0	19.0	99998.0	46.7	0.0
UE-250Z16(601.76)	UE-250Z16	15	407898.0	549484.0	08-Sep-93	28.6	420.0	8.20	20.6	5.1	80.1	99998.0	32.0	18.0	0.0	163.4	99998.0	20.0	99998.0	131.6	1.1
UE-250Z16(607.04)	UE-250Z16	16	407898.0	549484.0	01-Jul-93	28.7	530.0	8.28	17.0	2.4	99.0	99998.0	56.0	23.0	0.0	194.9	99998.0	18.0	99998.0	62.1	1.7
UE-250Z16(613.98)	UE-250Z16	17	407898.0	549484.0	06-May-93	26.8	550.0	8.18	3.4	0.3	78.7	99998.0	22.8	18.7	0.0	152.8	99998.0	16.1	99998.0	47.9	1.1
UE-250Z16(620.58)	UE-250Z16	18	407898.0	549484.0	28-Jun-93	28.9	490.0	8.28	4.4	0.6	95.0	99998.0	21.0	25.0	0.0	193.3	99998.0	18.0	99998.0	66.3	2.6
UE-250Z16(623.52)	UE-250Z16	19	407898.0	549484.0	18-May-93	26.9	530.0	8.37	3.6	0.9	114.8	99998.0	23.5	23.8	0.0	239.9	99998.0	18.5	99998.0	62.5	2.0
UE-250Z16(628.28)	UE-250Z16	21	407898.0	549484.0	07-Jul-93	27.0	550.0	8.27	5.0	0.5	124.0	99998.0	45.0	45.0	0.0	192.8	99998.0	25.0	99998.0	79.2	4.7
UE-250Z16(628.28)	UE-250Z16	22	407898.0	549484.0	05-Apr-94	27.0	710.0	8.50	5.0	0.4	145.0	99998.0	14.0	20.0	0.0	324.4	99998.0	16.0	99998.0	123.0	7.8
UE-250Z16(628.28)	UE-250Z16	23	407898.0	549484.0	28-Jul-93	27.0	580.0	8.35	3.3	0.3	104.0	99998.0	20.0	16.0	0.0	225.8	99998.0	14.0	99998.0	68.5	3.4
UE-250Z16(630.71)	UE-250Z16	24	407898.0	549484.0	16-Sep-93	27.1	450.0	8.25	1.2	0.1	101.0	99998.0	26.0	30.0	0.0	180.2	99998.0	24.0	99998.0	75.9	1.0
UE-250Z16(635.35)	UE-250Z16	25	407898.0	549484.0	14-Sep-93	27.2	570.0	8.43	1.9	0.1	134.0	99998.0	23.0	23.0	0.0	277.6	99998.0	19.0	99998.0	80.5	3.4
UE-250Z16(637.21)	UE-250Z16	26	407898.0	549484.0	13-Jul-93	27.2	550.0	8.36	3.2	0.6	113.0	99998.0	23.0	19.0	0.0	232.1	99998.0	16.0	99998.0	109.1	6.1
UE-250Z16(639.83)	UE-250Z16	27	407898.0	549484.0	17-Jun-93	27.2	550.0	8.24	1.7	0.8	79.9	99998.0	18.9	13.7	0.0	174.7	99998.0	11.3	99998.0	68.9	1.2
UE-250Z16(653.27)	UE-250Z16	28	407898.0	549484.0	21-Sep-93	27.5	360.0	8.07	6.3	0.8	79.5	99998.0	38.0	11.0	0.0	119.0	99998.0	6.0	99998.0	233.3	26.2
UE-250Z16(658.08)	UE-250Z16	29	407898.0	549484.0	30-Dec-93	28.1	570.0	8.24	10.0	0.3	100.0	99998.0	53.0	27.0	0.0	174.8	99998.0	13.0	99998.0	36.0	0.7
UE-250Z16(690.09)	UE-250Z16	30	407898.0	549484.0	24-Jan-94	28.1	660.0	8.30	25.0	0.3	108.0	99998.0	71.0	33.0	0.0	203.0	99998.0	10.0	99998.0	34.0	1.0
UE-250Z16(503.44)	UE-250Z16	32	407898.0	549484.0	15-Mar-94	28.4	420.0	8.22	17.3	0.3	66.0	99998.0	27.0	20.0	0.0	167.1	99998.0	6.0	99998.0	47.4	0.7
USWUZ-14(13.78)	USWUZ-14	33	4080262.0	546033.0	19-Sep-94	19.7	1320.0	8.35	18.6	6.1	249.3	99998.0	245.0	33.0	0.0	264.7	99998.0	35.0	99998.0	58.5	1.0
USWUZ-14(26.03)	USWUZ-14	34	4080262.0	546033.0	24-Mar-94	19.9	630.0	8.09	49.9	13.2	43.5	99998.0	60.0	66.0	0.0	142.7	99998.0	22.0	99998.0	88.8	0.3
USWUZ-14(27.8)	USWUZ-14	35	4080262.0	546033.0	17-Mar-94	19.9	530.0	7.87	40.7	10.1	37.1	99998.0	47.0	81.0	0.0	85.3	99998.0	26.0	99998.0	80.6	0.0
USWUZ-14(29.17)	USWUZ-14	36	4080262.0	546033.0	21-Apr-94	19.9	600.0	7.84	53.3	13.2	38.1	99998.0	78.0	83.0	0.0	81.3	99998.0	29.0	99998.0	81.5	0.0
USWUZ-14(29.38)	USWUZ-14	37	4080262.0	546033.0	03-May-94	19.9	550.0	7.91	46.9	12.7	33.6	99998.0	59.0	75.0	0.0	94.4	99998.0	26.0	99998.0	79.8	0.0
USWUZ-14(30.66)	USWUZ-14	38	4080262.0	546033.0	22-Mar-94	20.0	600.0	8.11	51.1	13.8	41.3	99998.0	44.0	83.0	0.0	148.8	99998.0	23.0	99998.0	91.8	0.0
USWUZ-14(35.02)	USWUZ-14	39	4080262.0	546033.0	01-Sep-94	20.0	540.0	7.81	49.0	10.5	35.9	99998.0	61.0	90.0	0.0	75.1	99998.0	25.0	99998.0	93.9	0.0
USWUZ-14(41.36)	USWUZ-14	40	4080262.0	546033.0	12-Apr-94	20.2	690.0	8.13	68.5	14.3	58.2	99998.0	83.0	96.0	0.0	159.2	99998.0	23.0	99998.0	92.0	0.0
USWUZ-14(44.2)	USWUZ-14	41	4080262.0	546033.0	11-Aug-94	20.2	650.0	8.02	65.5	12.0	48.2	99998.0	77.0	102.0	0.0	123.3	99998.0	22.0	99998.0	81.5	0.0
USWUZ-14(45.08)	USWUZ-14	42	4080262.0	546033.0	14-Apr-94	20.2	640.0	7.88	54.8	11.5	51.6	99998.0	83.0	102.0	0.0	88.7	99998.0	22.0	99998.0	77.3	0.0
USWUZ-14(54.19)	USWUZ-14	43	4080262.0	546033.0	12-Sep-94	20.4	730.0	7.67	67.8	11.3	48.7	99998.0	100.0	130.0	0.0	55.1	99998.0	23.0	99998.0	77.5	0.0
USWUZ-14(54.35)	USWUZ-14	44	4080262.0	546033.0	19-Apr-94	20.4	740.0	7.71	64.0	10.6	49.1	99998.0	97.0	120.0	0.0	60.6	99998.0	21.0	99998.0	93.1	0.0
USWUZ-14(55.81)	USWUZ-14	45	4080262.0	546033.0	21-Apr-94	20.6	710.0	7.67	65.5	10.7	39.4	99998.0	85.0	130.0	0.0	55.0	99998.0	14.0	99998.0	97.8	0.0
USWUZ-14(68.82)	USWUZ-14	46	4080262.0	546033.0	31-Oct-94	20.6	640.0	7.70	58.6	10.4	48.4	99998.0	93.0	116.0	0.0	58.3	99998.0	16.0	99998.0	91.2	0.0
USWUZ-14(71.72)	USWUZ-14	47	4080262.0	546033.0	02-Mar-94	20.7	630.0	7.82	67.0	10.5	29.0	99998.0	84.0	94.0	0.0	76.7	99998.0	15.0	99998.0	63.0	0.0
USWUZ-14(74.88)	USWUZ-14	49	4080262.0	546033.0	07-Feb-94	20.8	580.0	7.71	65.0	12.0	9.0	99998.0	77.0	79.0	0.0	59.9	99998.0	12.0	99998.0	46.0	0.0
USWUZ-14(43.72)	USWUZ-14	54	4080262.0	546033.0	22-Dec-94	27.1	410.0	8.26	20.0	0.8	68.0	99998.0	24.0	21.0	0.0	183.4	99998.0	6.0	99998.0	60.0	1.4
USWUZ-14(45.82)	USWUZ-14	55	4080262.0	546033.0	04-Apr-95	27.3	570.0	8.44	9.2	0.1	128.0	99998.0	24.2	37.3	0.0	280.6	99998.0	8.2	99998.0	68.7	1.2
USWUZ-14(45.95)	USWUZ-14	56	4080262.0	546033.0	11-Apr-95	27.5	500.0	8.42	2.1	0.0	122.0	99998.0	28.0	14.3	0.0	264.9	99998.0	10.8	99998.0	56.7	0.3
USWUZ-14(46.73)	USWUZ-14	57	4080262.0	546033.0	14-Apr-95	27.7	560.0	8.46	1.1	0.1	137.0	99998.0	26.2	22.3	0.0	290.2	99998.0	12.5	99998.0	54.8	1.1
USWUZ-14(47.01)	USWUZ-14	58	4080262.0	546033.0	25-Jul-94	27.8	760.0	8.63	3.6	0.5	207.0	99998.0	20.0	28.0	0.0	449.8	99998.0	4.0	99998.0	143.0	13.8
USWUZ-14(47.62)	USWUZ-14	59	4080262.0	546033.0	30-Aug-94	27.9	660.0	8.53	1.2	0.2	155.0	99998.0	16.0	14.0	0.0	341.9	99998.0	4.0	99998.0	72.0	13.9
USWUZ-14(47.92)	USWUZ-14	60	4080262.0	546033.0	23-Aug-94	27.9	590.0	8.44	1.3	0.2	129.0	99998.0	16.0	17.0	0.0	280.9	99998.0	4.0	99998.0	140.4	9.4
USWUZ-14(47.77)	USWUZ-14	61	4080262.0	546033.0	17-Aug-94	27.9	690.0	8.53	1.7	0.5	169.0	99998.0	23.0	30.0	0.0	349.3	99998.0	1.0	99998.0	54.0	15.5
USWUZ-14(48.31)	USWUZ-14	62	4080262.0	546033.0	14-Sep-94	28.0	460.0	8.39	0.9	0.3	106.8	99998.0	14.0	10.0	0.0	245.7	99998.0	7.0	99998.0	74.5	5.0
USWUZ-14(48.32)	USWUZ-14	63	4080262.0	546033.0	03-Oct-94	28.0	400.0	8.25	1.2	0.6	85.0	99998.0	11.0	9.0	0.0	175.9	99998.0	6.0	99998.0	75.0	16.3
USWUZ-14(48.95)	USWUZ-14	64	4080262.0	546033.0	07-Oct-94	28.1	470.0	8.29	1.0	0.3	87.8	99998.0	18.0	9.0	0.0	192.0	99998.0	6.0	99998.0	67.2	6.0
USWUZ-14(50.21)	USWUZ-14	65	4080262.0	546033.0	19-Jan-95	28.3	420.0	8.33	2.2	0.7	110.0	99998.0	14.0	9.0	0.0	212.1	99998.0	0.0	99998.0	74.0	30.9
USWUZ-14(51.54)	USWUZ-14	66	4080262.0	546033.0	24-Oct-94	28.5	99998.0	8.05	1.8	0.6	58.0	99998.0	10.0	9.0	0.0	110.0	99998.0	4.0	99998		

2/8/01
DRJ

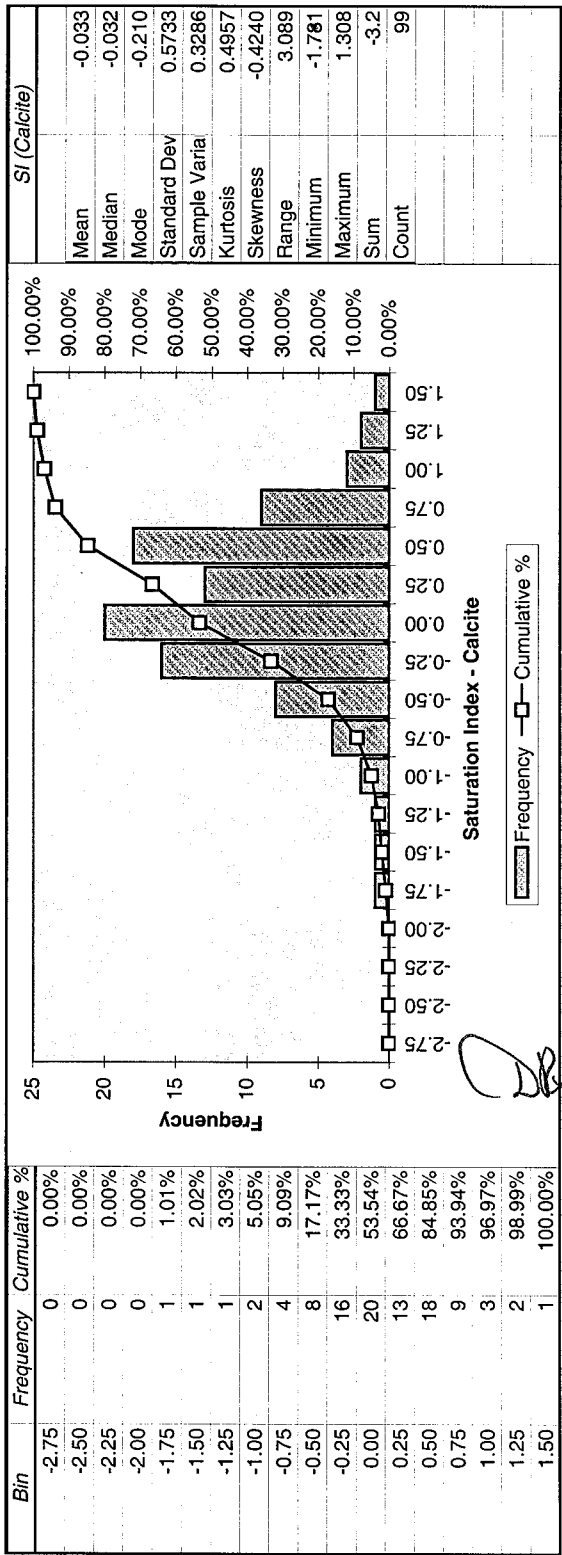
Histogram (Browning, pH, CO3)



Modified pH, CT
by Browning et al. (2000)

DRJ

2/8/01
DRJ



Calculated using data (not provided)
of Yong et al. (1996; 1998) as
modified by Browning et al. (2000)

DRJ

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JRS

Developing sorption coefficient statistics UZ matrix for input into TPA.

The approach described on pages (40-62) of this scientific notebook has been to modify UZ Kd distributions with one additional assumption. The porewater chemistry pH and C_T of Yang et al. (1996; 1998) has been modified using the methods outlined in Browning et al. (2000). Specifically, Browning et al. has equilibrated the porewaters with PCO2 reported for as a function of depth and used [H+] to balance charge. This gives a pH range that is much narrower than that reported by Yang et al. (1996; 1998). The pH range calculated by Browning et al. is also closer to a normal distribution (as opposed to the bimodal distribution of Yang et al.) and leads to a narrower, log-normal distribution in calculated Log Kd values. As before, we have used the method outlined in Pabalan et al. (1998), Bertetti et al. (1998), and Turner (1998), to model sorption for the range in UZ porewater chemistries represented by the data of Yang et al. (1996, 1998) as modified (pH, C_T) by Browning et al. (2000). All assumptions are the same as those outlined on page 40 of this scientific notebook.

With the DLM parameters presented in the previous table, MINTEQA2 input files were prepared for the data reported in Yang et al. (1996, 1998). These data were screened to exclude those data that did not report pH, carbonate, or Ca analyses (a reported value of 0 mg/L is considered to represent a measured value, although below detection limits). The mean solubility limit from TPA 3.1.4 is used for the radionuclide concentrations of Am(III), Pu(V), and Th(IV). Radionuclide concentrations for Np(V) and U(VI) were set at 1E-6 M. Work presented in Turner (1995) and Turner et al. (1998b) suggest sorption expressed in terms of K_D and K_A are relatively insensitive to radionuclide concentration:

Am(III)- γ alumina

UE-25UZ#16(49.9)										;SampID=UE-25UZ#16										;ArcID=7									
UTM=4076986.0 North; 549484.0 East; Date=02-Dec-92																													
20.30 MG/L 0.000 0.00000E-01																													
0 0 1 0 3 0 0 0 1 1 0 0 0																													
4 1 7																													
1.000E+00 13.00 0.000 0.000 81																													
330 0.000E-01 -7.96 y																				/H+1									
040 1.200E-01 -6.30 y																				/Am+3									
150 0.425E+02 -2.97 y																				/Ca+2									
460 0.134E+02 -3.26 y																				/Mg+2									
500 0.215E+02 -3.03 y																				/Na+1									
180 0.324E+02 -3.04 y																				/Cl-1									
732 0.723E+02 -3.12 y																				/SO4-2									
140 0.103E+03 -2.77 y																				/CO3-2									
492 0.231E+02 -3.43 y																				/NO3-1									
770 0.484E+02 -3.09 y																				/H4SiO4									
030 0.500E+00 -4.73 y																				/Al+3									
813 0.000E-01 0.00 y																				/ADS1PSIo									
811 4.986E-05 -4.30 y																				/ADS1TYP1									
3 1																													
330 7.9600 0.0000																				/H+1									
6 1																													
813 0.0000 0.0000																				/ADS1PSIo									
2 3																													
8113300 >AlO- 0.0000 -9.0500 0.000 0.000-1.00 0.00																													
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000																													
0.000 0 0.000 0 0 0.000 0 0.000 0 0.000																													
0 0.000 0 0.000 0 0.000 0																													
8113301 >AlOH2+ 0.0000 6.8500 0.000 0.000 1.00 0.00																													
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000																													
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000																													
0 0.000 0 0.000 0 0.000 0																													
8110400 >AlOAm+2 0.0000 4.6600 0.000 0.000 2.00 0.00																													
0.00 4 1.000 811 1.000 040 -1.000 330 2.000 813 0.000																													
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0 0.000																													
0 0.000 0 0.000 0 0.000 0																													

JRS

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JRS

Np(V)-montmorillonite

UE-25UZ#16(49.9) ;SampID=UE-25UZ#16 ;ArcID=7									
UTM=4076986.0 North; 549484.0 East; Date=02-Dec-92									
20.30 MG/L 0.000 0.00000E-01									
0 0 1 0 3 0 0 0 1 1 0 0 0									
4 1 7									
1.000E+00 9.70 0.000 0.000 81									
330	0.000E-01	-7.96 y							
150	0.425E+02	-2.97 y							
460	0.134E+02	-3.26 y							
500	0.215E+02	-3.03 y							
180	0.324E+02	-3.04 y							
732	0.723E+02	-3.12 y							
140	0.103E+03	-2.77 y							
492	0.231E+02	-3.43 y							
770	0.484E+02	-3.09 y							
030	0.500E+00	-4.73 y							
552	2.690E-01	-6.00 y							
813	0.000E-01	0.00 y							
811	1.687E-05	-4.77 y							
812	2.033E-05	-4.69 y							

pH=7.96
Ca=42.5mg/L
etc.

Compare
data on
pg. 63

JRS

2 4										
5523300	-10.0000	10.5015	/npo2 (oh)							
5521400	4.6000	12.7951	/npo2 (co3) -1							
5521401	7.0000	7.1390	/npo2 (co3) 2-3							
5521402	8.5000	6.2630	/npo2 (co3) 3-5							
3 1										
330	7.9600	0.0000	/H+1							
6 1										
813	0.0000	0.0000	/ADS1PSIo							
2 6										
5523301 npo2 (oh) 2-	0.0000	-22.4000	0.000	0.000-1.00	4.00	0.00	0.0000			
0.00 3 -2.000 330	1.000 552	2.000 2	0.000 0	0.000 0	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
8113300 >AlO-	0.0000	-9.7300	0.000	0.000-1.00	0.00	0.00	0.0000			
0.00 3 1.000 811	-1.000 330	-1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
8113301 >AlOH2+	0.0000	8.3300	0.000	0.000 1.00	0.00	0.00	0.0000			
0.00 3 1.000 811	1.000 330	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
8115520 >AlONpO2OH-	0.0000	-13.7900	0.000	0.000-1.00	0.00	0.00	0.0000			
0.00 5 1.000 811	1.000 552	1.000 2	-2.000 330	-1.000 813	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
8123300 >SiO-	0.0000	-7.2000	0.000	0.000-1.00	0.00	0.00	0.0000			
0.00 3 1.000 812	-1.000 330	-1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
8125520 >SiOHnpO2+	0.0000	4.0500	0.000	0.000 1.00	0.00	0.00	0.0000			
0.00 3 1.000 812	1.000 552	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.0000			
0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			
0 0.000 0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0 0.000 0	0.0000			

Pu(V)-γ alumina

UE-25UZ#16(49.9) ;SampID=UE-25UZ#16 ;ArcID=7
UTM=4076986.0 North; 549484.0 East; Date=02-Dec-92
20.30 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 13.00 0.000 0.000 81
330 0.000E-01 -7.96 y /H+1
642 1.200E-01 -6.36 y /PuO2+1
150 0.425E+02 -2.97 y /Ca+2
460 0.134E+02 -3.26 y /Mg+2
500 0.215E+02 -3.03 y /Na+1
180 0.324E+02 -3.04 y /Cl-1
732 0.723E+02 -3.12 y /SO4-2
140 0.103E+03 -2.77 y /CO3-2
492 0.231E+02 -3.43 y /NO3-1
770 0.484E+02 -3.09 y /H4SiO4
030 0.500E+00 -4.73 y /Al+3
813 0.000E-01 0.00 y /ADS1PSIo
811 4.986E-05 -4.30 y /ADS1TYP1

3 1
330 7.9600 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 3
8113300 >AlO- 0.0000 -9.0500 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 6.8500 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8116420 >AlOPuO2 0.0000 -2.1800 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 642 -1.000 330 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

Th(IV)-γ alumina

UE-25UZ#16(49.9) ;SampID=UE-25UZ#16 ;ArcID=7
UTM=4076986.0 North; 549484.0 East; Date=02-Dec-92
20.30 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 13.00 0.000 0.000 81
330 0.000E-01 -7.96 y /H+1
866 2.300E-01 -6.01 y /Th+4
150 0.425E+02 -2.97 y /Ca+2
460 0.134E+02 -3.26 y /Mg+2
500 0.215E+02 -3.03 y /Na+1
180 0.324E+02 -3.04 y /Cl-1
732 0.723E+02 -3.12 y /SO4-2
140 0.103E+03 -2.77 y /CO3-2
492 0.231E+02 -3.43 y /NO3-1
770 0.484E+02 -3.09 y /H4SiO4
030 0.500E+00 -4.73 y /Al+3
813 1.000E-07 -7.00 y /ADS1PSIo
811 4.986E-05 -4.30 y /ADS1TYP1

3 1
330 7.9600 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

2 3
8113300 >AlO- 0.0000 -9.0500 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 6.8500 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118660 >AlOTh+3 0.0000 15.3000 0.000 0.000 3.00 0.00 0.00 0.0000
0.00 4 1.000 811 1.000 866 -1.000 330 3.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

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U(VI)-montmorillonite

UE-25UZ#16(49.9) ;SampID=UE-25UZ#16 ;ArcID=7
UTM=4076986.0 North; 549484.0 East; Date=02-Dec-92
20.30 MG/L 0.000 0.00000E-01
0 0 1 0 3 0 0 0 1 1 0 0 0
4 1 7
1.000E+00 9.70 0.000 0.000 81
330 0.000E-01 -7.96 y /H+1
893 2.700E-01 -6.00 y /uo2+2
150 0.425E+02 -2.97 y /Ca+2
460 0.134E+02 -3.26 y /Mg+2
500 0.215E+02 -3.03 y /Na+1
180 0.324E+02 -3.04 y /Cl-1
732 0.723E+02 -3.12 y /SO4-2
140 0.103E+03 -2.77 y /CO3-2
492 0.231E+02 -3.43 y /NO3-1
770 0.484E+02 -3.09 y /H4SiO4
030 0.500E+00 -4.73 y /Al+3
813 0.000E-01 0.00 y /ADS1PSIo
811 1.687E-05 -5.57 y /ADS1TYP1
812 2.033E-05 -5.23 y /ADS1TYP2

2 1
8933301 -13.0000 18.0940 /uo2(oh)2
3 1
330 7.9600 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

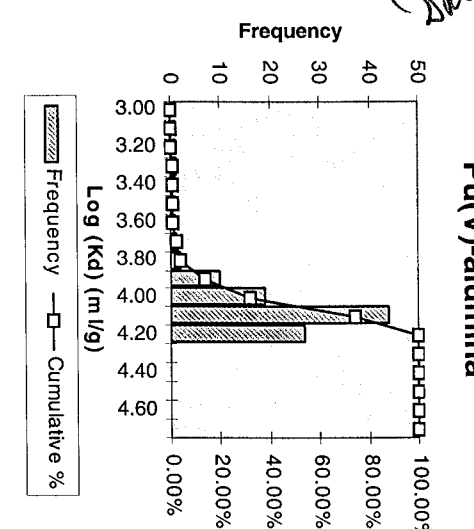
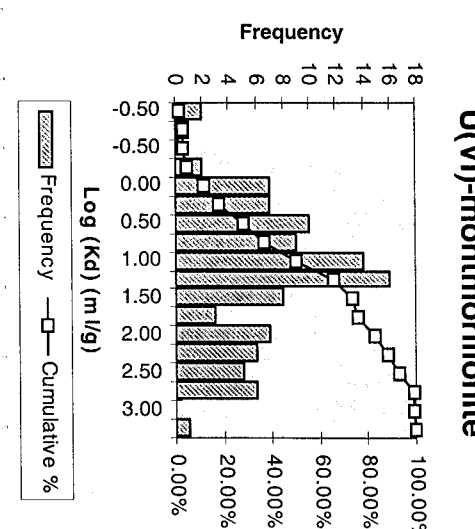
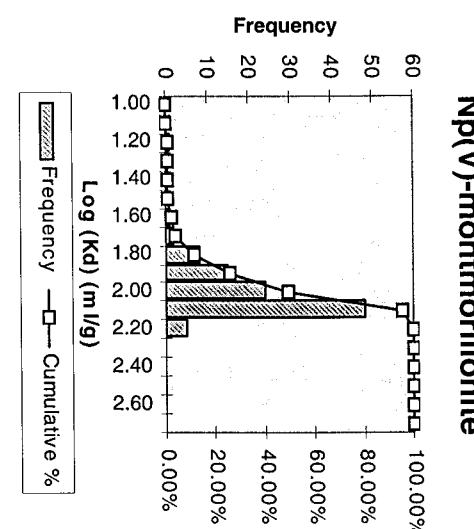
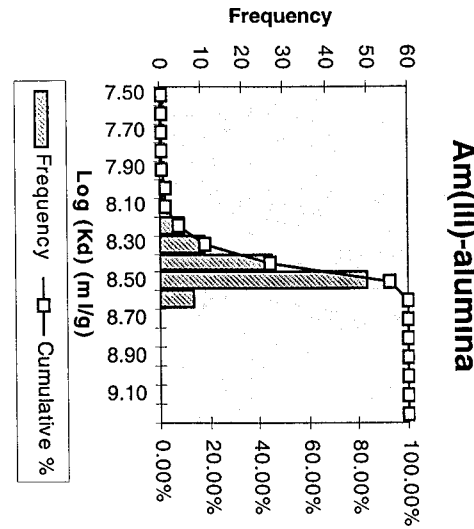
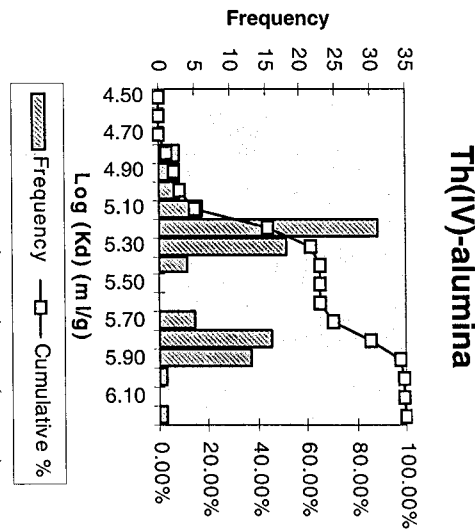
2 5
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0.00 3 1.000 812 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8128930 >SiOUO2+ 0.0000 2.6000 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 4 1.000 812 1.000 893 -1.000 330 1.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113300 >AlO- 0.0000 -9.7300 0.000 0.000-1.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >AlOH2+ 0.0000 8.3300 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118930 >AlOUO2+ 0.0000 2.7000 0.000 0.000 1.00 0.00 0.00 0.0000
0.00 4 1.000 811 1.000 893 -1.000 330 1.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

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Running these MINTEQA2 models allows generation of sorption coefficients for the observed ranges in water chemistry for the five radionuclide-mineral systems considered here. Normalized to effective surface area K_A of the minerals used in the calibration experiments, and assuming that the pH- and PCO_2 -dependent sorption behavior is similar for aluminosilicates, these sorption coefficient distributions can be recast in terms of K_D for each of the hydrostratigraphic units used in TPA.

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Calculated
using Browning et al. 2000
pH, G_T

DB

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DB

The log K_A distributions and descriptive statistics calculated using Microsoft Excel 97 are given here:

Descriptive Statistics					
log K_A (mL/m ²)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Mean	7.253	0.839	2.905	4.252	-0.071
Median	7.303	0.888	2.938	4.103	-0.101
Mode	7.318	#N/A	2.938	#N/A	#N/A
Standard Deviation	0.174	0.140	0.125	0.336	0.876
Sample Variance	0.030	0.019	0.016	0.113	0.768
Kurtosis	49.407	9.569	15.018	-0.764	-0.293
Skewness	-6.084	-2.402	-2.940	0.485	0.224
Range	1.622	0.950	0.918	1.604	4.603
Minimum	5.783	0.051	2.109	3.633	-2.198
Maximum	7.405	1.002	3.027	5.236	2.405
Sum	754.3	87.3	302.1	442.2	-7.4
Count	104	104	104	104	104

The final step in using this information in TPA is to apply this distribution to each hydrostratigraphic unit and transform the K_A into K_D (in mL/g). The relationship among porosity, dry density, and pore radius and parameters described on page (48) of this scientific notebook are used to calculate Kd values for the each radionuclide for each radionuclide (5 total) for each of seven hydrostratigraphic units (in m³/g = 1000 mL/g):

Log KD(m3/kg)	Am(III)-TSw	Am(III)-CHnv	Am(III)-CHnz	Am(III)-PPw	Am(III)-UCF	Am(III)-BFw	Am(III)-UFZ
Mean	4.716	5.198	5.156	5.073	5.092	4.700	4.684
Median	4.765	5.247	5.206	5.122	5.142	4.750	4.734
Mode	4.781	5.263	5.222	5.138	5.157	4.766	4.750
Standard Deviation	0.1743	0.1743	0.1743	0.1743	0.1743	0.1743	0.1743
Sample Variance	0.0304	0.0304	0.0304	0.0304	0.0304	0.0304	0.0304
Kurtosis	49.4067	49.4067	49.4067	49.4067	49.4067	49.4067	49.4067
Skewness	-6.0841	-6.0841	-6.0841	-6.0841	-6.0841	-6.0841	-6.0841
Range	1.622	1.622	1.622	1.622	1.622	1.622	1.622
Minimum	3.245	3.728	3.686	3.603	3.622	3.230	3.214
Maximum	4.867	5.349	5.308	5.224	5.244	4.852	4.836
Sum	490.4	540.5	536.2	527.6	529.6	488.8	487.2
Count	104	104	104	104	104	104	104

Log KD(m3/kg)	Np(V)-TSw	Np(V)-CHnv	Np(V)-CHnz	Np(V)-PPw	Np(V)-UCF	Np(V)-BFw	Np(V)-UFZ
Mean	-1.698	-1.216	-1.258	-1.341	-1.322	-1.714	-1.729
Median	-1.650	-1.168	-1.209	-1.293	-1.274	-1.665	-1.681
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.1395	0.1395	0.1395	0.1395	0.1395	0.1395	0.1395
Sample Variance	0.0195	0.0195	0.0195	0.0195	0.0195	0.0195	0.0195
Kurtosis	9.5689	9.5689	9.5689	9.5689	9.5689	9.5689	9.5689
Skewness	-2.4023	-2.4023	-2.4023	-2.4023	-2.4023	-2.4023	-2.4023
Range	0.950	0.950	0.950	0.950	0.950	0.950	0.950
Minimum	-2.486	-2.004	-2.046	-2.129	-2.110	-2.501	-2.517
Maximum	-1.536	-1.054	-1.095	-1.179	-1.159	-1.551	-1.567
Sum	-176.6	-126.5	-130.8	-139.5	-137.5	-178.2	-179.9
Count	104	104	104	104	104	104	104

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Log KD(m3/kg)	Pu(V)-TSw	Pu(V)-CHnv	Pu(V)-CHnz	Pu(V)-PPw	Pu(V)-UCF	Pu(V)-BFw	Pu(V)-UFZ
Mean	0.367	0.849	0.808	0.724	0.744	0.352	0.336
Median	0.400	0.882	0.841	0.757	0.776	0.385	0.369
Mode	0.400	0.882	0.841	0.757	0.776	0.385	0.369
Standard Deviation	0.1254	0.1254	0.1254	0.1254	0.1254	0.1254	0.1254
Sample Variance	0.0157	0.0157	0.0157	0.0157	0.0157	0.0157	0.0157
Kurtosis	15.0184	15.0184	15.0184	15.0184	15.0184	15.0184	15.0184
Skewness	-2.9395	-2.9395	-2.9395	-2.9395	-2.9395	-2.9395	-2.9395
Range	0.918	0.918	0.918	0.918	0.918	0.918	0.918
Minimum	-0.429	0.053	0.012	-0.072	-0.053	-0.444	-0.460
Maximum	0.489	0.971	0.930	0.846	0.866	0.474	0.458
Sum	38.2	88.3	84.0	75.3	77.3	36.6	34.9
Count	104	104	104	104	104	104	104

Log KD(m3/kg)	Th(IV)-TSw	Th(IV)-CHnv	Th(IV)-CHnz	Th(IV)-PPw	Th(IV)-UCF	Th(IV)-BFw	Th(IV)-UFZ
Mean	1.714	2.196	2.155	2.071	2.090	1.699	1.683
Median	1.565	2.047	2.006	1.922	1.942	1.550	1.534
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.3359	0.3359	0.3359	0.3359	0.3359	0.3359	0.3359
Sample Variance	0.1129	0.1129	0.1129	0.1129	0.1129	0.1129	0.1129
Kurtosis	-0.7635	-0.7635	-0.7635	-0.7635	-0.7635	-0.7635	-0.7635
Skewness	0.4851	0.4851	0.4851	0.4851	0.4851	0.4851	0.4851
Range	1.604	1.604	1.604	1.604	1.604	1.604	1.604
Minimum	1.095	1.577	1.536	1.452	1.471	1.080	1.064
Maximum	2.699	3.181	3.139	3.056	3.075	2.683	2.668
Sum	178.3	228.4	224.1	215.4	217.4	176.7	175.0
Count	104	104	104	104	104	104	104

Log KD(m3/kg)	U(VI)-TSw	U(VI)-CHnv	U(VI)-CHnz	U(VI)-PPw	U(VI)-UCF	U(VI)-BFw	U(VI)-UFZ
Mean	-2.609	-2.127	-2.168	-2.252	-2.232	-2.624	-2.640
Median	-2.639	-2.157	-2.198	-2.282	-2.263	-2.654	-2.670
Mode	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A
Standard Deviation	0.8761	0.8761	0.8761	0.8761	0.8761	0.8761	0.8761
Sample Variance	0.7675	0.7675	0.7675	0.7675	0.7675	0.7675	0.7675
Kurtosis	-0.2927	-0.2927	-0.2927	-0.2927	-0.2927	-0.2927	-0.2927
Skewness	0.2235	0.2235	0.2235	0.2235	0.2235	0.2235	0.2235
Range	4.603	4.603	4.603	4.603	4.603	4.603	4.603
Minimum	-4.736	-4.253	-4.295	-4.378	-4.359	-4.751	-4.767
Maximum	-0.133	0.349	0.308	0.224	0.244	-0.148	-0.164
Sum	-271.3	-221.2	-225.5	-234.2	-232.2	-272.9	-274.5
Count	104	104	104	104	104	104	104

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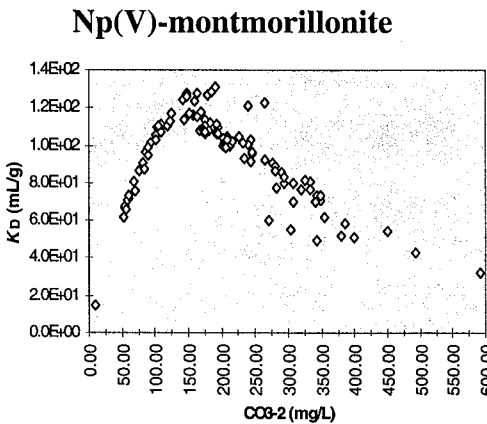
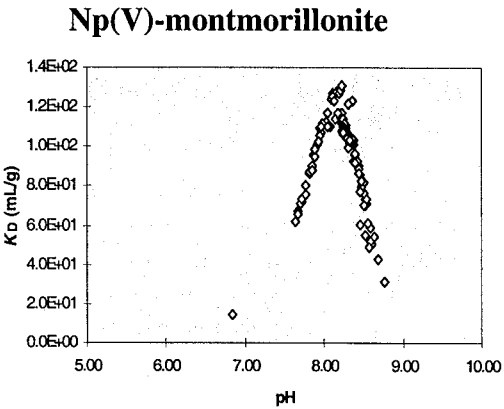
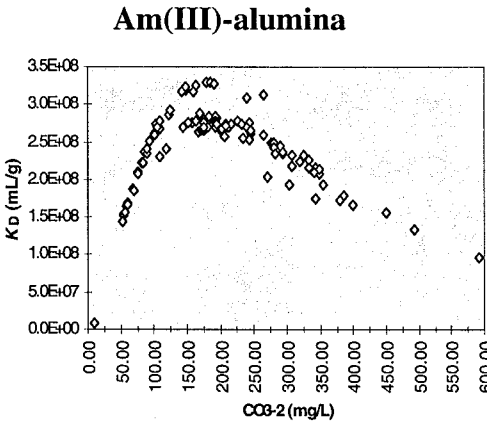
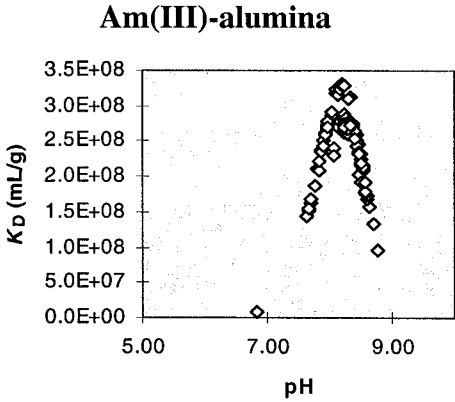
Using the data analysis tools in Microsoft Excel 97, the following correlation coefficients are developed for K_A (and therefore K_D):

Correlations based on Browning et al. 2000 interpretation of Yang et al. (96/98) UZ porewater data					
K_A (mL/m2)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.9449555	1			
Pu(V)	0.7494019	0.8839817	1		
Th(IV)	-0.3144929	-0.1063647	0.0942793	1	
U(VI)	-0.5460706	-0.3929841	-0.3343929	0.7872652	1

For log K_A (and log K_D), the correlation coefficients are different:

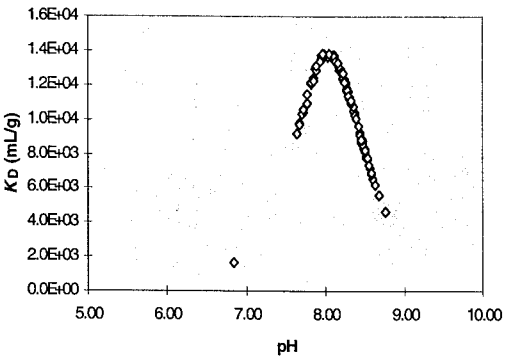
Log K_A (mL/m2)	Am(III)	Np(V)	Pu(V)	Th(IV)	U(VI)
Am(III)	1				
Np(V)	0.8924145	1			
Pu(V)	0.8341597	0.9260436	1		
Th(IV)	-0.1851512	0.1207744	0.2670366	1	
U(VI)	-0.1552063	0.1534478	0.2945488	0.9992569	1

These K_D distributions and correlation coefficients were passed to the PA element for incorporation in TPA 4.2.

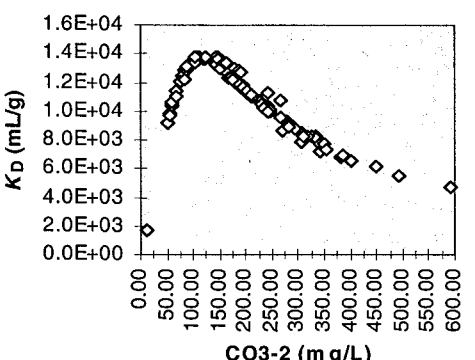


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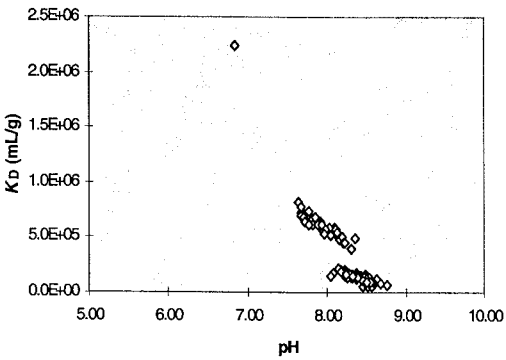
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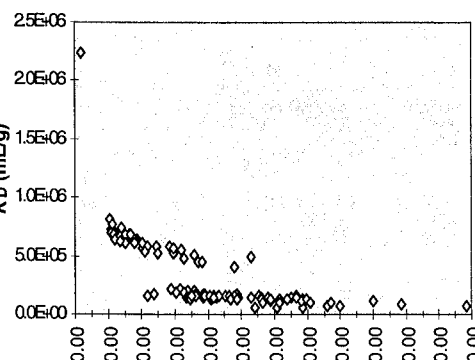
Pu(V)-alumina



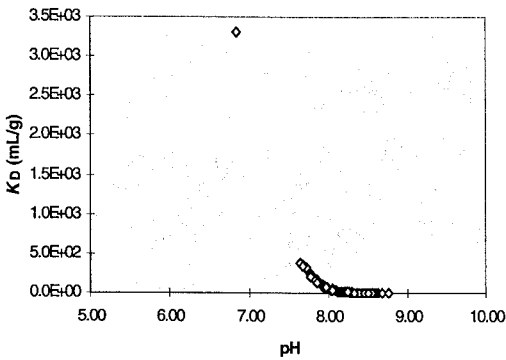
Th(IV)-alumina



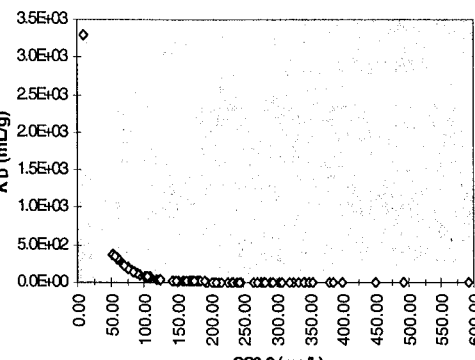
Th(IV)-alumina



U(VI)-montmorillonite



U(VI)-montmorillonite



References

Bertetti, F.P., R.T. Pabalan, and M.G. Almendarez. 1998. Studies of neptunium^V sorption on quartz, clinoptilolite, montmorillonite, and α -alumina. E.A. Jenne, ed. *Adsorption of Metals by Geomedia*. New York, NY: Academic Press, Inc.: 131-148.

Browning, L., W.M. Murphy, B.W. Leslie, and W.L. Dam. 2000. Thermodynamic interpretations of chemical analyses of unsaturated zone water from Yucca Mountain, Nevada. *Scientific Basis for Nuclear Waste Management XXIII*. R.W. Smith and D.W. Shoesmith, eds. Pittsburgh, PA: Materials Research Society: Symposium Proceedings 608: 237-242.

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. 1998. Uranium^{VI} sorption onto selected mineral surfaces. E.A. Jenne, ed. *Adsorption of Metals by Geomedia*. New York, NY: Academic Press, Inc.: 99-130.

Turner, D.R. 1995. *A Uniform Approach to Surface Complexation Modeling of Radionuclide Sorption*. CNWRA 95-001. San Antonio, TX: CNWRA.

Turner, D.R. 1998. *Radionuclide Sorption in Fractures at Yucca Mountain, Nevada: A Preliminary Demonstration of Approach for Performance Assessment*. CNWRA Letter Report. San Antonio, TX: CNWRA.

Turner, D.R., G.W. Wittmeyer, and F.P. Bertetti. 1998b. *Radionuclide Sorption in the Alluvium at Yucca Mountain, Nevada: A Preliminary Demonstration of Approach for Performance Assessment*. CNWRA Letter Report. San Antonio, TX: CNWRA.

Yang, I.C., G.W. Rattray, P. Yu., *Interpretation of Chemical and Isotopic Data from Boreholes in the Unsaturated Zone at Yucca Mountain, Nevada*, Water Resources Investigations Report 96-4058, Denver, CO: U.S. Geological Survey, 1996a.

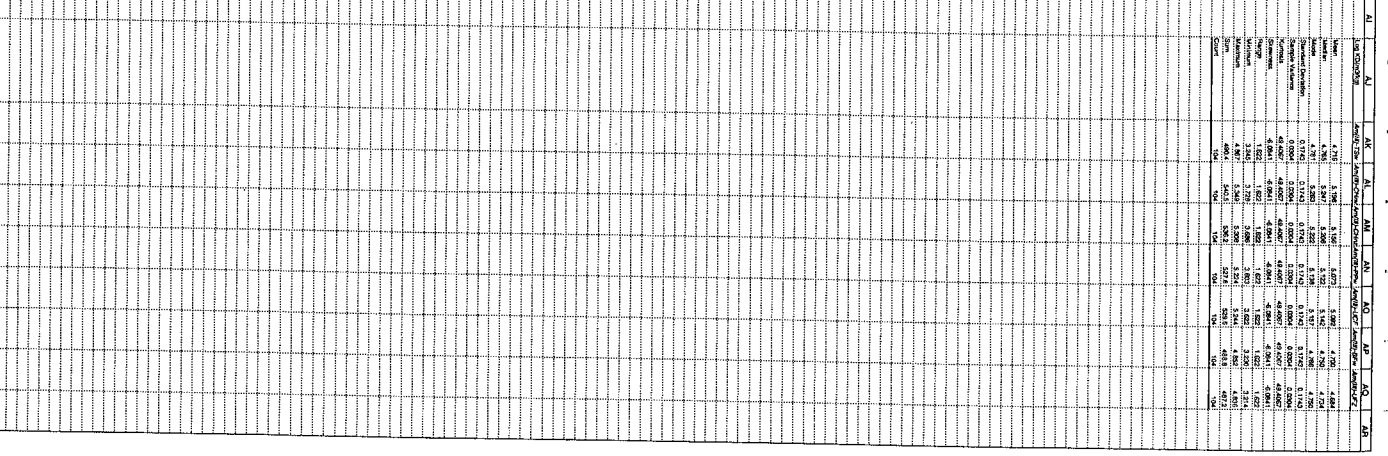
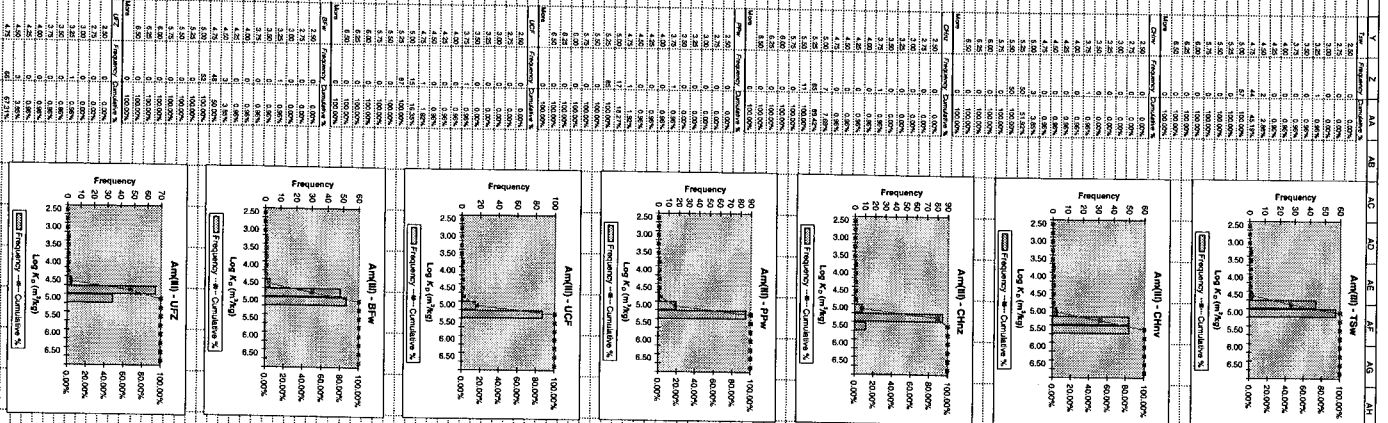
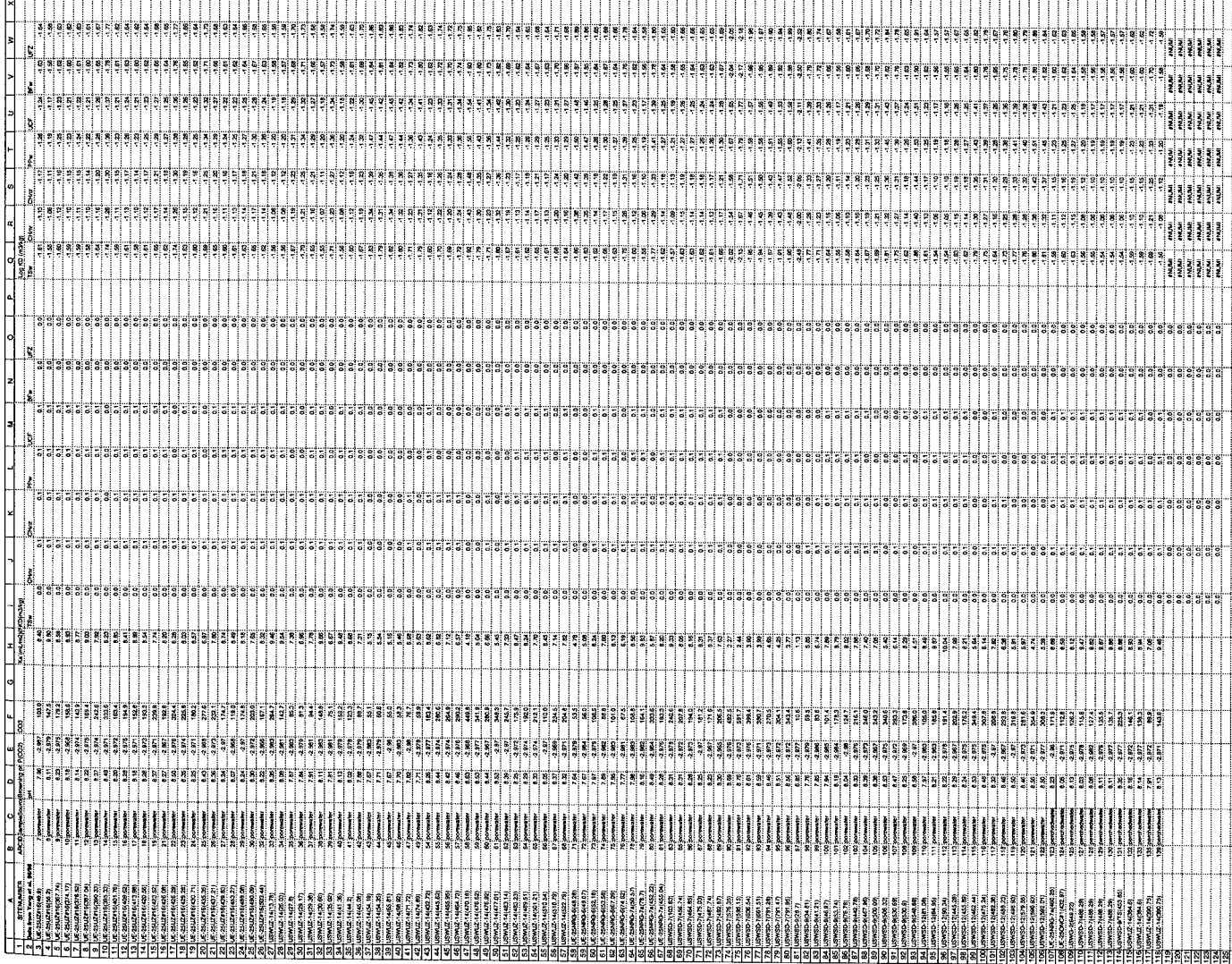
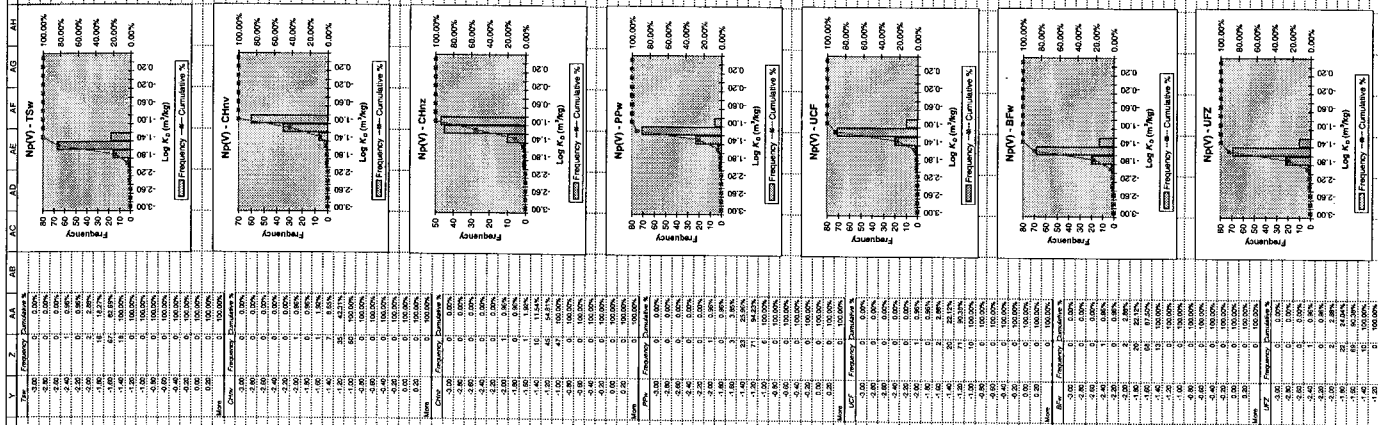
Yang, I.C., P. Yu, G.W. Rattray, J.S. Ferarese, J.N. Ryan, *Hydrochemical Investigations in Characterizing the Unsaturated Zone at Yucca Mountain, Nevada*, Water-Resources Investigations Report 98-4132, Denver, CO: U.S. Geological Survey, 1998.

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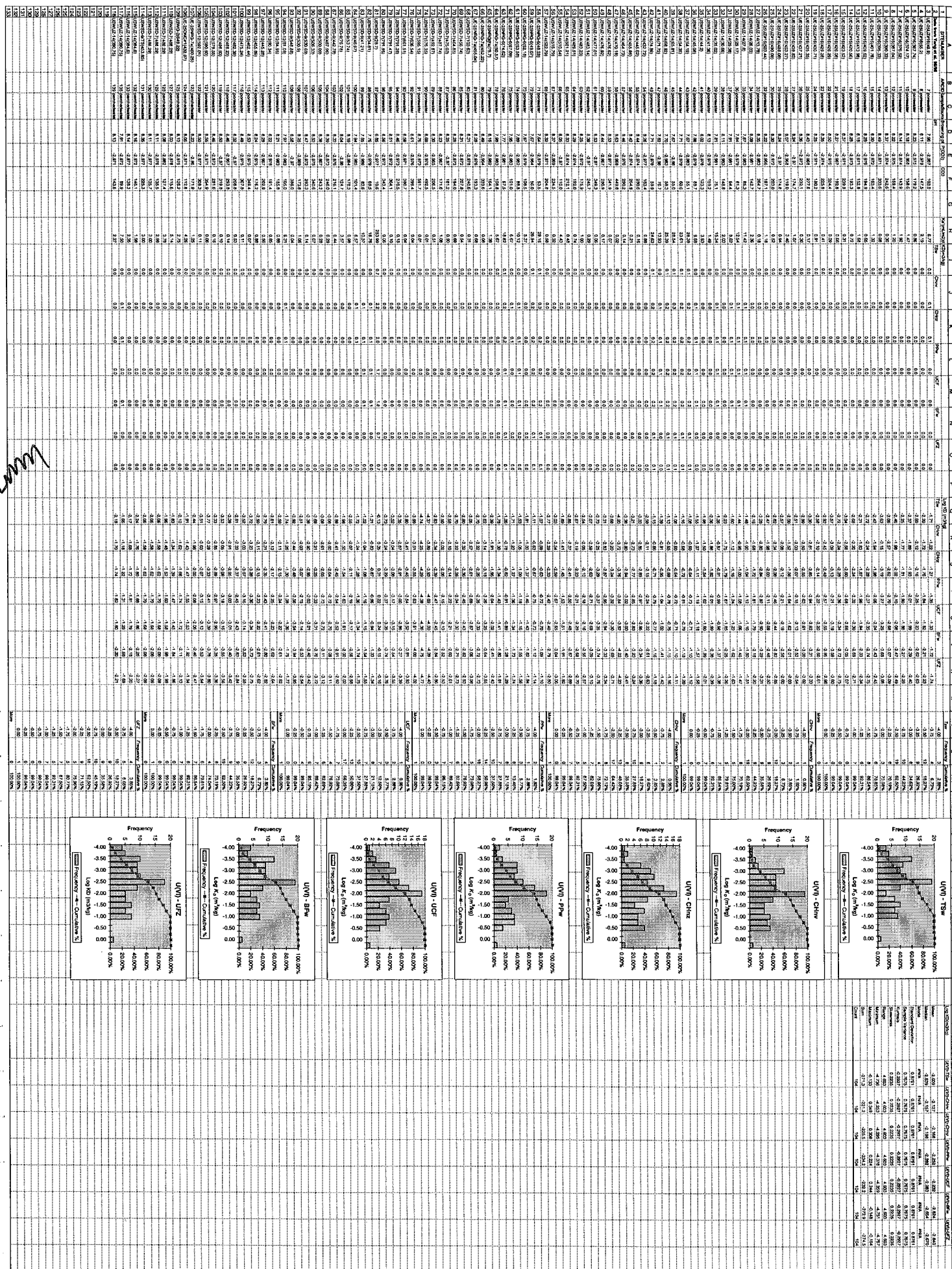
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Summary



Log KD(m/kg)	Am(III)-TSw	Am(III)-CHNv	Am(III)-CHNz	Am(III)-PPw	Am(III)-UCF	Am(III)-BFW	Am(III)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	4.71550636	5.19759104	5.15619835	5.0726523	5.09195745	4.70026639	4.68447213
Standard Deviation	0.17429616	0.17429616	0.17429616	0.17429616	0.17429616	0.17429616	0.17429616
Minimum	3.24546853	3.72755321	3.68616052	3.60261447	3.62191962	3.23022856	3.2144343
Maximum	4.86725	5.34933468	5.30794199	5.22439594	5.24370109	4.85201003	4.83621577
Log KD(m/kg)	Np(V)-TSw	Np(V)-CHNv	Np(V)-CHNz	Np(V)-PPw	Np(V)-UCF	Np(V)-BFW	Np(V)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	-1.69834607	-1.2162614	-1.25765408	-1.34120014	-1.32189498	-1.71358604	-1.72938031
Standard Deviation	0.13953695	0.13953695	0.13953695	0.13953695	0.13953695	0.13953695	0.13953695
Minimum	-2.48619998	-2.00411531	-2.04550799	-2.12905404	-2.10974889	-2.50143995	-2.51723422
Maximum	-1.53580848	-1.05372381	-1.0951165	-1.17866255	-1.15935739	-1.55104845	-1.56684272
Log KD(m/kg)	Pu(V)-TSw	Pu(V)-CHNv	Pu(V)-CHNz	Pu(V)-PPw	Pu(V)-UCF	Pu(V)-BFW	Pu(V)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	0.36706902	0.84915369	0.80776101	0.72421496	0.74352011	0.35182905	0.33603479
Standard Deviation	0.12543942	0.12543942	0.12543942	0.12543942	0.12543942	0.12543942	0.12543942
Minimum	-0.42900442	0.05308026	0.01168757	-0.07185848	-0.05255332	-0.44424438	-0.46003865
Maximum	0.48924053	0.9713252	0.92993252	0.84638647	0.86569162	0.47400056	0.4582063
Log KD(m/kg)	Th(IV)-TSw	Th(IV)-CHNv	Th(IV)-CHNz	Th(IV)-PPw	Th(IV)-UCF	Th(IV)-BFW	Th(IV)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	1.71399924	2.19608392	2.15469123	2.07114518	2.09045034	1.69875928	1.68296501
Standard Deviation	0.33593202	0.33593202	0.33593202	0.33593202	0.33593202	0.33593202	0.33593202
Minimum	1.09489902	1.57698369	1.535591	1.45204495	1.47135011	1.07965905	1.06386478
Maximum	2.69853975	3.18062443	3.13923174	3.05568569	3.07499084	2.68329979	2.66750552
Log KD(m/kg)	U(VI)-TSw	U(VI)-CHNv	U(VI)-CHNz	U(VI)-PPw	U(VI)-UCF	U(VI)-BFW	U(VI)-UFZ
Distribution	log normal	log normal	log normal	log normal	log normal	log normal	log normal
Mean	-2.60886144	-2.12677677	-2.16816945	-2.2517155	-2.23241035	-2.62410141	-2.63989568
Standard Deviation	0.87607364	0.87607364	0.87607364	0.87607364	0.87607364	0.87607364	0.87607364
Minimum	-4.73552548	-4.25344081	-4.29483349	-4.37837955	-4.35907439	-4.75076545	-4.76655972
Maximum	-0.13279384	0.34929083	0.30789814	0.22435209	0.24365725	-0.14803381	-0.16382808

Summary

Updating MINTEQA2 + PHREEQC databases to include NEA data for Am, Np, Pu, Tc, and U. Electronic files in database are included in packet at the back of this scientific notebook.

Drum

Am data

Silva et al. (1995)

NEA data

[illegible]

42

Selected americium data

Table III.2 (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_r H_m^\circ$ (kJ · mol ⁻¹)	$\Delta_r S_m^\circ$ (J · K ⁻¹ · mol ⁻¹)
Am(OH) ₃ (aq)	$\text{Am}^{3+} + 3 \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Am}(\text{OH})_3(\text{aq}) + 3 \text{H}^+$	-25.700 ±0.500	146.697 ±2.854		

Cross-check
Excel-calculated
Log k vs.
Silva et al reported value

DR

Pu - Data

NEA

Lemire et al
(2001)

Drum

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Lemire, R.J., J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, and H. Wanner. "Chemical Thermodynamics Series, Volume 4: Chemical Thermodynamics of Neptunium and Plutonium. Nuclear Energy Agency, Organization for Economic Cooperation and Development. Table 4.2.. New York, NY: Elsevier. p. 61. 2001.

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the following reference:

Information potentially subject to copyright protection was redacted from this location. The redacted material is from the following reference:

Rard, J.A. M.H. Rand, G. Anderegg, and H. Wanner. "Chemical Thermodynamics Series, Volume 3: Chemical Thermodynamics of Technetium. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York, NY: Elsevier. 1999.

TC Data: NEA
Rord et al. (1999)

Cross-check of reported $\log k^0$

4/26/2002

QPR

Uranium Data NEA
Grenthe et al. (1992)

Cross check w/ reported $\Delta G_k^\circ + \Delta H_r^\circ$

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4/24/2002
DRJ

NEA references.

Grenthe, I., J. Fuger, R. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. *Chemical Thermodynamics Series, Volume 1: Chemical Thermodynamics of Uranium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1992.

Lemire, R.J., J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, and H. Wanner. *Chemical Thermodynamics Series, Volume 4: Chemical Thermodynamics of Neptunium and Plutonium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 2001.

Rard, J.A., M.H. Rand, G. Anderegg, and H. Wanner. *Chemical Thermodynamics Series, Volume 3: Chemical Thermodynamics of Technetium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1999.

Silva, R.J., G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, and I. Puigdomenich. *Chemical Thermodynamics Series, Volume 2: Chemical Thermodynamics of Americium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1995.

JBL/mm

- Excel Spreadsheet to calculate $\log K^0/\Delta H^0$ from NEA databases included in back pocket to this scientific notebook (E:\Thermo\neadata.xls)

- MINTEQA2, Version 4.02 files (E:\MINTEQA2_V4.02_Configuration\ThermoData\

Thermo4_nea.dbs

Type64_nea.dbs

Redox4_nea.dbs

- PHREEQC, Version 2.4.2 files (E:\PHREEQC_Configuration\ThermoData\

phreeqc 2_42.dat

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JBL/mm

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4/30/2002

Database Check after CNLRA modifications
to make sure no errors introduced.

MS

Redline/strikeout
MINTEQA2 Test Problem 1b

Test1a.out
Comparison of Complete Output
(redline/strikeout)
① as distributed
② CNLRA modified database

PART 1 of OUTPUT FILE
MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5 JUN 2000~~ 13-FEB-2002 TIME: 147:-613:2738

Date/Time stamp

TEST1A - Compute total H+ of a solution of known pH.
This together with TEST1B illustrate a two run set to compute pH.
Component file (COMP.DBS): comp.dbs COMP v4.00-09/30/1999 02/12/2002
Thermodynamic file (THERMO.UNF): thermo.unf THERMO V4.00-09/30/1999 02/05/2002
Gaussian DOM file (GAUSSIAN.DBS): gaussian.dbs GAUSSIAN V4.00 09/30/1999
Solids file (TYPE6.UNF): type6.unf TYPE6 V4.00-09/30/1999 02/05/2002

}
Different
databases

Temperature (Celsius): 25.00
Units of concentration: MOLAL
Ionic strength to be computed.
If specified, carbonate concentration represents total inorganic carbon.
Do not automatically terminate if charge imbalance exceeds 30%
Precipitation is allowed only for those solids specified as ALLOWED
in the input file (if any).
Maximum iterations: 200
The method used to compute activity coefficients is: Davies equation
Intermediate output file

330 0.000E+00 -2.50
732 1.580E-03 -2.80
410 7.700E-05 -4.11
140 0.000E+00 -16.00

H2O has been inserted as a COMPONENT

3 2
3301403 21.6600 -0.5300
330 2.5000 0.0000

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	Name	ACTIVITY GUESS	log GUESS	ANAL TOTAL
330	H+1	3.162E-03	-2.500	0.000E+00
732	SO4-2	1.585E-03	-2.800	1.580E-03
410	K+1	7.762E-05	-4.110	7.700E-05
140	CO3-2	1.000E-16	-16.000	0.000E+00
2	H2O	1.000E+00	0.000	0.000E+00

Charge Balance: UNSPECIATED

Sum of CATIONS= 7.700E-05 Sum of ANIONS = 3.160E-03

PERCENT DIFFERENCE = 9.524E+01 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:
SO4-2 Log activity guess: -2.92
CO3-2 Log activity guess: -16.66

4/30/2002 Database Check after CNLRA modifications

to make sure no errors introduced.

PART 2 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5-JUN-2000~~13-FEB-2002 TIME: 147:-613:2739

CONSTRAINTS ON COMPONENT ACTIVITIES

As specified, this chemical system is OPEN with respect to the following components:

H2O

H+1

CO3-2

Activities of the following components are constrained by the species shown:

COMPONENT	SPECIES	TYPE
CO3-2	eo2 co2 (g)	3
H+1	H+1	3
H2O	H2O	3

CNLRA database changed
all species names to
lower case

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4/30/2002

Database Check after CNLWRA modifications

CPS

to make sure no errors introduced.

PART 2 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5 JUN 2000~~ 13-FEB-2002 TIME: 147:-613:2739

CONSTRAINTS ON COMPONENT ACTIVITIES

As specified, this chemical system is OPEN with respect to the following components:

H2O

H+1

CO3-2

Activities of the following components are constrained by the species shown:

COMPONENT	SPECIES	TYPE
CO3-2	e02 co2 (g)	3
H+1	H+1	3
H2O	H2O	3

CNLWRA database changed
all species names to
lower case

Database Check after CNLREA modifications

to make sure no errors introduced.

PART 3 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: -5-JUN-2000 13-FEB-2002 TIME: 147:-613:2739

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL mol/L	DIFF FXN	LOG ACTVITY	RESIDUAL
0	SO4-2	1.580E-03	6.594E-07	-2.91757	5.014E-07
1	SO4-2	1.580E-03	4.193E-04	-2.91775	4.192E-04
2	SO4-2	1.580E-03	8.125E-06	-3.01997	7.967E-06
3	SO4-2	1.580E-03	1.693E-07	-3.02220	1.135E-08

ID No	Name	Total Conc(M)	Conc (M)	log Activity	Diff fxn
410	K+1	7.700E-05	7.649E-05	-4.14759	5.093E-11
732	SO4-2	1.580E-03	1.266E-03	-3.02224	3.557E-09
2	H2O	0.000E+00	-1.049E-05	-0.00004	0.000E+00
330	H+1	0.000E+00	3.398E-03	-2.50000	0.000E+00
140	CO3-2	0.000E+00	2.916E-17	-16.66004	0.000E+00

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID No	Name	Conc (M)	log Act	Charge	Act Coef	New logK
330	H+1	3.398E-03	-2.50000	1.00	0.93070	0.031
732	SO4-2	1.266E-03	-3.02224	-2.00	0.75031	0.125
410	K+1	7.649E-05	-4.14759	1.00	0.93070	0.031
140	CO3-2	2.916E-17	-16.66004	-2.00	0.75031	0.125

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID No	Name	Conc (M)	log Act	Charge	Act Coef	New logK
3301400	HCO3-	1.588E-09	-8.83038	-1.00	0.93070	10.361
3301401	H2CO3 (aq)	1.048E-05	-4.97904	0.00	1.00102	16.681
3300020	OH-	3.421E-12	-11.49704	-1.00	0.93070	-13.966
3307320	H2SO4-hso4-	3.132E-04	-3.53530	-1.00	0.93070	2.018
4107320	K2SO4-kso4-	5.106E-07	-6.32310	-1.00	0.93070	0.878
3300020	oh-	3.421E-12	-11.49704	-1.00	0.93070	-13.966
3301400	hco3-	1.588E-09	-8.83038	-1.00	0.93070	10.361
3301401	h2co3 (aq)	1.048E-05	-4.97904	0.00	1.00102	16.681

Even though flagged in document compare, note that values match to 4 significant figures. Only lower case change triggered flagging

Type III - SPECIES WITH FIXED ACTIVITY

ID No	Name	Conc (M)	New logK	Enthalpy
2	H2O	-1.049E-05	0.000	0.000
330	H+1	-3.711E-03	2.500	0.000
3301403	CO2(g)	-1.049E-05	21.660	-0.530

All species changed to lower case in CNLREA modifications to THERM.DBS and TYPE6.DBS. All parameter values are unchanged.

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Database Check after CNLIRA modifications

DPS

to make sure no errors introduced.

PART 4 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5-JUN-2000~~13-FEB-2002 TIME: 147:-613:2739PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

K+1	99.3	Percent bound in species # 410	K+1
SO4-2	80.1	Percent bound in species # 732	SO4-2
	19.8	Percent bound in species #3307320	H SO4- <u>hso4-</u>
H2O	100.0	Percent bound in species #3300020	OH- <u>oh-</u>
H+1	91.0	Percent bound in species # 330	H+1
	8.4	Percent bound in species #3307320	H SO4- <u>hso4-</u>
CO3-2	100.0	Percent bound in species #3301401	H2CO3 <u>h2co3</u> (aq)

4/30/2002

Database Check after CNLRA modifications

SRS

to make sure no errors introduced

PART 5 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5-JUN-2000~~ 13-FEB-2002 TIME: 147:-613:2739-----
EQUILIBRATED MASS DISTRIBUTION -----

IDX	Name	DISSOLVED		SORBED		PRECIPITATED	
		mol/L	percent	mol/L	percent	mol/L	percent
410	K+1	7.700E-05	100.0	0.000E+00	0.0	0.000E+00	0.0
732	SO4-2	1.580E-03	100.0	0.000E+00	0.0	0.000E+00	0.0
2	H2O	3.421E-12	100.0	0.000E+00	0.0	0.000E+00	0.0
330	H+1	3.732E-03	100.0	0.000E+00	0.0	0.000E+00	0.0
140	CO3-2	1.049E-05	100.0	0.000E+00	0.0	0.000E+00	0.0

Charge Balance: SPECIATED

Sum of CATIONS = 3.474E-03 Sum of ANIONS 2.846E-03

PERCENT DIFFERENCE = 9.936E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 4.426E-03

EQUILIBRIUM pH = 2.500

DATE ID NUMBER: ~~20000605~~ 20020213TIME ID NUMBER: ~~14062757~~ 17133906

Note all data values identical except
Date/Time stamp and run ID numbers

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Database Check after CNLIRA modifications

DRS

to make sure no errors introduced

PART 6 of OUTPUT FILE

MINTEQA2 v4.02 DATE OF CALCULATIONS: ~~5-JUN-2000~~ 13-FEB-2002 TIME: 147:~~613:2739~~

Saturation indices and stoichiometry of all minerals

ID No	Name	SI	Composition by stoich. of components
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VALIDATING MINTEQA2, VERSION 4.02

This is intended to document the validation of MINTEQA2, Version 4.02 as outlined in the software validation test plan (Turner, 2002). MINTEQA2, Version 4.02 is an acquired code, originally developed by the USEPA (EPA, 1999a,b). CNWRA staff use the software to provide technical assistance to the NRC. All input and output files are included in electronic form on the zip disk in the pocket at the back of this scientific notebook.

THERMODYNAMIC DATA USED IN TESTING

The original MINTEQA2, Version 4.02 (and PHREEQC, Version 2.4.2) databases have been modified to include thermodynamic data (ΔH_f° and $\log K$) for almost 600 aqueous species and solids involving 14 potentially important radioelements, including U, Pu, Th, Np, Am, Sr, Cs, Ra, Sn, Zr, Tc, Ru, Eu, and Co. Thermodynamic data for U, Pu, Np, Am, and Tc are from the Nuclear Energy Agency (NEA) Thermodynamic Database Project (Grenthe et al., 1992; Silva et al., 1995; Rard et al., 1999; Lemire et al., 2001). With a few exceptions as noted in the thermodynamic reference file, the source for other data is the EQ3/6 database (Release Gembochs.v2-eq8-data0.alt.r2, 02Aug95). The electronic data for both CNWRA-modified MINTEQA2 and PHREEQC databases are included in the pocket at the back of this scientific notebook. Spreadsheet calculations for NEA data are included on pp. 82-89 of this scientific notebook (SN394). A redline/strikeout comparison of output for MINTEQA2 test problem 1b using the as-received database and the CNWRA-modified database is provided on pg. 90 of this scientific notebook. The agreement between the output indicates that no errors were introduced during modification of the database.

Installation Check—Results

The installation of MINTEQA2, Version 4.02 software was checked as part of bringing the code into configuration management under Technical Operating Procedure (TOP)-018 for the CNWRA. The results indicate that the code was installed correctly on the PC platform and produced the correct results for 12 different example problems provided with MINTEQA2, Version 4.02. The results are included in electronic format in the pocket at the end of this scientific notebook and are also documented in the configuration management package for MINTEQA2, Version 4.02 stored in the CNWRA QA Records Room.

Aqueous Speciation

We tested MINTEQA2, Version 4.02 results against an example test problem (Example 1) provided for the geochemical speciation code PHREEQC, Version 2.4.2 (Parkhurst and Appelo, 1999).

As originally posed in the PHREEQC, Version 2.4.2 user's manual (Parkhurst and Appelo, 1999), test Example 1 is designed to calculate the distribution of aqueous species in seawater and the saturation state of seawater at 25 °C relative to a set of minerals. Changes to the original problem formulation include:

- 1) With the update to both MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 to include data from the NEA thermodynamic databases (Grenthe et al., 1992; Silva et al., 1995; Rard et al., 1999; Lemire et al., 2001), we used the default values for uranium speciation.
- 2) The original formulation of Example 1 in the PHREEQC, Version 2.4.2 user's manual (Parkhurst and Appelo, 1999) also used the $\text{NO}_3^-/\text{NH}_4^+$ redox couple to control the oxidation state of uranium, while controlling the distribution of the other redox sensitive elements (Fe, Mn) by the overall redox equilibrium with atmospheric oxygen. MINTEQA2, Version 4.02 does not allow the user to specify separate redox controls, so the entire problem was formulated to control all redox reactions, including uranium speciation, only by atmospheric oxygen.

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Because of the large number of aqueous species in a multicomponent solution like seawater, only a few representative species concentrations are included in Table 1. Complete output is included in electronic form in the pocket at the back of this scientific notebook *and in spreadsheets on pp. 108-109 of this SN.*

Table 1. Comparison of MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 calculated concentrations of selected component species, carbonate species, and redox sensitive species. $T = 25\text{ }^{\circ}\text{C}$, $P_{\text{O}_2} = 10^{-0.66}\text{ atm}$.

Species	Aqueous Concentration (molal) MINTEQA2, Version 4.02	Aqueous Concentration (molal) PHREEQC, Version 2.4.2
Non-Redox/Non-Carbonate Species		
K^+	1.033×10^{-2}	1.040×10^{-2}
Na^+	4.766×10^{-1}	4.786×10^{-1}
Cl^-	5.656×10^{-1}	5.657×10^{-1}
Carbonate Species		
CO_3^{2-}	3.024×10^{-5}	3.728×10^{-5}
HCO_3^-	1.613×10^{-3}	1.480×10^{-3}
Na HCO_3	2.058×10^{-4}	1.626×10^{-4}
UO_2CO_3	1.242×10^{-12}	1.668×10^{-13}
Redox-Sensitive Species		
$\text{U(IV)}_{\text{total}}$	1.419×10^{-37}	6.233×10^{-38}
$\text{U(V)}_{\text{total}}$	5.437×10^{-28}	4.660×10^{-29}
$\text{U(VI)}_{\text{total}}$	1.267×10^{-8}	1.437×10^{-8}
$\text{U}^{\text{V}}\text{O}_2(\text{CO}_3)_3^{5-}$	1.071×10^{-21}	7.159×10^{-32}
$\text{U}^{\text{VI}}\text{O}_2(\text{CO}_3)_3^{4-}$	1.180×10^{-8}	1.422×10^{-8}
Saturation Indices (SI) with respect to solid phases		
Anhydrite	-0.68	-0.85
Calcite	0.88	0.79
Halite	-2.43	-2.51
Schoepite	-4.88	-5.86
Uraninite	-27.37	-28.38

A graphical comparison of the calculated concentration of more than 100 aqueous species (Figure 1a) shows a reasonable, although not perfect correlation among the results. Although there are some order of magnitude differences between calculated concentrations of several species (e.g., $\text{UO}_2(\text{CO}_3)_3^{5-}$ and UO_2CO_3), most calculated values agree within a factor of two. Calculated mineral saturations also show reasonable agreement, and MINTEQA2 results are consistent with PHREEQC predictions of saturation and

undersaturation. The discrepancies between the two codes appear to be due to two principal factors, differences in the thermodynamic databases and slight differences in activity coefficients.

The aqueous species included in the two thermodynamic databases are not identical. For example, MINTEQA2, Version 4.02 includes the nitrate species CaNO_3^+ , MnNO_3^+ , and FeNO_3^+ that are not part of the PHREEQC, Version 2.4.2 database, while PHREEQC, Version 2.4.2 includes KOH and the carbonate species FeCO_3 and MnCO_3 that are not in the MINTEQA2 database. Most of these species are present in small amounts and do not have a large effect on the overall speciation, but may still account for part of the observed differences in speciation.

Also, although the modifications made at the CNWRA have resulted in identical thermodynamic data for the uranium species, there are slight differences in the thermodynamic data for a number of common aqueous species, and the cumulative effect may be amplified. Although both MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 are reported to use the WATEQ data compilations, these types of small differences persist in thermodynamic data for many of the chemical component systems that are beyond the intended scope of the validation.

A second cause of the differences in the results from the two computer codes is likely to be due to differences in how activity coefficient corrections (γ) are calculated for aqueous species. The results from the two codes (Figure 1b) indicate that there are differences in calculated γ . Typically, MINTEQA2, Version 4.02 calculates a higher activity coefficient than PHREEQC, Version 2.4.2. The close agreement with the one-to-one correspondence line in Figure 1b indicates that the differences are generally small, but there are a few cases where the different formulations result in calculated values for γ that differ by a factor of two or more. Also, because of the z^2 term in the Davies equation, the differences in activity coefficient formulations between the two codes is more pronounced for highly charged aqueous species.

Mineral Solubility: Barite Solubility - Richardson and McSween (1989) and Blount (1977)

Two worked problems in Richardson and McSween (1989) consider the solubility of barite (BaSO_4) at 298 K in pure water (Worked Problem 3-7), and in a 0.2 m NaCl solution (Worked Problem 3-8). The results for barite solubility reported in Richardson and McSween (1989) differ slightly from the results calculated by

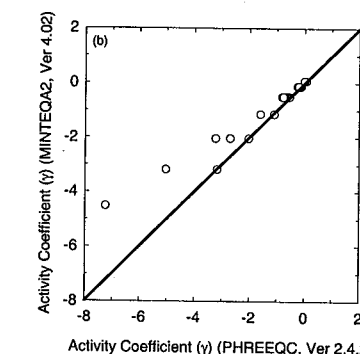
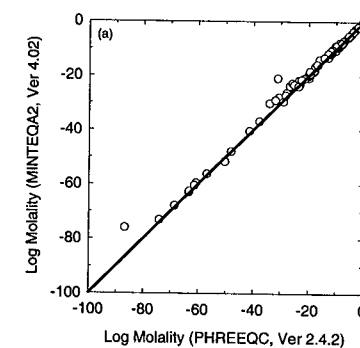


Figure 1. Comparison of aqueous speciation of seawater from MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2. (a) Comparison of concentration (log molality) of aqueous species; (b) Comparison of the calculated activity coefficients (γ) used by the two computer codes. The solid line indicates a one-to-one perfect correlation between model results.

MINTEQA2, Version 4.02 (Table 2). The results differ by less than 2%, and are likely due to slight differences in the activity coefficient formulation, and a more complete handling of the geochemical system in MINTEQA2, Version 4.02. Reevaluating the Richardson and McSween (1989) calculations using the activity coefficients calculated by MINTEQA2, Version 4.02 shows excellent agreement between the two sets of results (Table 2). Both the MINTEQA2, Version 4.02 and Richardson and McSween (1989) solubility calculations are in good agreement with the experimental data of Blount (1977) as reported in Richardson and McSween (1989).

Table 2. Comparison of barite solubility results for Richardson and McSween (1989) and MINTEQA2, Version 4.02.

	$m_{Ba^{2+}}$ (molal)	$m_{SO_4^{2-}}$ (molal)	$\gamma_{Ba^{2+}}$ (D-H)	$\gamma_{SO_4^{2-}}$ (D-H)
Problem 3-7 (pure H2O)				
MINTEQA2, Version 4.02	1.055×10^{-5}	1.055×10^{-5}	0.97018	0.97011
Richardson and McSween (1989)	1.051×10^{-5}	1.051×10^{-5}	0.9704	0.9704
Richardson & McSween calculations with MINTEQA2 activity coefficients	1.055×10^{-5}	1.055×10^{-5}	0.97018	0.97011
Blount (1977)	1.06×10^{-5}	1.06×10^{-5}	n.r.	n.r.
Problem 3-8 (0.2 m NaCl)				
MINTEQA2, Version 4.02	3.675×10^{-5}	3.675×10^{-5}	0.29726	0.26082
Richardson and McSween (1989)	3.611×10^{-5}	3.611×10^{-5}	0.2987	0.2671
Richardson & McSween calculations with MINTEQA2 activity coefficients	3.675×10^{-5}	3.675×10^{-5}	0.29726	0.26082
Blount (1977)	3.7×10^{-5}	3.7×10^{-5}	n.r.	n.r.

n.r. not reported

Gas Chemistry: Stumm and Morgan (1996), Example 7.8

Stumm and Morgan (1996) present Example 7.8, equilibrating calcite ($CaCO_3$) in sea water at 25 °C, and open to atmosphere (fixed $P_{CO_2} = 3.55 \times 10^{-4}$ atm). The seawater composition is not specified in the example problem, but a representative composition is provided in Table 15.2 of Stumm and Morgan (1996) and reproduced in Table 3.

Table 3. Representative seawater composition (Stumm and Morgan, 1996; Table 15.2).

Constituent	Concentration (mg/L)
Na+	10770
Mg ²⁺	1290
Ca ²⁺	412.1
K+	399
Sr ²⁺	7.9
Cl ⁻	19354
SO ₄ ²⁻	2712
HCO ₃ ⁻	142.4
Br ⁻	67.3
F ⁻	1.3
B	4.5

← Stumm+Morgan 96 do not specify that this is the seawater composition used in Example 7.8

As indicated in the problem formulation for Example 7.8, initial Ca^{2+} , HCO_3^- , and B were omitted. Results from Stumm and Morgan (1996) and MINTEQA2, Version 4.02 are compared in Table 4.

Table 4. Seawater in equilibrium with calcite at 25 °C, and open to atmosphere (fixed $P_{CO_2} = 3.55 \times 10^{-4}$ atm). All concentrations in molarity.

	pH	Ca^{2+} (total)	HCO_3^- (total)	CO_3^{2-} (total)	$H_2CO_3(aq)$ (total)
Problem 7.8					
MINTEQA2, Version 4.02	8.32	1.234×10^{-3}	1.93×10^{-3}	2.63×10^{-4}	1.03×10^{-5}
Stumm and Morgan (1996)	8.34	1.51×10^{-3}	2.77×10^{-3}	3.80×10^{-4}	1.05×10^{-5}

The model results agree very well for pH, Ca^{2+} and $H_2CO_3(aq)$, and agree within less than a factor of two for HCO_3^- and CO_3^{2-} concentrations. The differences in HCO_3^- and CO_3^{2-} are likely due to uncertainty in starting composition and slight differences in thermodynamic data for the aqueous carbonate system; Stumm and Morgan (1996) do not indicate the precise starting composition of the seawater used in their calculations. Because the details of the model inputs are not presented in Stumm and Morgan (1996), it is not possible to evaluate these differences in more detail.

Langmuir (1997) - calcite solubility, fresh H2O, variable fixed P_{CO_2}

Langmuir (1997) presents results for calcite solubility in fresh water at 25 °C, and under variable fixed P_{CO_2} . These results are easier to interpret than the seawater speciation in Stumm and Morgan (1996) due to the simpler geochemical system.

Again, there are slight differences (Table 5) due to thermodynamic data or different activity coefficient models, [Langmuir (1997) does not provide this information in Table 6.3], but at all three P_{CO_2} values covering two orders of magnitude, the agreement is within one percent (Table 5). The overall excellent agreement indicates that MINTEQA2, Version 4.02 is correctly implementing gas equilibria in aqueous speciation calculations.

Table 5. Fresh water in equilibrium with calcite at 25 °C, and variable P_{CO_2}

	pH	Ca^{2+} (mg/L)	HCO_3^- (mg/L)
$P_{CO_2} = 10^{-3.5}$ bar = $10^{-3.51}$ atm			
MINTEQA2, Version 4.02	8.284	19.8	58.1
Langmuir (1997); Table 6.3	8.29	20	58
$P_{CO_2} = 10^{-2.5}$ bar = $10^{-2.51}$ atm			
MINTEQA2, Version 4.02	7.628	43.8	131.1
Langmuir (1997); Table 6.3	7.62	44	131
$P_{CO_2} = 10^{-1.5}$ bar = $10^{-1.51}$ atm			
MINTEQA2, Version 4.02	6.976	100.5	300.0
Langmuir (1997); Table 6.3	6.97	100	298

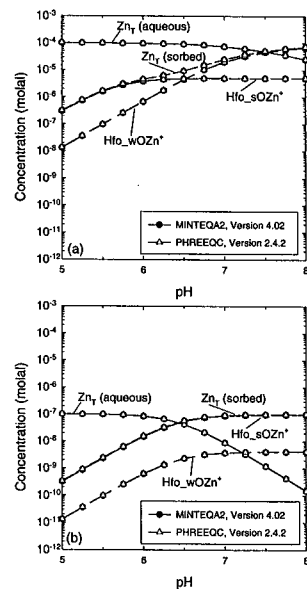


Figure 2. Comparison of Zn-ferrihydrite sorption results for MINTEQA2, Version 4.02 (circles) and PHREEQC, Version 2.4.2 (triangles). MINTEQA2, Version 4.02 thermodynamic data have been modified to match the PHREEQC, Version 2.4.2 database.

Zn Sorption—Surface Complexation Modeling: Dzombak and Morel (1990)

Dzombak and Morel (1990) described Zn²⁺ sorption on ferrihydrite (HFO) using the diffuse-layer surface complexation model. Sorption at 25 °C (298 K) is investigated for two Zn²⁺ concentrations (10⁻⁴ and 10⁻⁷ molal), and the results are presented in terms of dissolved and sorbed Zn²⁺ molality as a function of pH. For more direct comparison of model results, the input file for MINTEQA2, Version 4.02 includes modified equilibrium constants for Zn(OH)⁺, Zn(OH)₂(aq), Zn(OH)₃⁻, and Zn(OH)₄²⁻ that match those in the PHREEQC, Version 2.4.2 database. In addition, the species ZnNO₃⁺ and Zn(NO₃)₂(aq) are excluded from the MINTEQA2, Version 4.02 run since they are not included in the PHREEQC, Version 2.4.2 database. Model results are given in Table 6 (percent sorbed) and shown in Figure 2 (surface complex concentration).

Table 6. Comparison of MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 results for Zn sorption on ferrihydrite (percent sorbed). DLM constants from Dzombak and Morel (1990).

pH	Zn _T = 1 × 10 ⁻⁴ molal		Zn _T = 1 × 10 ⁻⁷ molal	
	MINTEQA2 (% sorbed)	PHREEQC (% sorbed)	MINTEQA2 (% sorbed)	PHREEQC (% sorbed)
5.00	0.3	0.3	0.3	0.3
5.25	0.8	0.8	0.9	0.9
5.50	1.7	1.7	2.4	2.4
5.75	3.0	3.0	6.2	6.3
6.00	4.5	4.5	15.3	15.5
6.25	6.2	6.3	33.0	33.2
6.50	9.2	9.3	57.3	57.6
6.75	15.1	15.2	78.7	78.9
7.00	24.8	25.0	91.1	91.2
7.25	37.4	37.6	96.6	96.7
7.50	50.4	50.6	98.8	98.8
7.75	62.4	62.5	99.6	99.6
8.00	72.3	72.4	99.8	99.8

The results from MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 show excellent agreement, indicating that the surface complexation modeling subroutines are performing as expected. The minor variations are likely due to differences in how the two codes sweep through a range in pH. In PHREEQC, Version 2.4.2, pH is fixed based on titration with 1.0 m NaOH, in contrast to MINTEQA2, Version 4.02, where pH is fixed externally by adjusting H⁺ activity. This leads to differences in both Na⁺ concentrations and ionic strength.

ZnT=1e-7	pH	mZn+2(tot)	Hfo_sOZn+	Hfo_wOZn+	%sorbed
20020321	5.00	9.97E-08	3.11E-10	1.30E-11	0.32%
20020321	5.25	9.91E-08	8.51E-10	3.57E-11	0.89%
20020321	5.50	9.76E-08	2.29E-09	9.60E-11	2.39%
20020321	5.75	9.37E-08	5.99E-09	2.51E-10	6.24%
20020321	6.00	8.46E-08	1.47E-08	6.17E-10	15.31%
20020321	6.25	6.70E-08	3.16E-08	1.33E-09	32.95%
20020321	6.50	4.26E-08	5.50E-08	2.33E-09	57.30%
20020321	6.75	2.13E-08	7.55E-08	3.21E-09	78.67%
20020321	7.00	8.85E-09	8.74E-08	3.72E-09	91.09%
20020321	7.25	3.34E-09	9.27E-08	3.96E-09	96.63%
20020321	7.50	1.21E-09	9.47E-08	4.04E-09	98.77%
20020321	7.75	4.27E-10	9.55E-08	4.08E-09	99.56%
20020321	8.00	1.50E-10	9.58E-08	4.09E-09	99.84%
ZnT=1e-4					
20020321	5.00	9.97E-05	2.93E-07	1.30E-08	0.31%
20020321	5.25	9.92E-05	7.27E-07	3.56E-08	0.76%
20020321	5.50	9.83E-05	1.57E-06	9.61E-08	1.67%
20020321	5.75	9.70E-05	2.75E-06	2.56E-07	3.01%
20020321	6.00	9.55E-05	3.82E-06	6.75E-07	4.49%
20020321	6.25	9.37E-05	4.47E-06	1.76E-06	6.23%
20020321	6.50	9.06E-05	4.78E-06	4.43E-06	9.21%
20020321	6.75	8.47E-05	4.90E-06	1.02E-05	15.07%
20020321	7.00	7.47E-05	4.95E-06	1.99E-05	24.84%
20020321	7.25	6.20E-05	4.97E-06	3.24E-05	37.37%
20020321	7.50	4.86E-05	4.98E-06	4.54E-05	50.41%
20020321	7.75	3.61E-05	4.99E-06	5.74E-05	62.35%
20020321	8.00	2.53E-05	4.99E-06	6.73E-05	72.27%

MINTEQA2, valid65, Zn-HFO

ZnT=1e-7	pH	m_Zn+2	m_Hfo_wO	m_Hfo_sOZn	%sorbed
1	5.00	9.97E-08	1.32E-11	3.15E-10	0.33%
1	5.25	9.91E-08	3.61E-11	8.62E-10	0.90%
1	5.50	9.76E-08	9.72E-11	2.32E-09	2.42%
1	5.75	9.37E-08	2.54E-10	6.06E-09	6.32%
1	6.00	8.45E-08	6.24E-10	1.49E-08	15.48%
1	6.25	6.67E-08	1.34E-09	3.19E-08	33.24%
1	6.50	4.23E-08	2.34E-09	5.53E-08	57.61%
1	6.75	2.11E-08	3.22E-09	7.57E-08	78.88%
1	7.00	8.75E-09	3.73E-09	8.75E-08	91.20%
1	7.25	3.30E-09	3.96E-09	9.27E-08	96.66%
1	7.50	1.19E-09	4.04E-09	9.47E-08	98.78%
1	7.75	4.21E-10	4.08E-09	9.55E-08	99.56%
1	8.00	1.48E-10	4.09E-09	9.57E-08	99.84%
ZnT=1e-4					
2	5.00	9.97E-05	1.32E-08	2.96E-07	0.31%
2	5.25	9.92E-05	3.61E-08	7.35E-07	0.77%
2	5.50	9.83E-05	9.73E-08	1.59E-06	1.68%
2	5.75	9.69E-05	2.59E-07	2.77E-06	3.02%
2	6.00	9.54E-05	6.83E-07	3.83E-06	4.51%
2	6.25	9.37E-05	1.78E-06	4.48E-06	6.26%
2	6.50	9.06E-05	4.48E-06	4.78E-06	9.26%
2	6.75	8.46E-05	1.03E-05	4.91E-06	15.17%
2	7.00	7.46E-05	2.00E-05	4.95E-06	24.99%
2	7.25	6.18E-05	3.26E-05	4.97E-06	37.55%
2	7.50	4.84E-05	4.56E-05	4.98E-06	50.58%
2	7.75	3.59E-05	5.75E-05	4.99E-06	62.50%
2	8.00	2.51E-05	6.74E-05	4.99E-06	72.39%

PHREEQC, Valid65, Zn-HFO

Excel 97 spreadsheet to calculate sorption %. Electronic file in validation.xls on zip disk at back of this notebook.

Redox Conditions: Stumm and Morgan (1996), Examples 8.2 and 8.4

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Example 8.2 presents three different geochemical problems to calculate electron activity (pe) for Fe and Mn systems open to atmosphere. Simple thermodynamic calculations can be used to calculate pe.

Example 8.2(a). An acid solution with {Fe³⁺} = 10⁻⁵ M; {Fe²⁺} = 10⁻³ M

$$pe = \log K + \frac{\log \{Fe^{3+}\}}{\log \{Fe^{2+}\}} \quad \log K = 13.0 \quad [2]$$

Example 8.2(b). Natural water with pH = 7.5 in equilibrium with atmosphere (Po₂ = 0.22 atm)

$$pe = \frac{1}{2} \log K + \frac{1}{4} \log Po_2 - pH \quad [3]$$

Example 8.2(c). Natural water with pH = 8 in equilibrium with γ-MnO₂

$$pe = \frac{1}{2} \log K - 2pH + \frac{1}{2} \log \{Mn^{2+}\} \quad [4]$$

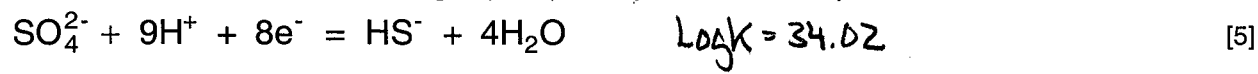
Equilibrium constants (log K) were modified in the MINTEQA2, Version 4.02 input files to match the values provided in Stumm and Morgan (1996). Formation of ferric- and ferrous-hydroxy species was suppressed in the MINTEQA2, Version 4.02 simulation of Example 8.2(a) to match the geochemical equilibrium model used in Stumm and Morgan (1996). Also, a dilute NaCl (10⁻³ M) solution was added to the natural water in Example 8.2(b) to avoid problems with creating a singular matrix in the MINTEQA2, Version 4.02 simulation. Comparison of model results in Table 7 show that there are slight differences in calculated pe values. In Stumm and Morgan (1996), the assumption is that the activity coefficients for all of the components are unity (γ = 1.0), while MINTEQA2, Version 4.02 uses the Davies equation to correct for ionic strength effects. Incorporating activity coefficients calculated with the Davies equation improves the agreement significantly.

Table 7. Calculated electron activity (pe) for Example 8.2 in Stumm and Morgan (1996).

Geochemical System	pe calculation		
	MINTEQA2, Version 4.02	Hand Calculation (γ = 1.0)	Hand Calculation (γ from Davies equation)
Example 8.2(a) (Equation[2])			
{Fe ²⁺ } = 10 ⁻³ M {Fe ³⁺ } = 10 ⁻⁵ M	10.891	11.01	10.89
Example 8.2(b) (Equation[3])			
pH = 7.5 Po ₂ = 0.22 atm	13.106	12.94	13.106
Example 8.2(c) (Equation[4])			
{Mn ²⁺ } = 10 ⁻⁵ M Equilibrium with γ-MnO ₂	6.925	6.92	6.925

Example 8.4 (Stumm and Morgan, 1996) calls for a simple calculation of the speciation of HS⁻ and SO₄²⁻ as a function of pe, with pH = 10, and {HS⁻} + {SO₄²⁻} = 10⁻⁴ M. Aqueous speciation log K values for the

reaction in Equation [5] were modified in the MINTEQA2, Version 4.02 input file to match the values (log K = 34.02) provided in Stumm and Morgan (1996). Based on the redox equilibrium reaction



pe can be expressed in terms of pH and component activity

$$pe = \frac{1}{8} (\log K + pH + \log [SO_4^{2-}] + \log [HS^-]) \quad [6]$$

The results from MINTEQA2, Version 4.02 are compared with hand calculations (Equation [6]).

Table 8. Calculated HS⁻-SO₄²⁻ speciation as a function of electron activity (pe) for Example 8.4 in Stumm and Morgan (1996). Calculations in spreadsheet on next page (100) of this SO.

pe	MINTEQA2, Version 4.02		Hand Calculation (γ = 1.0)		Hand Calculation (γ from Davies equation)	
	mHS ⁻ (molal)	mSO ₄ ²⁻ (molal)	mHS ⁻ (molal)	mSO ₄ ²⁻ (molal)	mHS ⁻ (molal)	mSO ₄ ²⁻ (molal)
-9.0	1.00E-4	9.89E-21	1.00E-4	9.55E-21	1.00E-4	9.89E-21
-8.8	1.00E-4	3.94E-19	1.00E-4	3.80E-19	1.00E-4	3.94E-19
-8.6	1.00E-4	1.57E-17	1.00E-4	1.51E-17	1.00E-4	1.57E-17
-8.4	1.00E-4	6.24E-16	1.00E-4	6.03E-16	1.00E-4	6.24E-16
-8.2	1.00E-4	2.48E-14	1.00E-4	2.40E-14	1.00E-4	2.48E-14
-8.0	1.00E-4	9.89E-13	1.00E-4	9.55E-13	1.00E-4	9.89E-13
-7.8	1.00E-4	3.94E-11	1.00E-4	3.80E-11	1.00E-4	3.94E-11
-7.6	1.00E-4	1.57E-9	1.00E-4	1.51E-9	1.00E-4	1.57E-9
-7.4	9.99E-4	6.24E-8	9.99E-4	6.02E-8	9.99E-4	6.24E-8
-7.2	9.76E-5	2.43E-6	9.77E-5	2.34E-6	9.76E-5	2.43E-6
-7.0	5.00E-5	5.00E-5	5.12E-5	4.88E-5	5.00E-5	5.00E-5
-6.8	2.43E-6	9.76E-5	2.56E-6	9.74E-5	2.43E-6	9.76E-5
-6.6	6.25E-8	9.99E-5	6.60E-8	9.99E-5	6.25E-8	9.99E-5
-6.4	1.57E-9	1.00E-4	1.66E-9	1.00E-4	1.57E-9	1.00E-4
-6.2	3.95E-11	1.00E-4	4.17E-11	1.00E-4	3.95E-11	1.00E-4
-6.0	9.91E-13	1.00E-4	1.05E-12	1.00E-4	9.91E-13	1.00E-4
-5.8	2.49E-14	1.00E-4	2.63E-14	1.00E-4	2.49E-14	1.00E-4
-5.6	6.26E-16	1.00E-4	6.61E-16	1.00E-4	6.26E-16	1.00E-4
-5.4	1.57E-17	1.00E-4	1.66E-17	1.00E-4	1.57E-17	1.00E-4
-5.2	3.95E-17	1.00E-4	4.17E-17	1.00E-4	3.95E-17	1.00E-4
-5.0	9.91E-21	1.00E-4	1.05E-20	1.00E-4	9.91E-21	1.00E-4

Comparison of the results in Table 8 show that there is very good agreement. MINTEQA2, Version 4.02 correctly predicts the crossover point (pe = -7.0) where the concentrations of HS⁻ and SO₄²⁻ are equal. There is a slight discrepancy when unity activity coefficients (γ = 1) were assumed for the hand calculations. Performing the hand calculations with the activity coefficients derived for each pe value by MINTEQA2, Version 4.02 using the Davies equation results in a match to the HS⁻ and SO₄²⁻ concentrations predicted by MINTEQA2, Version 4.02 to at least three significant figures (Table 8). Concentration-pe plots comparing MINTEQA2, Version 4.02 and hand calculation results (Figure 3)

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[illegible]

Redox, Ex. 8.4, Stumm & Morgan 96

demonstrate the excellent agreement, indicating that MINTEQA2, Version 4.02 correctly implements redox equilibria reactions.

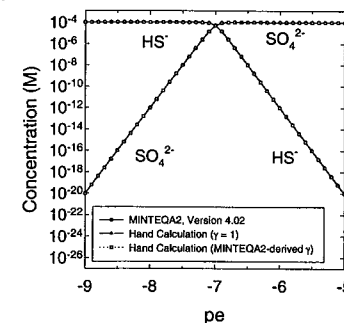


Figure 3. Calculated HS^- – SO_4^{2-} speciation as a function of electron activity (pe) for Example 8.4 in Stumm and Morgan (1996).

reaction (ΔH_f°) to correct equilibrium constants for the effects of temperature and also use a polynomial expression to correct equilibrium constants for the effects of temperature:

$$\text{Log } K_T = A_1 + A_2T + \frac{A_3}{T} + A_4\text{Log}(T) + A_5T^2 + \frac{A_6}{T^2} + A_7\sqrt{T} \quad [8]$$

where K_T is the equilibrium constant at a given temperature T in Kelvin.

In conducting this validation exercise, the same thermodynamic constants and polynomial expressions were used for anhydrite and gypsum.

Comparing the results in Table 9 and Figure 4(a) shows a slight discrepancy between the SI values calculated by MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2. This discrepancy is likely due to differences in the aqueous speciation and differences in how the two codes calculate the activity of water. The PHREEQC, Version 2.4.2 database includes the aqueous species CaHSO_4^+ , which is not included in the MINTEQA2, Version 4.02 database. In addition, there are slight differences in the equilibrium constants and analytic temperature effect corrections for the aqueous species $\text{CaSO}_4(\text{aq})$, HSO_4^- , and CaOH^+ . In calculating the concentrations of individual ionic species to correct the activity of water, MINTEQA2, Version 4.02 includes the concentrations of the two minerals anhydrite and gypsum (1.0 moles of each). This gives a larger correction to unit activity ($a_{\text{H}_2\text{O}} = 0.949$), and results in a constant variation in the calculated SI values. If, however, gypsum or anhydrite is assigned to be present in an infinite amount in the MINTEQA2, Version 4.02 input file, then the activity correction for water does not include the minerals, and the agreement with PHREEQC, Version 2.4.2 is much better (Figure 4b).

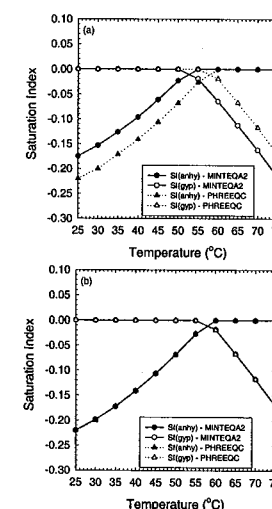


Figure 4. Comparison of saturation indexes (SI) calculated by MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 for anhydrite and gypsum as a function of temperature. (a) 1.0 moles anhydrite + 1 mol gypsum; (b) infinite gypsum (25° to 55 °C), infinite anhydrite (60° to 75 °C).

Table 9. Comparison of saturation indexes (SI) calculated by MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2 for anhydrite and gypsum as a function of temperature.

T(°C)	MINTEQA2, Version 4.02			PHREEQC, Version 2.4.2		
	pH	SI(Anhy)	SI(Gyp)	pH	SI(Anhy)	SI(Gyp)
25	7.08	-0.175	0.000	7.07	-0.220	0.000
30	7.01	-0.153	0.000	7.00	-0.200	0.000
35	6.94	-0.126	0.000	6.94	-0.171	0.000
40	6.88	-0.096	0.000	6.88	-0.141	0.000
45	6.82	-0.061	0.000	6.82	-0.106	0.000
50	6.76	-0.023	0.000	6.77	-0.068	0.000
55	6.70	0.000	-0.019	6.72	-0.026	0.000
60	6.65	0.000	-0.064	6.67	0.000	-0.019
65	6.59	0.000	-0.112	6.62	0.000	-0.067
70	6.54	0.000	-0.162	6.57	0.000	-0.117
75	6.49	0.000	-0.216	6.53	0.000	-0.170

Modified Database: Neptunium and Uranium Aqueous Speciation

The main code function to be checked in this section of the test plan is to ensure that the MINTEQA2, Version 4.02 database modified to include NEA radionuclide thermodynamic data is correct and produces reasonable results. If thermodynamic data are the same, different geochemical equilibrium speciation codes should produce similar results. The most straightforward way to test this is to compare aqueous speciation results from several different codes. This approach has been used before (Turner, 1993; Turner et al., 1993) to examine the modified MINTEQA2, Version 3.11/3.12 database.

Speciation checks for uranium and neptunium were performed using MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2. Identical thermodynamic data from the Nuclear Energy Agency (NEA) thermodynamic database for neptunium and uranium (Grenthe et al., 1992; Lemire et al., 2001) were used to examine speciation as a function of pH under atmospheric CO₂ (10^{-3.5} atm) and O₂ (10^{-0.66} atm) conditions. Temperature were fixed at 25 °C (298 K). Low concentrations were used to avoid the complications of precipitation of pure phases, and the redox couples were allowed to establish the distribution among the different oxidation states of Np and U. The focus of the check is the CNWRA-modifications to the MINTEQA2, Version 4.02 database, and very simple solutions of 0.1 M NaNO₃ were used to minimize the effects of major ions such as Ca²⁺, Mg²⁺.

Comparison of the predicted speciation indicates good agreement between PHREEQC, Version 2.4.2 and MINTEQA2, Version 4.02 for Np and U (Figure 5). With atmospheric oxygen (Po₂ = 10^{-0.66} atm), both codes calculate similar pe values for the system over the pH range. Not only is there good agreement with aqueous speciation as a function of pH, but there is also good agreement between the two codes in simulating the changing dominance of different oxidation states for redox sensitive elements like Np and U.

For example, both codes predict a change from Np(V)-dominance at pH < 8 to Np(VI)-dominance of NpO₂(CO₃)₂²⁻ and NpO₂(CO₃)₃²⁻ at pH > 8. There are minor differences that are most likely due to activity coefficient calculation. Also, there are slight differences in calculated ionic strength due to differences in how pH is determined. Finally, there are differences in how the two codes handle the activity of the neutral species UO₂(OH)₂(aq) and UO₂CO₃(aq). While PHREEQC, Version 2.4.2 assigns γ = 1 to neutral species, MINTEQA2, Version 4.02 corrects for ionic strength effects using the relationship

$$\log \gamma = 0.1(I.S.)$$
 [9]

where I.S. is the ionic strength of the solution. For the ionic strength used in the simulation (0.1 m NaNO₃), the activity coefficient for UO₂(OH)₂(aq) and UO₂CO₃(aq) is 1.02.

Despite these small differences, the agreement is excellent for a system open to atmosphere over the range in pH, even for very complicated redox-sensitive aqueous systems such as neptunium and uranium. This indicates that the databases are correctly formatted for both MINTEQA2, Version 4.02 and PHREEQC, Version 2.4.2, both codes are correctly reading the modified databases, and both codes are calculating aqueous speciation in a similar fashion.

REFERENCES

Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems*. Version 3.0 User's Manual. EPA/600/3-91/021. Athens, Georgia: U.S. Environmental Protection Agency. 1991.

Blount, C.W. Barite solubilities and thermodynamic quantities up to 300 °C and 1400 bars. *American Mineralogist* 272: 438-475. 1977.

CNWRA. *Technical Operating Procedure (TOP-18): Development and Control of Scientific and Engineering Software, Revision 8, Change 0 (October 5, 2001)*. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 2001.

Dzombak, D.A. and Morel, F.M.M. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons. 1990.

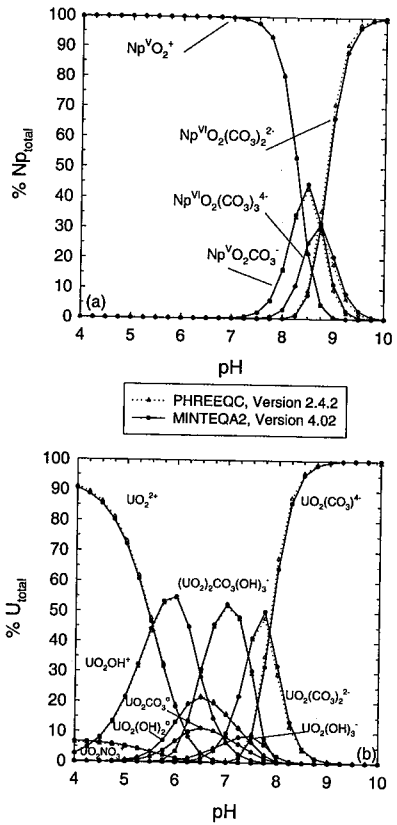


Figure 5. Aqueous speciation predicted by MINTEQA2, Version 4.02 (solid line, filled circles) and PHREEQC, Version 2.4.2 (dotted line, open triangles) as a function of pH. T = 25 °C, PCO₂ = 10^{-3.5} atm, PO₂ = 10^{-0.66} atm, (a) Neptunium speciation with Np_{total} = 10⁻⁷ m. Neptunium oxidation states change with pH and both Np(V)-species and Np(VI)-species are shown; (b) Uranium speciation with U_{total} = 10⁻⁷ m. Uranium speciation is dominated by U(VI) over entire pH range, and only U(VI) species are shown.

4/30/2002

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Grenthe, I., J. Fuger, R. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. *Chemical Thermodynamics Series, Volume 1: Chemical Thermodynamics of Uranium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1992.

Langmuir, D. *Aqueous Environmental Geochemistry*. Englewood Cliffs, New Jersey: Prentice-Hall, Inc. 1997.

Lemire, R.J., J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, and H. Wanner. *Chemical Thermodynamics Series, Volume 4: Chemical Thermodynamics of Neptunium and Plutonium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 2001.

Parkhurst, D.L. and C.A.J. Appelo. *User's Guide to PHREEQC (Version 2)—A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, And Inverse Geochemical Calculations*. Water-Resources Investigations Report 99-4259. Denver, Colorado: U.S. Geological Survey. 1999.

Rard, J.A., M.H. Rand, G. Anderegg, and H. Wanner. *Chemical Thermodynamics Series, Volume 3: Chemical Thermodynamics of Technetium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1999.

Richardson, S.M. and H.Y. McSween, Jr. *Geochemistry: Pathways and Processes*. Englewood Cliffs, New Jersey: Prentice-Hall, Inc. 1989.

Silva, R.J., G. Bidoglio, M.H. Rand, P.B. Robouch, H. Wanner, and I. Puigdomenich. *Chemical Thermodynamics Series, Volume 2: Chemical Thermodynamics of Americium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1995.

Stumm, W. and J.J. Morgan. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. 3rd Edition. New York, New York: Wiley-Interscience. 1996.

Turner, D.R., T. Griffin, and T.B. Dietrich. Radionuclide sorption modeling using the MINTEQA2 speciation code. *Scientific Basis for Nuclear Waste Management—XVI*. C. Interrante and R. Pabalan, eds. Symposium Proceedings. Pittsburgh, Pennsylvania: Material Research Society. pp. 783-789. 1993.

Turner, D.R. *Mechanistic Approaches to Radionuclide Sorption Modeling*. CNWRA 93-019. San Antonio, Texas: Center for Nuclear Waste Regulatory Analyses. 1993.

Turner, D.R. *Software Validation Test Plan for MINTEQA2, Version 4.02*. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 2001.

U.S. Environmental Protection Agency. "MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999a.

U.S. Environmental Protection Agency. "Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999b.

$$\text{Np(VI)}$$
$$Np(11)$$

pH	pe	m_NpO2+	%_NpO2+	m_NpO2OI	%_NpO2OI	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2C	%_NpO2C	m_NpO2(CO3)3-4	
4.00	16.61	9.98E-08	99.77	3.80E-15	0.00	2.49E-23	0.00	2.04E-16	0.00	1.24E-27	0.00	1.36E-40	0.00	1.01E-38	0.00	3.66E-21	0.00	1.13E-30	0.00	99.77	
4.25	16.36	9.99E-08	99.87	6.77E-15	0.00	7.88E-23	0.00	6.47E-16	0.00	1.24E-26	0.00	4.29E-39	0.00	1.01E-37	0.00	2.06E-20	0.00	2.01E-29	0.00	99.87	
4.50	16.11	9.99E-08	99.92	1.20E-14	0.00	2.49E-22	0.00	2.05E-15	0.00	1.24E-25	0.00	1.36E-37	0.00	1.01E-36	0.00	1.16E-19	0.00	3.58E-28	0.00	99.92	
4.75	15.86	1.00E-07	99.95	2.14E-14	0.00	7.89E-22	0.00	6.48E-15	0.00	1.24E-24	0.00	4.29E-36	0.00	1.01E-35	0.00	6.51E-19	0.00	6.37E-27	0.00	99.95	
5.00	15.61	1.00E-07	99.97	3.81E-14	0.00	2.49E-21	0.00	2.05E-14	0.00	1.24E-23	0.00	1.36E-34	0.00	1.01E-34	0.00	3.66E-18	0.00	1.13E-25	0.00	99.97	
5.25	15.36	1.00E-07	99.98	6.78E-14	0.00	7.89E-21	0.00	6.48E-14	0.00	1.24E-22	0.00	4.29E-33	0.00	1.01E-33	0.00	2.06E-17	0.00	2.02E-24	0.00	99.98	
5.50	15.11	1.00E-07	99.98	1.21E-13	0.00	2.49E-20	0.00	2.05E-13	0.00	1.24E-21	0.00	1.36E-31	0.00	1.01E-32	0.00	1.16E-16	0.00	3.58E-23	0.00	99.98	
5.75	14.86	1.00E-07	99.99	2.14E-13	0.00	7.89E-20	0.00	6.48E-13	0.00	1.24E-20	0.00	4.29E-30	0.00	1.01E-31	0.00	6.52E-16	0.00	6.37E-22	0.00	99.99	
6.00	14.61	1.00E-07	99.99	3.81E-13	0.00	2.50E-19	0.00	2.05E-12	0.00	1.24E-19	0.00	1.36E-28	0.00	1.01E-30	0.00	3.66E-15	0.00	1.13E-20	0.00	99.99	
6.25	14.36	1.00E-07	99.98	6.78E-13	0.00	7.89E-19	0.00	6.48E-12	0.01	1.24E-18	0.00	4.29E-27	0.00	1.01E-29	0.00	2.06E-14	0.00	2.02E-19	0.00	99.99	
6.50	14.11	1.00E-07	99.97	1.21E-12	0.00	2.49E-18	0.00	2.05E-11	0.02	1.24E-17	0.00	1.36E-25	0.00	1.01E-28	0.00	1.16E-13	0.00	3.58E-18	0.00	99.99	
6.75	13.86	9.99E-08	99.92	2.14E-12	0.00	7.88E-18	0.00	6.47E-11	0.06	1.24E-16	0.00	4.29E-24	0.00	1.01E-27	0.00	6.51E-13	0.00	6.37E-17	0.00	99.99	
7.00	13.61	9.98E-08	99.78	3.80E-12	0.00	2.49E-17	0.00	2.04E-10	0.20	1.23E-15	0.00	1.35E-22	0.00	1.01E-26	0.00	3.66E-12	0.00	1.13E-15	0.00	99.99	
7.25	13.36	9.93E-08	99.31	6.73E-12	0.01	7.84E-17	0.00	6.44E-10	0.64	1.23E-14	0.00	4.26E-21	0.00	1.00E-25	0.00	2.05E-11	0.02	2.00E-14	0.00	99.98	
7.50	13.11	9.79E-08	97.85	1.18E-11	0.01	2.44E-16	0.00	2.01E-09	2.01	1.21E-13	0.00	1.33E-19	0.00	9.89E-25	0.00	1.13E-10	0.11	3.51E-13	0.00	99.96	
7.75	12.86	9.33E-08	93.29	2.00E-11	0.02	7.36E-16	0.00	6.05E-09	6.05	1.16E-12	0.00	4.01E-18	0.00	9.44E-24	0.00	6.08E-10	0.61	5.96E-12	0.01	99.97	
8.00	12.61	8.04E-08	80.41	3.06E-11	0.03	2.01E-15	0.00	1.65E-08	16.47	9.96E-12	0.01	1.10E-16	0.00	8.15E-23	0.00	2.95E-09	2.95	9.15E-11	0.09	99.96	
8.25	12.36	5.33E-08	53.27	3.61E-11	0.04	4.20E-15	0.00	3.45E-08	34.52	6.61E-11	0.07	2.31E-15	0.00	5.41E-22	0.00	1.10E-08	10.99	1.08E-09	1.08	99.96	
8.50	12.11	2.18E-08	21.80	2.63E-11	0.03	5.44E-15	0.00	4.47E-08	44.66	2.71E-10	0.27	3.01E-14	0.00	2.23E-21	0.00	2.53E-08	25.31	7.90E-09	7.90	99.97	
8.75	11.86	4.84E-09	4.84	1.04E-11	0.01	3.82E-15	0.00	3.14E-08	31.35	6.06E-10	0.61	2.15E-13	0.00	4.99E-21	0.00	3.17E-08	31.66	3.15E-08	31.53	99.95	
9.00	11.61	5.61E-10	0.56	2.13E-12	0.00	1.40E-15	0.00	1.15E-08	11.50	7.11E-10	0.71	8.17E-13	0.00	5.92E-21	0.00	2.07E-08	20.74	6.65E-08	66.49	100.00	
9.25	11.36	3.99E-11	0.04	2.68E-13	0.00	3.15E-16	0.00	2.59E-09	2.59	5.19E-10	0.52	1.99E-12	0.00	4.43E-21	0.00	8.38E-09	8.38	8.85E-08	88.47	100.00	
9.50	11.11	2.17E-12	0.00	2.57E-14	0.00	5.42E-17	0.00	4.45E-10	0.45	3.02E-10	0.30	4.16E-12	0.00	2.72E-21	0.00	2.63E-09	2.63	9.66E-08	96.62	100.00	
9.75	10.86	9.52E-14	0.00	1.95E-15	0.00	7.51E-18	0.00	6.17E-11	0.06	1.53E-10	0.15	8.95E-12	0.01	1.57E-21	0.00	6.84E-10	0.68	9.91E-08	99.10	100.01	
10.00	10.61	3.49E-15	0.00	1.20E-16	0.00	8.70E-19	0.00	7.14E-12	0.01	7.07E-11	0.07	2.08E-11	0.02	8.89E-22	0.00	1.54E-10	0.15	9.98E-08	99.75	100.00	

1.20E-16

U speciation, MINTEQA2, 4.0.2

pH	pe	m_UO2+2	%_UO2+2	m_UO2NO	%_UO2NO	m_UO2CO3	%_UO2CO3	m_UO2(Cr)	%_UO2(Cr)	m_UO2(Cr)_UO2(OH)	%_UO2(Cr)_UO2(OH)	m_UO2(OH)	%_UO2(OH)	m_UO2(OH)_UO2(OH)	%_UO2(OH)_UO2(OH)	m_UO2(OH)_UO2(OH)_UO2(OH)	%_UO2(OH)_UO2(OH)_UO2(OH)	m_UO2(OH)_UO2(OH)_UO2(OH)_UO2(OH)	%_UO2(OH)_UO2(OH)_UO2(OH)_UO2(OH)	Total						
4.00	16.61	9.06E-08	90.56	6.72E-09	6.72	3.46E-12	0.00	3.98E-18	0.00	7.96E-26	0.00	4.46E-18	0.00	2.71E-09	2.71	6.52E-12	0.01	2.69E-15	0.00	8.93E-25	0.00	7.26E-13	0.00	1.35E-18	0.00	100.00
4.25	16.36	8.87E-08	88.67	6.58E-09	6.58	1.07E-11	0.01	3.90E-17	0.00	7.46E-24	0.00	7.60E-17	0.00	4.72E-09	4.72	2.02E-11	0.02	1.48E-14	0.00	8.75E-24	0.00	2.20E-12	0.00	2.29E-17	0.00	100.00
4.50	16.11	8.55E-08	85.46	6.34E-09	6.34	3.26E-11	0.03	3.78E-16	0.00	7.51E-23	0.00	1.26E-15	0.00	8.09E-09	8.09	6.15E-11	0.06	8.04E-14	0.00	8.43E-23	0.00	6.47E-12	0.01	3.60E-16	0.00	100.00
4.75	15.86	8.02E-08	80.22	5.95E-09	5.95	6.69E-11	0.10	3.53E-15	0.00	2.23E-21	0.00	1.97E-14	0.00	1.35E-08	13.51	1.83E-10	0.18	4.24E-13	0.00	7.91E-22	0.00	1.80E-11	0.04	5.30E-15	0.00	100.00
5.00	15.61	7.22E-08	72.15	5.35E-09	5.35	2.76E-10	0.28	3.17E-14	0.00	6.34E-20	0.00	2.83E-13	0.00	2.16E-08	21.60	5.20E-10	0.52	2.15E-12	0.00	7.12E-21	0.00	4.61E-11	0.09	6.85E-14	0.00	99.99
5.25	15.36	6.08E-08	60.78	4.51E-09	4.51	7.34E-10	0.73	2.67E-13	0.00	1.69E-18	0.00	3.57E-12	0.01	3.24E-08	32.36	1.38E-09	1.38	1.02E-11	0.01	6.00E-20	0.00	1.04E-10	0.21	7.28E-13	0.00	99.99
5.50	15.11	4.67E-08	46.67	3.46E-09	3.46	1.78E-09	1.78	2.05E-12	0.00	4.10E-17	0.00	3.74E-11	0.07	4.42E-08	44.19	3.36E-09	3.36	4.39E-11	0.04	4.60E-19	0.00	1.93E-10	0.39	5.87E-12	0.00	99.99
5.75	14.86	3.17E-08	31.72	2.35E-09	2.35	3.83E-09	3.83	1.39E-11	0.01	8.81E-16	0.00	3.08E-10	0.62	5.34E-08	53.41	7.22E-09	7.22	1.68E-10	0.17	1.33E-18	0.00	2.82E-10	0.56	3.27E-11	0.10	99.99
6.00	14.61	1.83E-08	18.33	1.36E-09	1.36	7.00E-09	7.00	8.06E-11	0.08	1.61E-14	0.00	1.83E-09	3.65	5.49E-08	54.89	1.32E-08	13.20	5.45E-10	0.55	1.81E-17	0.00	2.98E-10	0.60	1.12E-10	0.34	99.99
6.25	14.36	8.44E-09	8.44	6.26E-10	0.63	1.02E-08	10.19	3.71E-10	0.37	2.34E-13	0.00	6.89E-09	13.78	4.50E-08	44.96	1.92E-08	19.23	1.41E-09	1.41	8.33E-17	0.00	2.00E-10	0.40	1.95E-10	0.59	100.00
6.50	14.11	2.99E-09	2.99	2.22E-10	0.22	1.14E-08	11.42	1.32E-09	1.32	2.63E-12	0.00	1.54E-08	30.76	2.83E-08	28.32	2.15E-08	21.54	2.81E-09	2.81	2.95E-16	0.00	7.93E-11	0.16	1.54E-10	0.46	100.00
6.75	13.86	8.85E-10	0.86	6.42E-11	0.06	1.04E-08	10.44	3.80E-09	3.80	2.40E-11	0.02	2.29E-08	45.72	1.46E-08	14.56	1.97E-08	19.70	4.57E-09	4.57	6.53E-16	0.00	2.10E-11	0.04	6.64E-11	0.20	99.99
7.00	13.61	2.20E-10	0.22	1.63E-11	0.02	8.39E-09	8.39	9.66E-09	9.66	1.93E-10	0.19	2.63E-08	52.50	6.58E-09	6.58	1.58E-08	15.83	6.54E-09	6.54	2.17E-15	0.00	4.28E-12	0.01	1.94E-11	0.06	100.00
7.25	13.36	4.99E-11	0.05	3.70E-12	0.00	6.03E-09	6.03	2.20E-08	21.95	1.39E-09	1.39	2.41E-09	48.18	2.66E-09	2.66	1.14E-08	11.37	3.85E-09	8.35	4.93E-15	0.00	6.99E-13	0.00	4.04E-12	0.01	99.99
7.50	13.11	9.40E-12	0.01	6.97E-13	0.00	3.59E-09	3.59	4.13E-08	41.31	8.26E-09	8.26	1.52E-09	30.34	8.90E-10	0.89	6.77E-09	6.77	8.84E-09	8.84	9.27E-15	0.00	7.82E-14	0.00	4.78E-13	0.00	100.00
7.75	12.86	1.14E-12	0.00	8.46E-14	0.00	1.38E-09	1.38	5.01E-08	50.14	3.17E-08	31.72	3.97E-09	7.95	1.92E-10	0.19	2.60E-09	2.60	6.03E-09	6.03	1.13E-14	0.00	3.64E-15	0.00	1.52E-14	0.00	100.00
8.00	12.61	7.31E-14	0.00	5.42E-15	0.00	2.79E-10	0.28	3.21E-08	32.11	6.43E-08	64.31	2.90E-10	0.58	2.19E-11	0.02	5.26E-10	0.53	2.17E-09	2.17	7.21E-15	0.00	4.72E-17	0.00	7.09E-17	0.00	100.00
8.25	12.36	3.08E-15	0.00	2.28E-16	0.00	3.71E-11	0.04	1.35E-08	13.52	8.58E-08	85.84	9.12E-12	0.02	1.64E-12	0.00	6.99E-11	0.07	5.14E-10	0.51	3.04E-15	0.00	2.65E-19	0.00	9.40E-20	0.00	100.00
8.50	12.11	1.07E-16	0.00	7.94E-18	0.00	4.09E-12	0.00	4.72E-09	4.72	9.52E-08	95.17	1.97E-13	0.00	1.02E-13	0.00	7.71E-12	0.01	1.01E-10	0.10	1.06E-15	0.00	1.02E-21	0.00	7.09E-23	0.00	100.00
8.75	11.86	3.48E-18	0.00	2.57E-19	0.00	4.18E-13	0.00	1.53E-09	1.53	9.85E-08	98.45	3.67E-15	0.00	5.84E-15	0.00	7.88E-13	0.00	1.83E-11	0.02	3.44E-16	0.00	3.38E-24	0.00	4.27E-26	0.00	100.00
9.00	11.61	1.09E-19	0.00	8.02E-21	0.00	4.12E-14	0.00	4.81E-10	0.48	9.95E-08	99.52	6.37E-17	0.00	3.25E-16	0.00	7.78E-14	0.00	3.22E-12	0.00	1.08E-16	0.00	1.05E-26	0.00	2.31E-29	0.00	100.00
9.25	11.36	3.33E-21	0.00	2.41E-22	0.00	3.92E-15	0.00	1.47E-10	0.15	9.99E-08	99.85	1.03E-18	0.00	1.74E-17	0.00	7.38E-15	0.00	5.47E-13	0.00	3.29E-17	0.00	3.03E-29	0.00	1.12E-32	0.00	100.00
9.50	11.11	9.58E-23	0.00	6.71E-24	0.00	3.44E-16	0.00	4.21E-11	0.04	1.00E-07	99.96	1.43E-20	0.00	8.69E-19	0.00	6.48E-16	0.00	8.63E-14	0.00	9.46E-18	0.00	7.68E-32	0.00	4.34E-36	0.00	100.00
9.75	10.86	2.43E-24	0.00	1.58E-25	0.00	2.54E-17	0.00	1.07E-11	0.01	1.00E-07	99.99	1.44E-22	0.00	3.71E-20	0.00	4.79E-17	0.00	1.17E-14	0.00	2.40E-18	0.00	1.46E-34	0.00	1.03E-39	0.00	100.00
10.00	10.61	5.43E-26	0.00	3.15E-27	0.00	1.55E-18	0.00	2.39E-12	0.01	1.00E-07	100.00	1.04E-24	0.00	1.35E-21	0.00	2.93E-18	0.00	1.34E-15	0.00	5.36E-19	0.00	2.04E-37	0.00	1.48E-43	0.00	100.00

Sturm

4/30/2002
SRI

Np(VI)
 \downarrow

$$\text{Np(VI)} \downarrow$$

pH	pe	m_NpO2+	%_NpO2+	m_NpO2O1	%_NpO2O1	m_NpO2(C	%_NpO2(C	m_NpO2C(%_NpO2C(m_NpO2(C	%_NpO2(C	m_NpO2(C	%_NpO2(C	m_NpO2(C	%_NpO2(C	m_NpO2(C	%_NpO2(C	m_NpO2(C	%_NpO2(C	(CO3)3-4	
4.00	16.6157	9.98E-08	99.77	3.83E-15	0.00	2.49E-23	0.00	1.98E-16	0.00	1.31E-27	0.00	1.76E-40	0.00	1.18E-34	0.00	3.66E-21	0.00	1.31E-30	0.00		99.7
4.25	16.3657	9.99E-08	99.87	6.83E-15	0.00	7.88E-23	0.00	6.28E-16	0.00	1.31E-26	0.00	5.57E-39	0.00	2.10E-33	0.00	2.06E-20	0.00	2.33E-29	0.00		99.8
4.50	16.1157	9.99E-08	99.92	1.21E-14	0.00	2.49E-22	0.00	1.99E-15	0.00	1.31E-25	0.00	1.76E-37	0.00	3.73E-32	0.00	1.16E-19	0.00	4.15E-28	0.00		99.9
4.75	15.8657	1.00E-07	99.95	2.16E-14	0.00	7.89E-22	0.00	6.29E-15	0.00	1.31E-24	0.00	5.58E-36	0.00	6.64E-31	0.00	6.52E-19	0.00	7.38E-27	0.00		99.9
5.00	15.6157	1.00E-07	99.97	3.84E-14	0.00	2.49E-21	0.00	1.99E-14	0.00	1.31E-23	0.00	1.76E-34	0.00	1.18E-29	0.00	3.66E-18	0.00	1.31E-25	0.00		99.9
5.25	15.3657	1.00E-07	99.98	6.83E-14	0.00	7.89E-21	0.00	6.29E-14	0.00	1.31E-22	0.00	5.58E-33	0.00	2.10E-28	0.00	2.06E-17	0.00	2.33E-24	0.00		99.9
5.50	15.1157	1.00E-07	99.98	1.22E-13	0.00	2.49E-20	0.00	1.99E-13	0.00	1.31E-21	0.00	1.76E-31	0.00	3.74E-27	0.00	1.16E-16	0.00	4.15E-23	0.00		99.9
5.75	14.8657	1.00E-07	99.99	2.16E-13	0.00	7.89E-20	0.00	6.29E-13	0.00	1.31E-20	0.00	5.58E-30	0.00	6.64E-26	0.00	6.52E-16	0.00	7.38E-22	0.00		99.9
6.00	14.6157	1.00E-07	99.99	3.84E-13	0.00	2.49E-19	0.00	1.99E-12	0.00	1.31E-19	0.00	1.76E-28	0.00	1.18E-24	0.00	3.67E-15	0.00	1.31E-20	0.00		99.9
6.25	14.3657	1.00E-07	99.98	6.83E-13	0.00	7.89E-19	0.00	6.29E-12	0.01	1.31E-18	0.00	5.58E-27	0.00	2.10E-23	0.00	2.06E-14	0.00	2.33E-19	0.00		99.9
6.50	14.1157	1.00E-07	99.97	1.22E-12	0.00	2.49E-18	0.00	1.99E-11	0.02	1.31E-17	0.00	1.77E-25	0.00	3.74E-22	0.00	1.16E-13	0.00	4.15E-18	0.00		99.9
6.75	13.8657	9.99E-08	99.92	2.16E-12	0.00	7.88E-18	0.00	6.28E-11	0.06	1.31E-16	0.00	5.58E-24	0.00	6.64E-21	0.00	6.51E-13	0.00	7.38E-17	0.00		99.9
7.00	13.6157	9.98E-08	99.78	3.83E-12	0.00	2.49E-17	0.00	1.98E-10	0.20	1.31E-15	0.00	1.76E-22	0.00	1.18E-19	0.00	3.66E-12	0.00	1.31E-15	0.00		99.9
7.25	13.3657	9.93E-08	99.33	6.79E-12	0.01	7.84E-17	0.00	6.25E-10	0.62	1.30E-14	0.00	5.56E-21	0.00	2.09E-18	0.00	2.05E-11	0.02	2.32E-14	0.00		99.9
7.50	13.1157	9.79E-08	97.91	1.19E-11	0.01	2.44E-16	0.00	1.95E-09	1.95	1.28E-13	0.00	1.74E-19	0.00	3.67E-17	0.00	1.14E-10	0.11	4.08E-13	0.00		99.9
7.75	12.8658	9.35E-08	93.46	2.02E-11	0.02	7.37E-16	0.00	5.88E-09	5.88	1.23E-12	0.00	5.26E-18	0.00	6.24E-16	0.00	6.10E-10	0.61	6.93E-12	0.01		99.9
8.00	12.6158	8.08E-08	80.78	3.10E-11	0.03	2.02E-15	0.00	1.61E-08	16.06	1.06E-11	0.01	1.45E-16	0.00	9.63E-15	0.00	2.97E-09	2.97	1.07E-10	0.11		99.9
8.25	12.3658	5.37E-08	53.70	3.67E-11	0.04	4.24E-15	0.00	3.38E-08	33.77	7.10E-11	0.07	3.07E-15	0.00	1.15E-13	0.00	1.11E-08	11.11	1.27E-09	1.27		99.9
8.50	12.1158	2.18E-08	21.75	2.64E-11	0.03	5.43E-15	0.00	4.32E-08	43.25	2.89E-10	0.29	4.02E-14	0.00	8.36E-13	0.00	2.54E-08	25.36	9.29E-09	9.29		99.9
8.75	11.8659	4.58E-09	4.58	9.87E-12	0.01	3.62E-15	0.00	2.88E-08	28.82	6.18E-10	0.62	2.79E-13	0.00	3.22E-12	0.00	3.02E-08	30.21	3.57E-08	35.75		99.9
9.00	11.616	4.85E-10	0.48	1.85E-12	0.00	1.21E-15	0.00	9.64E-09	9.64	6.73E-10	0.67	1.02E-12	0.00	6.39E-12	0.01	1.82E-08	18.17	7.10E-08	71.02		100.0
9.25	11.3663	3.09E-11	0.03	2.08E-13	0.00	2.44E-16	0.00	1.94E-09	1.94	4.58E-10	0.46	2.49E-12	0.00	8.17E-12	0.01	6.67E-09	6.67	9.09E-08	90.88		99.9
9.50	11.1171	1.40E-12	0.00	1.64E-14	0.00	3.48E-17	0.00	2.77E-10	0.28	2.41E-10	0.24	5.66E-12	0.01	8.76E-12	0.01	1.80E-09	1.80	9.76E-08	97.65		99.9
9.75	10.8697	3.83E-14	0.00	7.59E-16	0.00	3.00E-18	0.00	2.40E-11	0.02	9.76E-11	0.10	1.58E-11	0.02	8.87E-12	0.01	3.22E-10	0.32	9.94E-08	99.44		99.9
10.00	10.6355	2.98E-16	0.00	9.07E-18	0.00	7.18E-20	0.00	5.83E-13	0.00	2.12E-11	0.02	8.89E-11	0.09	8.53E-12	0.01	2.11E-11	0.02	9.92E-08	99.16		99.3

99.44	
99.16	

Shuman

U(VI) Speciation, PHREEQC, 2.4.2

[illegible]

0.00 0.00E+00 0

Shuman

4/30/2002
JRW

Validation Test Case 1.

The installation of MINTEQA2, Version 4.02 software was checked as part of bringing the code into configuration management under Technical Operating Procedure (TOP)-018 for the CNWRA. The results indicate that the code was installed correctly on the PC platform and produced the correct results for 12 different example problems provided with MINTEQA2, Version 4.02. The results are documented in the configuration management package for MINTEQA2, Version 4.02 stored in the CNWRA QA Records Room.

4/30/2002

DPS

Validation Test Case 2a—Aqueous Speciation. PHREEQC, Version 2.4.2 input file for seawater speciation check (from Parkhurst and Appelo, 1999)

TITLE Modified Example 1.--Add uranium and speciate seawater.
SOLUTION 1 SEAWATER FROM NORDSTROM ET AL. (1979)

units	ppm		
pH	8.22		
pe	8.451		
density	1.000		
temp	25.0		
redox	O(0)/O(-2)		
Ca	412.3		
Mg	1291.8		
Na	10768.0		
K	399.1		
Fe	0.002		
Mn	0.0002		
Si	4.28		
Cl	19353.0		
C(4)	141.682	as HCO3	
S(6)	2712.0		
N(5)	0.29	gfw	62.0
N(-3)	0.03	as	NH4
U	3.3	ppb	
O(0)	1.0	O2(g)	-0.66

END

DPS

Validation Test Case 2b—Aqueous Speciation. MINTEQA2, Version 4.02 input file for seawater speciation check (from Parkhurst and Appelo, 1999)

Add U and speciate seawater (Nordstrom et al., 1979)
Modified PHREEQC 2.4.2 Ex. 1 (Parkhurst and Appelo, 1999)

25.00 PPM 0.000 0.00000E+00

0 0 1 0 1 0 0 0 1 1 0 0 0

0 0 0

330	0.000E+00	-8.22 y	/H+1
150	4.123E+02	-1.99 y	/Ca+2
460	1.292E+03	-1.27 y	/Mg+2
500	1.077E+04	-0.33 y	/Na+1
410	3.991E+02	-1.99 y	/K+1
280	0.000E+00	-11.75	/Fe+2
281	2.000E-03	-7.45 y	/Fe+3
470	2.000E-04	-8.44 y	/Mn+2
471	0.000E+00	-11.74 y	/Mn+3
770	4.280E+00	-3.82 y	/H4SiO4
180	1.935E+04	-0.26 y	/Cl-1
140	1.393E+02	-2.63 y	/CO3-2
732	2.712E+03	-1.55 y	/SO4-2
492	2.900E-01	-5.33 y	/NO3-1
490	3.000E-02	-5.78 y	/NH4+1
891	0.000E+00	-12.43 y	/U+4
892	0.000E+00	-12.43 y	/UO2+1
893	3.300E-03	-7.86 y	/UO2+2
1	0.000E+00	-7.00 y	/E-1

3	6		
3300021	-82.4318	571.6600	/O2 (g)
2802810	13.0320	-42.7000	/fe+2/fe+3
4704710	25.3500	-107.8000	/mn+2/mn+3
8918930	9.0400	-143.8600	/u+4/uo2+2
8928930	1.4800	-6.1300	/uo2+/uo2+2
330	8.2200	0.0000	/H+1
6	1		
1	0.0000	0.0000	/E-1

Species Concentration in Solution			MINTEQA2, Version 4.02 Output			PHREEQC, Version 2.4.2 Output		
ID	Name		Molality	Log Molality	Activity	Log Activity	Molality	Log Molality
330 H+1			8.08E-09	-8.092	6.03E-09	-8.22	7.98E-09	-8.098
3300020 oh-			2.20E-06	-5.658	1.64E-06	-5.78564	2.67E-06	-5.786
8931404 (uo2)11(c03)8(oh)12-2			1.00E-76	-76.000	3.09E-77	-76.51015	0.00E+00	-86.792
8933305 (uo2)2(c03)2++			2.20E-22	-21.647	6.97E-23	-22.15706	4.20E-24	-23.377
8931405 (uo2)2(c03)3-			8.17E-15	-14.088	6.09E-15	-14.21532	9.41E-17	-16.026
8933304 (uo2)2(oh)++			5.01E-27	-26.301	3.56E-28	-27.44842	1.51E-28	-27.821
8931403 (uo2)3(c03)6-6			9.42E-22	-21.026	2.41E-26	-25.61732	2.77E-22	-21.557
8933306 (uo2)3(c03)4++			1.04E-28	-27.984	3.20E-29	-28.49424	1.99E-31	-30.702
8933307 (uo2)3(oh)5+			1.57E-24	-23.805	1.17E-24	-23.93288	2.02E-27	-26.695
8933308 (uo2)3(oh)7-			1.47E-23	-22.833	1.10E-23	-22.96017	1.90E-26	-25.722
8933309 (uo2)4(oh)7+			6.13E-31	-30.213	4.57E-31	-30.34006	8.13E-35	-34.09
1504902 ca(nh3)2+2			5.41E-17	-16.267	1.67E-17	-16.77736	9.52E-03	-2.021
150 Ca+2			8.79E-03	-2.056	2.71E-03	-2.56639	2.94E-05	-4.531
1501401 cac03			3.09E-05	-4.510	3.60E-05	-4.44349	4.97E-05	-4.304
1501400 cahco3+			4.54E-05	-4.343	3.38E-05	-4.47096		
1504901 canh3+2			1.23E-09	-8.912	3.79E-10	-9.42188		
1504921 cano3+			4.13E-08	-7.385	3.07E-08	-7.51216	9.30E-08	-7.031
1503300 caoh+			1.19E-07	-6.924	8.87E-08	-7.05204	1.00E-08	-2.974
1507320 caso4			1.80E-03	-2.745	2.10E-03	-2.67824	5.66E-01	-0.247
180 Cl-1			5.68E-01	-0.247	4.22E-01	-0.37500	4.12E-05	-4.385
2803302 fe(oh)2			5.45E-24	-23.264	6.35E-24	-23.19734	2.29E-09	-8.641
2813301 fe(oh)2+			1.55E-08	-7.810	1.16E-08	-7.93707	6.95E-24	-23.158
2813302 fe(oh)2+			4.41E-24	-23.355	3.29E-24	-23.48299	2.77E-08	-7.557
2803301 fe(oh)3-			4.16E-09	-8.381	3.10E-09	-8.50836	7.11E-09	-8.148
2813303 fe(oh)4-			6.28E-20	-19.202	4.68E-20	-19.32949	5.94E-20	-19.226
2817321 fe(so4)2-			2.42E-19	-18.616	7.48E-20	-19.12606	4.98E-19	-18.304
280 Fe+2			2.41E-19	-18.616	1.71E-20	-19.76578	7.40E-26	-25.131
281 Fe+3			1.20E-24	-23.922	1.09E-26	-25.96285	3.42E-19	-18.466
2813305 fe3(oh)4+5			2.81E-30	-29.551	1.82E-33	-32.73993	2.35E-24	-23.63
2811800 feoh+2			7.07E-19	-18.151	2.18E-19	-18.66078	7.42E-20	-19.129
2811801 feoh+2+			5.52E-19	-18.258	4.11E-19	-18.38578	1.04E-29	-28.982
2811802 feoh+3			1.49E-20	-19.827	1.73E-20	-19.76078	1.50E-18	-17.824
2801400 fehco3+			1.52E-21	-20.819	1.13E-21	-20.94667	1.50E-18	-17.824
2814921 feno3+2			1.99E-24	-23.701	6.14E-25	-24.21155	6.90E-19	-18.161
2803300 feoh+			6.54E-21	-20.184	4.88E-21	-20.31170	1.38E-20	-19.185
2813300 feoh+2			5.87E-14	-13.231	1.81E-14	-13.74143	2.01E-20	-19.697
2807320 feso4			5.32E-20	-19.274	6.20E-20	-19.20791	1.68E-20	-19.774
2817320 feso4+			8.71E-19	-18.060	6.49E-19	-18.18764	1.50E-18	-17.824
3301401 h2co3			1.40E-05	-4.855	1.63E-05	-4.78861	1.77E-04	-3.752
3307701 h2so4-2			1.12E-09	-8.950	3.47E-10	-9.45973	4.75E-02	-1.323
3307700 h3so4-			1.37E-06	-5.864	1.02E-06	-5.99139	9.63E-05	-4.016
770 H4SiO4			4.48E-05	-4.349	5.22E-05	-4.28239	1.85E-05	-4.735
3301400 hco3-			1.61E-03	-2.792	1.20E-03	-2.91996	2.82E-09	-8.627
3307320 hso4-			2.65E-09	-8.577	1.97E-09	-8.70491	1.04E-02	-1.983
410 K+1			1.03E-02	-1.986	7.70E-03	-2.11328	3.15E-09	-8.504
4107320 kso4-			2.45E-04	-3.611	1.83E-04	-3.73840	1.77E-04	-3.752
460 Mg+2			4.71E-02	-1.327	1.45E-02	-1.83763	4.75E-02	-1.323
4601400 mgco3			1.11E-04	-3.954	1.30E-04	-3.88758	9.63E-05	-4.016
4601401 mgohco3+			2.73E-04	-3.564	2.03E-04	-3.69205	2.82E-04	-3.55
4603300 mgoh+			5.21E-06	-5.283	3.88E-06	-5.41078	1.15E-05	-4.939
4607320 mgs04			7.66E-03	-2.116	8.92E-03	-2.04948	7.18E-03	-2.144
4704920 mn(n03)2			2.82E-20	-19.550	3.28E-20	-19.48360	1.13E-20	-19.947
4703301 mn(oh)3-			5.88E-20	-19.230	4.39E-20	-24.63464	4.21E-20	-19.376
4703302 mn(oh)4-2			7.51E-25	-24.124	2.32E-25	-24.63464	1.78E-09	-8.749
470 Mn+2			2.08E-09	-8.682	6.43E-10	-9.19206	3.98E-22	-21.401
471 Mn+3			9.96E-22	-21.002	7.08E-23	-22.14979	8.85E-10	-9.053
4701800 mncl+			4.58E-10	-9.340	3.41E-10	-9.46706	7.75E-11	-10.111
4701801 mncl2			1.74E-10	-9.759	2.03E-10	-9.69206		
4701802 mncl3-			3.17E-11	-10.499	2.36E-11	-10.62706	1.33E-11	-10.878
4701400 mnhco3+			2.07E-11	-10.685	1.54E-11	-10.81267	2.39E-10	-9.622
4704921 mnno3+			4.89E-15	-14.310	3.65E-15	-14.43783	6.06E-11	-10.218
4700020 mnco4-			6.73E-10	-9.172	5.01E-10	-9.29978	5.51E-10	-9.259
4700021 mnco4-2			1.55E-12	-11.809	4.79E-13	-12.31935	1.61E-12	-11.793
4703300 mnoh+			3.55E-12	-11.450	2.64E-12	-11.57771	2.58E-12	-11.589
4707320 mns04			3.31E-10	-9.480	3.86E-10	-9.41392	1.62E-10	-9.79
500 Na+1			4.77E-01	-0.322	3.55E-01	-0.44940	4.79E-01	-0.32
5001400 naco3-			8.29E-05	-4.081	6.18E-05	-4.20901	8.00E-05	-4.097
5001401 nahco3			2.06E-04	-3.687	2.40E-04	-3.62001	1.80E-04	-3.745
5007320 nas04-			8.64E-03	-2.064	6.44E-03	-2.19126	3.11E-07	-6.507
3304900 nh3			9.50E-08	-7.022	1.11E-07	-6.95570	6.54E-03	-2.184
490 NH4+1			1.57E-06	-5.804	1.27E-06	-5.93148	7.31E-08	-7.136
4907320 nh4so4-			5.68E-08	-7.246	4.03E-08	-7.37333	1.61E-06	-5.795
492 NO3-1			4.81E-06	-5.318	3.58E-06	-5.44577	4.57E-08	-7.34
732 SO4-2			1.09E-02	-1.962	3.37E-03	-2.47185	4.85E-06	-5.314
8911400 u(c03)4+4			9.02E-49	-48.045	8.21E-51	-50.08559	1.43E-02	-1.845
8911401 u(c03)5-6			1.80E-52	-51.744	4.62E-57	-56.33520	0.00E+00	-48.015
8914921 u(n03)2++			6.78E-74	-73.169	2.10E-74	-73.67868	0.00E+00	-50.276
8913303 u(oh)4(aq)			1.42E-37	-36.848	1.65E-37	-36.78172	0.00E+00	-74.125
8913304 u(oh)5-			3.61E-41	-40.443	2.69E-41	-40.57036	1.65E-38	-37.783
8917321 u(so4)2(aq)			2.59E-60	-59.587	3.01E-60	-59.52085	0.00E+00	-61.371
891 U+4			8.98E-64	-63.047	8.18E-66	-66.08714	0.00E+00	-60.748
8914920 u(n03)3++			2.55E-63	-62.594	1.81E-64	-63.74214	0.00E+00	-63.394
8931401 uo2(c03)2-2			1.22E-68	-67.915	8.65E-70	-69.06291	0.00E+00	-63.219
8931402 uo2(c03)3-4			8.15E-10	-9.089	2.52E-10	-9.59911	0.00E+00	-68.562
8921400 uo2(c03)3-5			1.18E-08	-7.928	1.07E-10	-9.96872	1.40E-10	-9.856
8933301 uo2(h2)2(aq)			1.07E-21	-20.970	6.94E-25	-24.15872	1.42E-08	-7.847
8933302 uo2(h2)3-			3.77E-11	-10.424	4.39E-11	-10.35717	7.16E-32	-31.145
8933303 uo2(h2)4-2			1.21E-11	-10.918	9.00E-12	-11.04582	4.52E-12	-11.345
8937321 uo2(so4)2-2			7.51E-17	-16.124	2.32E-17	-16.63446	1.47E-12	-11.832
892 UO2+1			1.69E-17	-16.773	5.20E-18	-17.28359	1.52E-17	-16.817
893 UO2+2			5.44E-28	-27.265	4.05E-28	-27.39216	2.04E-18	-17.691
8931800 uo2oh+			1.07E-16	-15.970	3.31E-17	-16.47989	6.52E-29	-28.186
8931801 uo2cl2(aq)			2.77E-17	-16.557	2.07E-17	-16.68489	2.17E-17	-16.663
8931400 uo2co3(aq)			4.01E-19	-18.396	4.68E-19	-18.32989	2.82E-18	-17.549
8934920 uo2no3+			1.24E-12	-11.906	1.45E-12	-11.83950	3.37E-20	-19.473
8933300 uo2oh+			3.18E-22	-21.498	2.37E-22	-21.62565	1.37E-13	-12.864
8931406 (uo2)3co2(oh)5+			4.56E-14	-13.341	3.40E-14	-13.46853	3.07E-23	-22.512
8937320 uo2so4(aq)			8.58E-30	-29.066	6.40E-30	-29.19385	5.68E-15	-14.255
8913300 uoh++			1.35E-16	-15.868	1.58E-16	-15.80174	1.02E-32	-31.993
8917320 uo4++			5.40E-57	-56.268	3.84E-58	-57.41579	1.25E-17	-16.902
8917320 uo4++			3.40E-61	-60.469	1.05E-61	-60.97900	0.00E+00	-56.815
Total Concentration of Component Species								
140 CO3-2			2.41E-03					
150 Ca+2			1.07E-02					
180 Cl-1			5.66E-01					
280 Fe+2			3.03E-19					
281 Fe+3			3.71E-08					
410 K+1			1.06E-02					
460 Mg+2			5.51E-02					
470 Mn+2			3.77E-09					
471 Mn+3			9.96E-22					
490 NH4+1			1.72E-06					
492 NO3-1			4.85E-06					
500 Na+1			4.86E-01					
732 SO4-2			2.93E-02					
770 H4SiO4			4.62E-05					
891 U+4			1.42E-37					
892 UO2+1			5.44E-28					
893 UO2+2			1.27E-08					

4/30/2002
JRS

Validation Test Case 3a—Mineral Solubility. MINTEQA2, Version 4.02 input file. Barite Solubility in pure H2O comparison to Richardson and McSween (1989) (Worked Problem 3-7):

Validation for Barite (BaSO4) solubility
Solubility comparison to Richardson & McSween (1989)
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 0 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
100 0.000E+00 -7.00 y /Ba+2
732 0.000E+00 -7.00 y /SO4-2

3 1
6010000 9.9800 -23.0000 /barite(baso4)
6 2
3307320 1.9900 22.0000 /hso4-
1003300 -13.3570 60.8100 /baoh+

Note: HSO4- and BaOH+ are aqueous species included in the MINTEQA2, Version 4.02 database, but excluded in this calculation for direct comparison to the results of Richardson and McSween (1989). Also, although the Davies equation is the MINTEQA2, Version 4.02 default, a flag is set to use extended Debye-Hückel approach to calculate activity coefficients as a more direct comparison to Richardson and McSween (1989).

Validation Test Case 3b—Mineral Solubility. MINTEQA2, Version 4.02 input file. Barite Solubility in 0.2 m NaCl comparison to Richardson and McSween (1989) (Worked Problem 3-8):

Validation for Barite solubility in 0.2m NaCl solution
Solubility comparison to Richardson & McSween (1989)
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 0 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
100 0.000E+00 -7.00 y /Ba+2
732 0.000E+00 -7.00 y /SO4-2
500 2.000E-01 -0.70 /Na+1
180 2.000E-01 -0.70 y /Cl-1

3 1
6010000 9.9800 -23.0000 /barite(baso4)
6 3
3307320 1.9900 22.0000 /hso4-
1003300 -13.3570 60.8100 /baoh+
5007320 0.7300 1.0000 /nasO4-

Stumm

Note: HSO4-, BaOH+, and NaOH+ are aqueous species included in the MINTEQA2, Version 4.02 database, but excluded in this calculation for direct comparison to the results of Richardson and McSween (1989). Also, although the Davies equation is the MINTEQA2, Version 4.02 default, a flag is set to use extended Debye-Huckel approach to calculate activity coefficients as a more direct comparison to Richardson and McSween (1989).

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JRS

Validation Test Case 4a—Gas Chemistry. MINTEQA2, Version 4.02 input file. Aqueous speciation of seawater in equilibrium with calcite at 25 °C, and open to atmosphere (fixed P_{CO2} = 3.55 × 10⁻⁴ atm) (Stumm and Morgan, 1996; Example 7.8).

Calcite-Seawater with PCO2 = 1E-3.5 atm
Example 7.8; Stumm&Morgan(1996); Seawater from Table 15.2
25.00 PPM 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
500 1.077E+04 -0.33 y /Na+1
460 1.290E+03 -1.28 y /Mg+2
410 3.990E+02 -1.99 y /K+1
800 7.900E+00 -4.04 y /Sr+2
180 1.935E+04 -0.26 y /Cl-1
732 2.712E+03 -1.55 y /SO4-2
270 1.300E+00 -4.16 y /F-1
130 6.730E+01 -3.07 y /Br-1
150 0.000E+00 -11.60 /Ca+2
140 0.000E+00 -7.00 y /CO3-2

3 2
5015001 8.4800 8.0000 /calcite
3301403 21.5968 -4.0600 /CO2 (g)

Note: The data from Table 15.2 in Stumm and Morgan (1996) are reported in g/L. These values are converted to molality by MINTEQA2, assuming that the density of water ~1 g/mL. This assumption is slightly inaccurate for seawater, where the density of water is slightly > 1g/mL.

Validation Test Case 4b—Gas Chemistry. MINTEQA2, Version 4.02 input file. Aqueous speciation of fresh water in equilibrium with calcite at 25 °C, and variable P_{CO2} (Langmuir, 1997; Table 6.3).

Calcite solubilty in fresh water, 25C with PCO2=1e-3.5 bar
Langmuir (1997), Calculated values in Table 6.3
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 4 3
ccsol.csv 140 150 3301400 3301401
0 0 0
150 0.000E+00 -11.60 y /Ca+2
140 0.000E+00 -7.00 y /CO3-2
330 0.000E+00 -7.00 y /H+1

3 2
5015001 8.4800 8.0000 /calcite
3301403 21.6530 -4.0600 /CO2 (g)

Stumm

Calcite solubilty in fresh water, 25C with PCO2=1e-2.5 bar
Langmuir (1997), Calculated values in Table 6.3
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 4 3
ccsol.csv 140 150 3301400 3301401
0 0 0
150 0.000E+00 -11.60 y /Ca+2
140 0.000E+00 -7.00 y /CO3-2
330 0.000E+00 -7.00 y /H+1

3 2
5015001 8.4800 8.0000 /calcite
3301403 20.6530 -4.0600 /CO2 (g)

Calcite solubilty in fresh water, 25C with PCO2=1e-1.5 bar
Langmuir (1997), Calculated values in Table 6.3
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 4 3
ccsol.csv 140 150 3301400 3301401
0 0 0
150 0.000E+00 -11.60 y /Ca+2
140 0.000E+00 -7.00 y /CO3-2
330 0.000E+00 -7.00 y /H+1

3 2
5015001 8.4800 8.0000 /calcite
3301403 19.6530 -4.0600 /CO2 (g)

Note: The partial pressures in Langmuir (1997) are presented in terms of bars, while MINTEQA2 reads pressures in terms of atmospheres. For conversion, 1 bar = 0.98692 atm.

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DJS

Validation Test Case 6a—Redox Equilibria. MINTEQA2, Version 4.02 input file for redox Example 8.2 in Stumm and Morgan (1996). The simulation is intended to determine electron activity (pe).

Calculate electron activity (pe) for 10-5 M Fe(III) and 10-3 M Fe(II) Example 8.2 from Stumm and Morgan (1996)

```
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
281 1.000E-05 -5.00 y /Fe+3
280 1.000E-03 -3.00 y /Fe+2
1 0.000E+00 -7.00 /E-1

3 1
2802810 13.0000 -42.7000 /fe2/fe3
6 10
1 0.0000 0.0000 /E-1
2813300 -2.1870 41.8100 /feoh+2
2813301 -4.5940 0.0000 /fe(oh)2+
2813302 -12.5600 103.8000 /fe(oh)3 (aq)
2813303 -21.5880 0.0000 /fe(oh)4-
2813304 -2.8540 57.6200 /fe2(oh)2+4
2813305 -6.2880 65.2400 /fe3(oh)4+5
2803300 -9.3970 55.8100 /feoh+
2803301 -28.9910 126.4300 /fe(oh)3-
2803302 -20.4940 119.6200 /fe(oh)2 (aq)
```

Calculate electron activity (pe) for pH=7.5, pO2=0.22 atm Example 8.2 from Stumm and Morgan (1996)

```
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.50 y /H+1
1 0.000E+00 -7.00 /E-1
500 1.000E-03 -3.00 /Na+1
180 1.000E-03 -3.00 /Cl-1

3 2
3300021 -82.4222 571.6600 /O2 (g)
330 7.5000 0.0000 /H+1
6 1
1 0.0000 0.0000 /E-1
```

Calculate electron activity (pe) for 10-5 M Mn(II) and pyrolusite Example 8.2 from Stumm and Morgan (1996)

```
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -8.00 y /H+1
1 0.000E+00 -7.00 /E-1
470 1.000E-05 -5.00 /Mn+2

3 2
2047000 -40.8400 272.0000 /pyrolusite
330 8.0000 0.0000 /H+1
6 1
1 0.0000 0.0000 /E-1
```

Validation Test Case 6b—Redox Equilibria. MINTEQA2, Version 4.02 input file for redox Example 8.4 in Stumm and Morgan (1996). The simulation is intended to determine HS⁻-SO₄²⁻ speciation as a function of electron activity (pe).

Redox equilibria test; 10-4 M SO4-2/HS- system Based on Example 8.4 from Stumm and Morgan (1996)

```
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 1 2 2
48 E-1 ACTIVITY mol/L
1 1 1.000
-9.00 0.10
valid66.123 730 732
0 0 0
330 0.000E+00 -10.00 y /H+1
730 1.000E-04 -4.00 y /HS-1
732 0.000E+00 -16.00 y /SO4-2
1 0.000E+00 -7.00 y /E-1

3 3
7307320 34.0200 -60.1400 /hs-/so4-2
330 10.0000 0.0000 /H+1
1 7.0000 0.0000 /E-1

6 3
3307300 7.0200 -22.0000 /h2s (aq)
3307320 1.9900 22.0000 /hso4-
3307301 -17.3000 49.4000 /s-2
```

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DJS

Validation Test Case 7a—Temperature Effects. PHREEQC, Version 2.4.2 input file for temperature effects on saturation of gypsum and anhydrite. Pure water with 1.0 moles of anhydrite and 1.0 moles of gypsum. This input file is from Example 2 in the PHREEQC, Version 2.4.2 installation test problems (Parkhurst and Appelo, 1999).

```
TITLE Example 2.--Temperature dependence of solubility of gypsum and anhydrite
SOLUTION 1 Pure water
pH 7.0
temp 25.0
EQUILIBRIUM_PHASES 1
Gypsum 0.0 1.0
Anhydrite 0.0 1.0
REACTION_TEMPERATURE 1
25.0 75.0 in 51 steps
SELECTED_OUTPUT
-file ex2.sel
-si anhydrite gypsum
END
```

Validation Test Case 7a—Temperature Effects. MINTEQA2, Version 4.02 input file for temperature effects on saturation of gypsum and anhydrite. Pure water with 1.0 moles of anhydrite and 1.0 moles of gypsum, based on Example 2 in the PHREEQC, Version 2.4.2 installation test problems (Parkhurst and Appelo, 1999). Thermodynamic data modified to match PHREEQC, Version 2.4.2.

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
30.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
35.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
40.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
45.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
```

```
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
50.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
55.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
60.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
65.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
70.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0 0 0
330 0.000E+00 -7.00 y /H+1
150 0.000E+00 -7.00 y /Ca+2
732 0.000E+00 -7.00 y /SO4-2

4 2
6015000 4.3600 7.1550 1.000E+00 /anhydrite
6015001 4.5800 0.4560 1.000E+00 /gypsum
```

```
Anhydrite/Gypsum solubility as function of temperature
Test Example 2 for PHREEQC, Version 2.4.2
75.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
```


[Signature]

```

50.00 MOLAL  0.000  0.00000E+00
0 0 1 0 1 0 0 0 1 1 0 0 0
0  0  0

```

Use Solution 1	
EQUILIBRIUM_PHASES 1	
Fix_H+	-4.00
NaOH	10.0
CO2(g)	-3.5
	1.0

[Signature]

Validation Test Case 8a—Np and U speciation. PHREEQC, Version 2.4.2 input files for neptunium and uranium speciation as a function of pH. T = 25 °C, PCO2 = 10^{-3.5} atm, PO2 = 10^{-6.86} atm, (a) Neptunium speciation with Np_{total} = 10⁻⁷ m. Neptunium oxidation states change with pH and both Np(V)-species and Np(VI)-species are written to the output file np_phrq2.123; (b) Uranium speciation with U_{total} = 10⁻⁷ m. Uranium speciation is dominated by U(VI) over entire pH range, an only U(VI) species are written to u_phrq2.123.

TITLE Test Example: Speciation of Np(V), 1.0e-7 molal NpO2+, \ PCO2=1e-3.5; Speciation over pH range

```
SOLUTION 1
-units      mol/kgw
pH          7.00
redox       0(0)/O(-2)
temp        25.0
Na          0.100      charge
N(+5)       0.100      as NO3-
Np(+5)      0.0000001  as NpO2+
O(0)        1.0       O2(g) -0.66
```

```
PHASES 1
Fix_H+
H+ = H+
log_k = 0.0
END
```

```
SELECTED_OUTPUT
-file np_phrq2.123
-molalities NpO2+ NpO2OH NpO2(OH)2- NpO2CO3- NpO2(CO3)2-3
NpO2(CO3)3-5 \
NpO2(CO3)2(OH)-4 NpO2(CO3)2-2 NpO2(CO3)3-4
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -6.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -6.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -6.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -6.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -7.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -7.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -7.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -7.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -8.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -8.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -8.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -8.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -9.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -9.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -9.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -9.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -10.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

TITLE Test Example: Speciation of U(VI), 1.0e-7 molal UO2+2, \ PCO2=1e-3.5; Speciation over pH range

```
SOLUTION 1
-units      mol/kgw
pH          7.00
redox       0(0)/O(-2)
temp        25.0
Na          0.100      charge
N(+5)       0.100      as NO3
U(+6)       0.0000001  as UO2
O(0)        1.0       O2(g) -0.66
```

```
SOLUTION_SPECIES
UO2+2 + 2H2O = UO2(OH)2 + 2H+
log_k -11.7000
delta_h 18.095 kcal
-gamma 3.0 0
```

```
PHASES 1
Fix_H+
H+ = H+
log_k = 0.0
END
```

```
SELECTED_OUTPUT
-file u_phrq2.123
-molalities UO2+2 UO2NO3+ UO2CO3 UO2(CO3)2-2 UO2(CO3)3-4 \
(UO2)2CO3(OH)3- UO2OH+ UO2(OH)2 UO2(OH)3- UO2(OH)4-2 \
(UO2)2(OH)2+2 (UO2)3(OH)5+
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.50 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.75 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.00 NaOH 10.0
CO2(g) -3.5 1.0
END
```

```
Use Solution 1
EQUILIBRIUM_PHASES 1
Fix_H+ -5.25 NaOH 10.0
CO2(g) -3.5 1.0
END
```

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```

END      CO2(g)   -3.5   1.0

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -5.50   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -5.75   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -6.00   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -6.25   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -6.50   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -6.75   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -7.00   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -7.25   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -7.50   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -7.75   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -8.00   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -8.25   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -8.50   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -8.75   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -9.00   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -9.25   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -9.50   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -9.75   NaOH  10.0
  CO2(g)   -3.5   1.0
END

Use Solution 1
EQUILIBRIUM_PHASES 1
  Fix_H+   -10.00  NaOH  10.0
  CO2(g)   -3.5   1.0
END

```

Validation Test Case 8b—Np and U speciation. MINTEQA2, Version 4.02 input files for neptunium and uranium speciation as a function of pH. T = 25 °C, PCO₂ = 10^{-3.5} atm, PO₂ = 10^{-0.66} atm, (a) Np speciation with Np_{total} = 10⁻⁷ m. (b) U speciation with U_{total} = 10⁻⁷ m.

```

Np(V) speciation, Np = 1e-7 M, PCO2=1e-3.5 atm
Variable pH, T = 25C, PO2=0.22 atm

25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 1 6 3
25 H+1
1 330 1.000
4.00 0.25
np_mint2.123 552 5523300 5523301 5521400 5521401 5521402
0 0 0
330 0.000E+00 -4.00 y /H+1
552 1.000E-07 -7.00 y /NpO2+
500 1.000E-01 -1.00 y /Na+1
492 1.000E-01 -1.00 y /NO3-1
140 0.000E+00 -7.00 y /CO3-2
1 0.000E+00 -7.00 y /E-1
551 0.000E+00 -7.00 y /Np+4
553 0.000E+00 -7.00 y /NpO2+2

3 5
3301403 21.6470 -4.0600 /CO2 (g)
5525510 -10.2100 149.5000 /npO2+1/np+4
5535510 -29.8000 266.9500 /npO2+2/np+4
3300021 -82.4318 571.6600 /O2 (g)
330 4.0000 0.0000 /H+1
6 1
1 0.0000 0.0000 /E-1

Np(V) speciation, Np = 1e-7 M, PCO2=1e-3.5 atm
Variable pH, T = 25C, PO2=0.22 atm

25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 1 3 3
25 H+1
1 330 1.000
4.00 0.25
np_mint2.123 5521403 5531401 5531402
0 0 0
330 0.000E+00 -4.00 y /H+1
552 1.000E-07 -7.00 y /NpO2+
500 1.000E-01 -1.00 y /Na+1
492 1.000E-01 -1.00 y /NO3-1
140 0.000E+00 -7.00 y /CO3-2
1 0.000E+00 -7.00 y /E-1
551 0.000E+00 -7.00 y /Np+4
553 0.000E+00 -7.00 y /NpO2+2

3 5
3301403 21.6470 -4.0600 /CO2 (g)
5525510 -10.2100 149.5000 /npO2+1/np+4
5535510 -29.8000 266.9500 /npO2+2/np+4
3300021 -82.4318 571.6600 /O2 (g)
330 4.0000 0.0000 /H+1
6 1
1 0.0000 0.0000 /E-1

U(VI) speciation, U = 1e-7 M, PCO2=1e-3.5 atm
Variable pH, T = 25C, PO2=0.22 atm

25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 1 6 3
25 H+1
1 330 1.000
4.00 0.25
u_mint2.123 893 8934920 8931400 8931401 8931402 8931405
0 0 0
330 0.000E+00 -4.00 y /H+1
893 1.000E-07 -7.00 y /UO2+2
500 1.000E-01 -1.00 y /Na+1
492 1.000E-01 -1.00 y /NO3-1
140 0.000E+00 -7.00 y /CO3-2
1 0.000E+00 -7.00 y /E-1
891 0.000E+00 -7.00 y /U+4
892 0.000E+00 -7.00 y /UO2+1

2 1
8933301 -11.7000 75.7100 /uo2(oh)2(aq)
3 5
3301403 21.6470 -4.0600 /CO2 (g)

```

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3300021	-82.4318	571.6600	/O2 (g)
8918930	9.0400	-143.8600	/u+4/uo2+2
8928930	1.4800	-6.1300	/uo2+/uo2+2
330	4.0000	0.0000	/H+1
6 1			
1	0.0000	0.0000	/E-1

U(VI) speciation, U = 1e-7 M, PCO2=1e-3.5 atm

Variable pH, T = 25C, PO2=0.22 atm

25.00 MOLAL 0.000 0.00000E+00

0 0 1 0 1 0 0 0 1 1 1 6 3

25 H+1 ACTIVITY mol/L

1 330 1.000

4.00 0.25

u_mint2.123 8933300 8933301 8933302 8933303 8933305 8933307

0 330	0.000E+00	-4.00 y	/H+1
893	1.000E-07	-7.00 y	/UO2+2
500	1.000E-01	-1.00 y	/Na+1
492	1.000E-01	-1.00 y	/NO3-1
140	0.000E+00	-7.00 y	/CO3-2
1	0.000E+00	-7.00	/E-1
891	0.000E+00	-7.00 y	/U+4
892	0.000E+00	-7.00 y	/UO2+1

2 1			
8933301	-11.7000	75.7100	/uo2(ch)2(aq)

3 5			
3301403	21.6470	-4.0600	/CO2 (g)

3300021	-82.4318	571.6600	/O2 (g)
---------	----------	----------	---------

8918930	9.0400	-143.8600	/u+4/uo2+2
---------	--------	-----------	------------

8928930	1.4800	-6.1300	/uo2+/uo2+2
---------	--------	---------	-------------

330	4.0000	0.0000	/H+1
-----	--------	--------	------

6 1			
1	0.0000	0.0000	/E-1

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NEA SORPTION EXERCISE
TEST CASE 1: Np(V) SORPTION ON HEMATITE

As described by the technical direction team for the Nuclear Energy Agency (NEA) sorption exercise, the model teams are to simulate the Np-hematite sorption data of Kohler et al. (1999) using: (1) an electrostatic surface complexation model, and (2) a nonelectrostatic model. The modeling assumptions used in Test Case 1 by the Center for Nuclear Waste Regulatory Analyses (CNWRA) modeling team are summarized below. Detailed model results are provided in the accompanying electronic files.

ELECTROSTATIC MODEL: MODELING DECISIONS

Mineral-Radioelement System

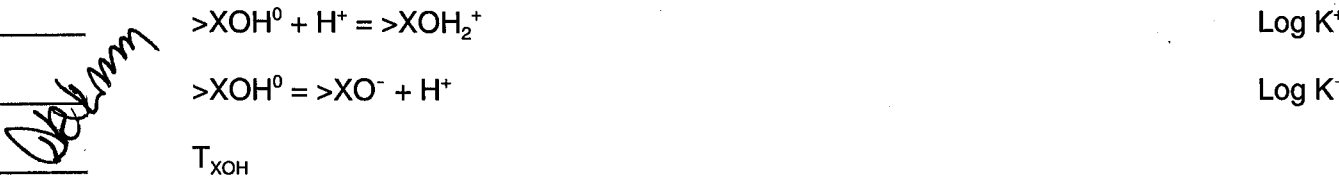
Np(V) sorption on hematite (Kohler et al., 1999).

Model Selected

Diffuse Layer Model (DLM) with electrostatic corrections.

Potentiometric Titration Parameters using FITEQL, Version 2.0

The nonlinear parameter optimization code FITEQL, Version 2.0 (Westall, 1982a,b) was used to fit potentiometric titration data for hematite. Adjustable parameters include:



The potentiometric titration data for all three ionic strengths were entered into FITEQL input files. The data for $I = 0.01$ M included more than the maximum number of 50 allowed by FITEQL, so every seventh data point was omitted for the optimization runs. FITEQL was allowed to fit each of three adjustable parameters: Log K^+ , Log K^- , and T_{XOH} .

The results from the FITEQL runs were combined using the weighting scheme developed in Dzombak and Morel (1990).

Determining Np-Hematite DLM parameters using FITEQL, Version 2.0

A two-site model was selected for the analysis. This included strong ($>\text{XOH}_s^0$) and weak ($>\text{XOH}_w^0$) sites as described in Dzombak and Morel (1990). Protonation and deprotonation constants for both site types were assumed to be equal and set at the weighted average values determined by the potentiometric titration data. The total site density ($T_{\text{XOH}_s} + T_{\text{XOH}_w}$) was assumed to be equal to the weighted average values determined from the potentiometric titration data (2.69×10^{-6} mol sites/m²).

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The Np(V)-hematite sorption data for CO₂-free atmosphere, $M/V = 0.1$ g/L, $I = 0.1$ M NaClO₄, and $\text{Np}_{\text{total}} = 1.24 \times 10^{-6}$ M was selected for optimization using FITEQL. The reason for selecting this sorption data set is that it offers the highest sorption density (highest concentration, lowest M/V), and demonstrates behavior consistent with saturation of the $>\text{XOH}_s^0$ site type.

A simplified modeling approach was used. A single type of mononuclear, monodentate sorption reaction was assumed to form on both sorption sites:



FITEQL, Version 2.0 was used to solve for the binding constants for the postulated sorption reactions. Additional input data include the surface protonation/deprotonation constants and total site concentration determined from the potentiometric titration data, and thermodynamic data for Np(V) from the NEA thermodynamic database (Lemire et al., 2001). Ionic strength activity coefficients were determined using the Davies Equation as identified in Table 2.13 of Dzombak and Morel (1990). An additional adjustable parameter (for a total of three) included the total concentration of the strong site type (T_{XOH_s}).

Summary of Model Results

As developed for this test case, the electrostatic DLM describes complex sorption behavior over a range in chemical conditions using a relatively simple postulated surface chemistry: NpO_2^+ sorbed on two different sorption sites. The model required fitting potentiometric titration data to determine surface acidity constants and total site concentration (three parameters). Once these are determined, the Np(V)-sorption data were described by an additional three fitted parameters, Log $K_{\text{XOs-NpO}_2}$, Log $K_{\text{XOw-NpO}_2}$, and strong site concentration (T_{XOH_s}) (Table 1). Determining these three parameters requires a Np-sorption data set over a sufficiently wide pH range, with surface loadings high enough to achieve saturation of the strong sites.

Table 1. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 1 (Np-Hematite). Diffuse Layer Model with Electrostatic Double Layer (EDL)

Par #	Surface Reaction/Fitted Parameter	Log K (I=0)	Site Concentration	Comment
1	$>\text{XOH}^0 + \text{H}^+ = >\text{XOH}_2^+$	9.56	-	Determined using FITEQL, v. 2.0 and potentiometric titration data at $I=0.01, 0.1$, and 0.27 . Weighted average using Dzombak and Morel (1990). One-site model.
2	$>\text{XOH}^0 = >\text{XO}^- + \text{H}^+$	-10.21	-	Determined using FITEQL, v. 2.0 and potentiometric titration data at $I=0.01, 0.1$, and 0.27 . Weighted average using Dzombak and Morel (1990). One-site model.
3	$>\text{XOH}_s^0 + \text{NpO}_2^+ = >\text{XO}_s\text{-NpO}_2^0 + \text{H}^+$	-0.46	-	Determined using CO ₂ -free, $M/V = 0.1$ g/L, $I = 0.1$ M NaClO ₄ , and $\text{Np}_{\text{total}} = 1.24 \times 10^{-6}$ M with FITEQL 2.0
4	$>\text{XOH}_w^0 + \text{NpO}_2^+ = >\text{XO}_w\text{-NpO}_2^0 + \text{H}^+$	-3.62	-	Determined using CO ₂ -free, $M/V = 0.1$ g/L, $I = 0.1$ M NaClO ₄ , and $\text{Np}_{\text{total}} = 1.24 \times 10^{-6}$ M with FITEQL 2.0
5	T_{XOH_s}	-	1.81×10^{-7} mol/m ²	Determined using CO ₂ -free, $M/V = 0.1$ g/L, $I = 0.1$ M NaClO ₄ , and $\text{Np}_{\text{total}} = 1.24 \times 10^{-6}$ M with FITEQL 2.0
6	T_{XOH_w}	-	2.51×10^{-6} mol/m ²	Determined by subtracting T_{XOH_s} from T_{total} (2.69×10^{-6}) determined by fitting potentiometric titration data

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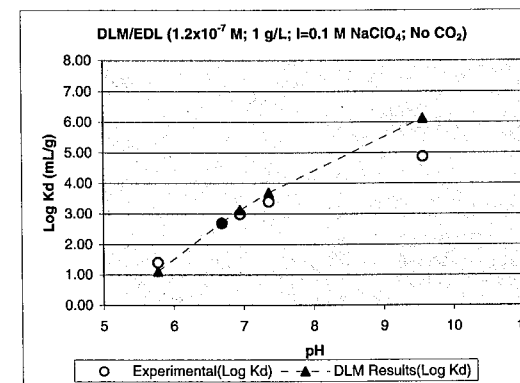
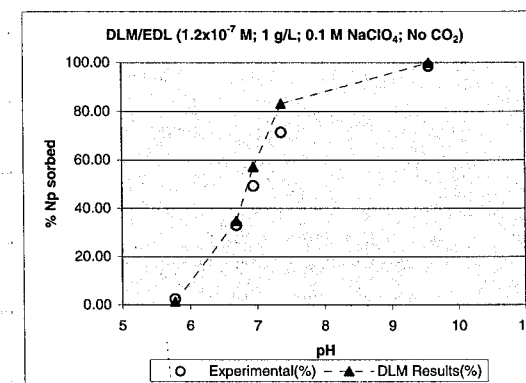
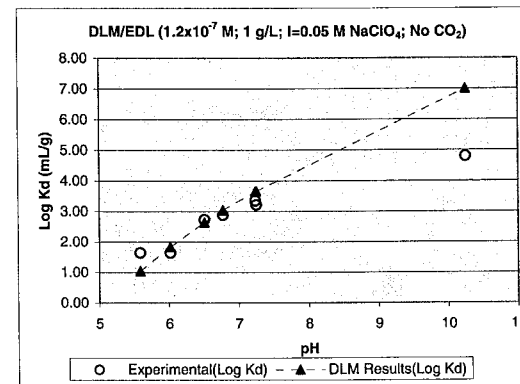
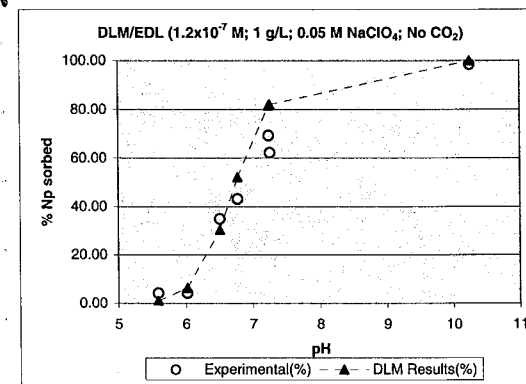
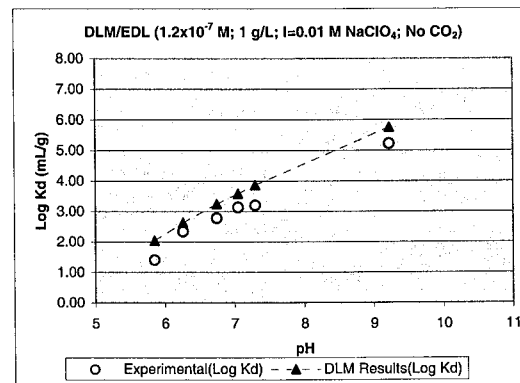
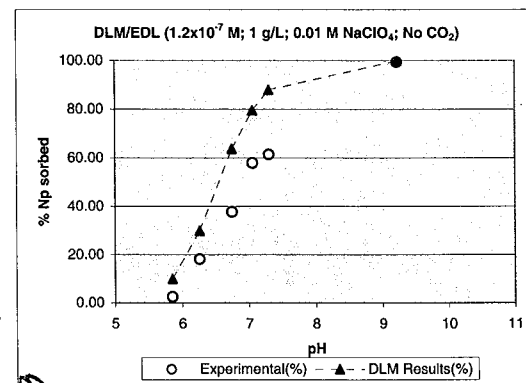
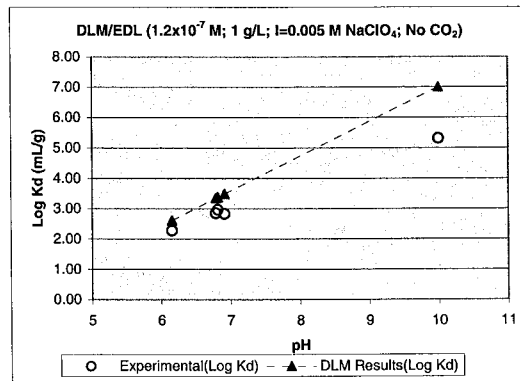
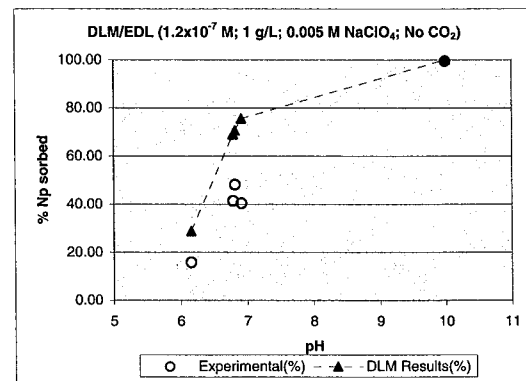
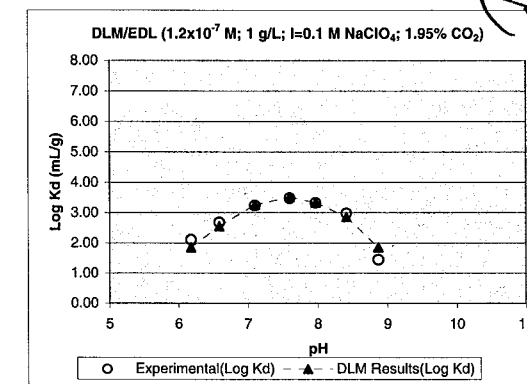
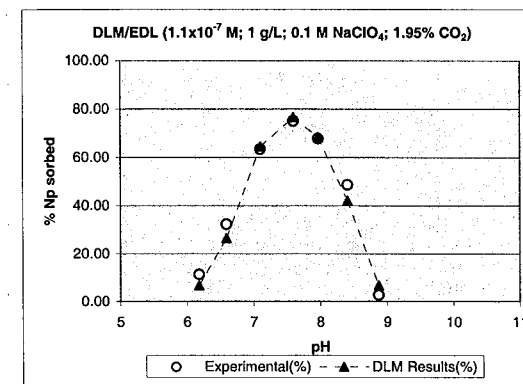
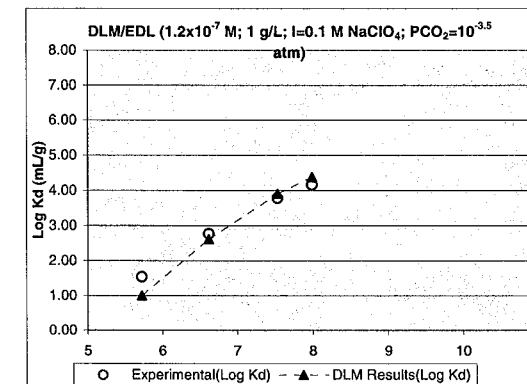
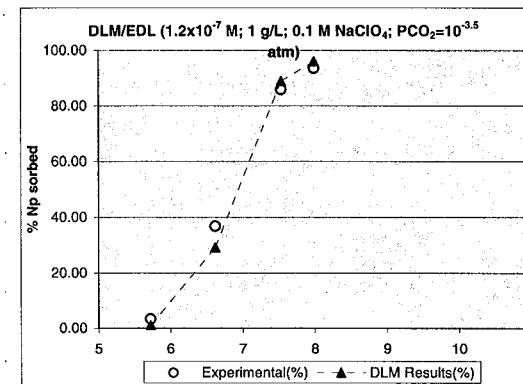
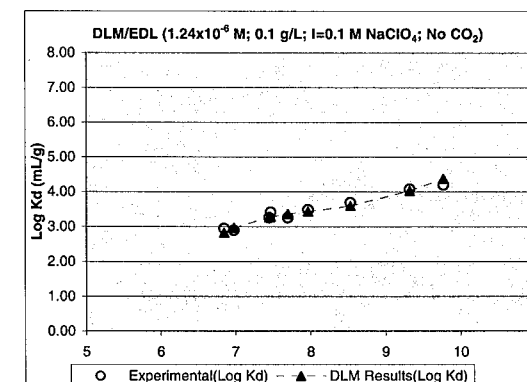
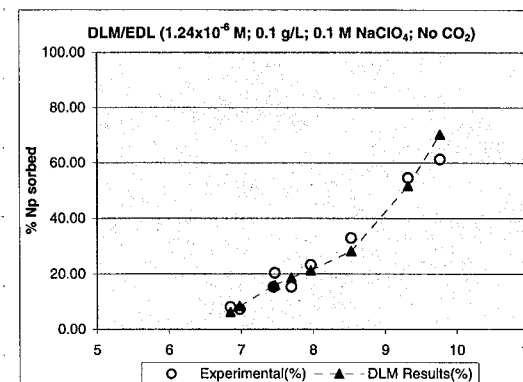
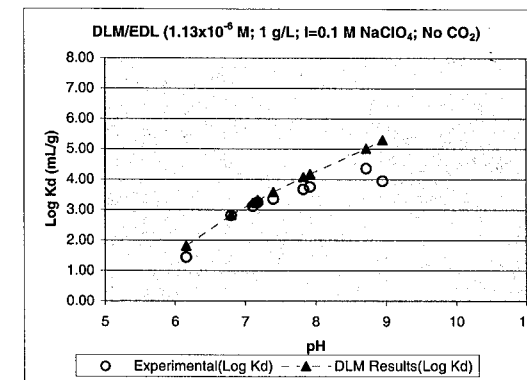
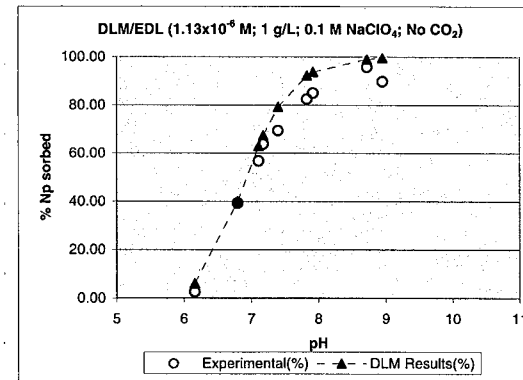
The model was applied using MINTEQA2, Version 4.02 (EPA, 1999a,b) with thermodynamic data from the NEA thermodynamic data base for neptunium (Lemire et al., 2001). As indicated in the instructions from the technical direction team, only Np(V) was modeled in the exercise.

Example MINTEQA2 Input File (Model 1, DLM with EDL)

Np-Hematite Sorption Exp. 1: 1 g/L; I=0.005 M NaClO4
No CO2; Np=1.2E-7 M; 2-site model
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 5 3
5 H+1 ACTIVITY mol/L
1 330 1.000
6.16 6.79 6.82 6.92 9.99
np01_edl.123 8115520 8125520 552 5523300 5523301
4 1 7
1.000E+00 14.40 0.000 0.000 81
330 0.000E+00 -5.00 y /H+1
500 5.000E-03 -2.30 y /Na+1
181 5.000E-03 -2.30 y /ClO4-
552 1.200E-07 -6.92 y /NpO2+1
813 0.000E+00 0.00 y /ADS1PSIo
811 2.612E-06 -5.58 y /ADS1TYP1
812 3.613E-05 -4.44 y /ADS1TYP2
3 1
330 5.0000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo
2 6
8113300 x0(s)- 0.0000 -10.2100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 xoh2+(s) 0.0000 9.5600 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8115520 x0(s)-np02 0.0000 -0.4600 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 4 1.000 811 1.000 552 -1.000 330 0.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8123300 x0(w)- 0.0000 -10.2100 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 812 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8123301 xoh2(w)+ 0.0000 9.5600 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 812 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8125520 x0(w)-np02 0.0000 -3.6210 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 4 1.000 812 1.000 552 -1.000 330 0.000 813 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0

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Species	log K	log a	log f	log g	log h	log i	log j	log k	log l	log m	log n	log o	log p	log q	log r	log s	log t	log u	log v	log w	log x	log y	log z	log A	log B	log C	log D	log E	log F	log G	log H	log I	log J	log K	log L	log M	log N	log O	log P	log Q	log R	log S	log T	log U	log V	log W	log X	log Y	log Z	log AA	log AB	log AC	log AD	log AE	log AF	log AG	log AH	log AI	log AJ	log AK	log AL	log AM	log AN	log AO	log AP	log AQ	log AR	log AS	log AT	log AU	log AV	log AW	log AX	log AY	log AZ	log BA	log BB	log BC	log BD	log BE	log BF	log BG	log BH	log BI	log BJ	log BK	log BL	log BM	log BN	log BO	log BP	log BQ	log BR	log BS	log BT	log BU	log BV	log BW	log BX	log BY	log BZ	log CA	log CB	log CC	log CD	log CE	log CF	log CG	log CH	log CI	log CJ	log CK	log CL	log CM	log CN	log CO	log CP	log CQ	log CR	log CS	log CT	log CU	log CV	log CW	log CX	log CY	log CZ	log DA	log DB	log DC	log DD	log DE	log DF	log DG	log DH	log DI	log DJ	log DK	log DL	log DM	log DN	log DO	log DP	log DQ	log DR	log DS	log DT	log DU	log DV	log DW	log DX	log DY	log DZ	log EA	log EB	log EC	log ED	log EE	log EF	log EG	log EH	log EI	log EJ	log EK	log EL	log EM	log EN	log EO	log EP	log EQ	log ER	log ES	log ET	log EU	log EV	log EW	log EX	log EY	log EZ	log FA	log FB	log FC	log FD	log FE	log FF	log FG	log FH	log FI	log FJ	log FK	log FL	log FM	log FN	log FO	log FP	log FQ	log FR	log FS	log FT	log FU	log FV	log FW	log FX	log FY	log FZ	log GA	log GB	log GC	log GD	log GE	log GF	log GG	log GH	log GI	log GJ	log GK	log GL	log GM	log GN	log GO	log GP	log GQ	log GR	log GS	log GT	log GU	log GV	log GW	log GX	log GY	log GZ	log HA	log HB	log HC	log HD	log HE	log HF	log HG	log HH	log HI	log HJ	log HK	log HL	log HM	log HN	log HO	log HP	log HQ	log HR	log HS	log HT	log HU	log HV	log HW	log HX	log HY	log HZ	log IA	log IB	log IC	log ID	log IE	log IF	log IG	log IH	log II	log IJ	log IK	log IL	log IM	log IN	log IO	log IP	log IQ	log IR	log IS	log IT	log IU	log IV	log IW	log IX	log IY	log IZ	log JA	log JB	log JC	log JD	log JE	log JF	log JG	log JH	log JI	log JJ	log JK	log JL	log JM	log JN	log JO	log JP	log JQ	log JR	log JS	log JT	log JU	log JV	log JW	log JX	log JY	log JZ	log KA	log KB	log KC	log KD	log KE	log KF	log KG	log KH	log KI	log KJ	log KK	log KL	log KM	log KN	log KO	log KP	log KQ	log KR	log KS	log KT	log KU	log KV	log KW	log KX	log KY	log KZ	log LA	log LB	log LC	log LD	log LE	log LF	log LG	log LH	log LI	log LJ	log LK	log LM	log LN	log LO	log LP	log LQ	log LR	log LS	log LT	log LU	log LV	log LW	log LX	log LY	log LZ	log MA	log MB	log MC	log MD	log ME	log MF	log MG	log MH	log MI	log MJ	log MK	log ML	log MM	log MN	log MO	log MP	log MQ	log MR	log MS	log MT	log MU	log MV	log MW	log MX	log MY	log MZ	log NA	log NB	log NC	log ND	log NE	log NF	log NG	log NH	log NI	log NJ	log NK	log NL	log NM	log NN	log NO	log NP	log NQ	log NR	log NS	log NT	log NU	log NV	log NW	log NX	log NY	log NZ	log OA	log OB	log OC	log OD	log OE	log OF	log OG	log OH	log OI	log OJ	log OK	log OL	log OM	log ON	log OO	log OP	log OQ	log OR	log OS	log OT	log OU	log OV	log OW	log OX	log OY	log OZ	log PA	log PB	log PC	log PD	log PE	log PF	log PG	log PH	log PI	log PJ	log PK	log PL	log PM	log PN	log PO	log PP	log PQ	log PR	log PS	log PT	log PU	log PV	log PW	log PX	log PY	log PZ	log QA	log QB	log QC	log QD	log QE	log QF	log QG	log QH	log QI	log QJ	log QK	log QL	log QM	log QN	log QO	log QP	log QQ	log QR	log QS	log QT	log QU	log QV	log QW	log QX	log QY	log QZ	log RA	log RB	log RC	log RD	log RE	log RF	log RG	log RH	log RI	log RJ	log RK	log RL	log RM	log RN	log RO	log RP	log RQ	log RR	log RS	log RT	log RU	log RV	log RW	log RX	log RY	log RZ	log SA	log SB	log SC	log SD	log SE	log SF	log SG	log SH	log SI	log SJ	log SK	log SL	log SM	log SN	log SO	log SP	log SQ	log SR	log SS	log ST	log SU	log SV	log SW	log SX	log SY	log SZ	log TA	log TB	log TC	log TD	log TE	log TF	log TG	log TH	log TI	log TJ	log TK	log TL	log TM	log TN	log TO	log TP	log TQ	log TR	log TS	log TT	log TU	log TV	log TW	log TX	log TY	log TZ	log UA	log UB	log UC	log UD	log UE	log UF	log UG	log UH	log UI	log UJ	log UK	log UL	log UM	log UN	log UO	log UP	log UQ	log UR	log US	log UT	log UY	log UZ	log VA	log VB	log VC	log VD	log VE	log VF	log VG	log VH	log VI	log VJ	log VK	log VL	log VM	log VN	log VO	log VP	log VQ	log VR	log VS	log VT	log VU	log VV	log VW	log VX	log VY	log VZ	log WA	log WB	log WC	log WD	log WE	log WF	log WG	log WH	log WI	log WJ	log WK	log WL	log WM	log WN	log WO	log WP	log WQ	log WR	log WS	log WT	log WU	log WV	log WW	log WX	log WY	log WZ	log XA	log XB	log XC	log XD	log XE	log XF	log XG	log XH	log XI	log XJ	log XK	log XL	log XM	log XN	log XO	log XP	log XQ	log XR	log XS	log XT	log XU	log XV	log XW	log XX	log XY	log XZ	log YA	log YB	log YC	log YD	log YE	log YF	log YG	log YH	log YI	log YJ	log YK	log YL	log YM	log YN	log YO	log YP	log YQ	log YR	log YS	log YT	log YU	log YV	log YW	log YX	log YY	log YZ	log ZA	log ZB	log ZC	log ZD	log ZE	log ZF	log ZG	log ZH	log ZI	log ZJ	log ZK	log ZL	log ZM	log ZN	log ZO	log ZP	log ZQ	log ZR	log ZS	log ZT	log ZU	log ZV	log ZW	log ZX	log ZY	log ZZ
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When expressed as percent sorbed, the electrostatic DLM, fitted to data obtained under CO₂-free conditions, does a good job of fitting the data over most of the observed pH range, and provides an excellent prediction of the effects of CO₂. Under CO₂-free conditions at high pH values, however, where sorption is very high, the model tends to overpredict K_d by one to two orders of magnitude. This is perhaps not surprising at high sorption values. As defined,

$$K_d \text{ (mL / g)} = \frac{\text{equilibrium mass of radionuclide sorbed on solid}}{\text{equilibrium mass of radionuclide in solution}} \times \left(\frac{V}{M} \right)$$

calculating K_d at very high sorption values involves a very small number in the denominator of the Equation. Small variations in sorption as reported (or calculated) on a percent sorbed basis can therefore result in a large shift in K_d. For example, assuming a 1 g/L mineral suspension, the difference between 99.6% and 99.7% sorption results in an increase in calculated K_d from 249,000 mL/g to 332,333 mL/g.

The technical direction team defined a quantitative measure of goodness-of-fit that compares the predicted sorption coefficient (K_d, in mL/g) with the experimental distribution coefficient R_d (mL/g):

$$\text{Goodness-of-Fit} = [\text{Log} (K_{d,\text{model}}/R_{d,\text{experiment}})]^2$$

Smaller values indicate a better prediction of the observed sorption behavior. The goodness-of-fit calculated using this measure is typically small, in most cases ranging from 10⁻⁴ to 10⁻¹.

The model predictions are relatively insensitive to ionic strength, tending to overpredict sorption at ionic strength values lower than the fitted data set (0.1 M NaClO₄). Ionic strength is included in the electrostatic term of the DLM, but unlike multilayer models like the Triple-Layer Model, the DLM does not explicitly consider the sorption of background electrolytes. The DLM also does not allow the treatment of inner and outer layer complexes. A model like the Triple-Layer Model might better simulate sorption at different ionic strengths, but the number of fitted parameters and data requirements would increase.

The model is chemically plausible with regard to Np(V) speciation. The dominant Np species is NpO₂⁺ for pH up to about 8, and continues to be a significant species over the range of experimental conditions. As discussed previously, the model does not consider sorption of background electrolytes, and does not invoke sorption of carbonate species such as NpO₂(CO₃)₂³⁻, CO₃²⁻, or HCO₃⁻. The model accurately predicts decreasing NpO₂⁺ sorption under increasing CO₂ by increasing competition of aqueous neptunyl carbonate species for available NpO₂⁺. The postulated surface reactions are also consistent with EXAFS data on Np-sorption on goethite (Combes et al., 1992).

Based on the modeling results, the DLM developed here is applicable over a broad range in pH, surface loading, and P_{CO2}. Results suggest, however, that there are limitations with regard to ionic strength. More complicated multilayer models are likely to be more suitable for modeling ionic strength effects, but will require additional parameters. One thing worth noting as a possible future area of investigation is the possibility of Np(VI) in the solution. The DLM developed here assumed only Np(V) in solution. However, modeling Np speciation under atmospheric oxygen and CO₂ using the NEA thermodynamic database (Lemire et al., 2001) suggests that Np(VI)-carbonate species form at higher pH.

NONELECTROSTATIC MODEL: MODELING DECISIONS

Model Selected

Non-electrostatic model (NEM). Surface reactions are represented in the same manner as aqueous reactions.

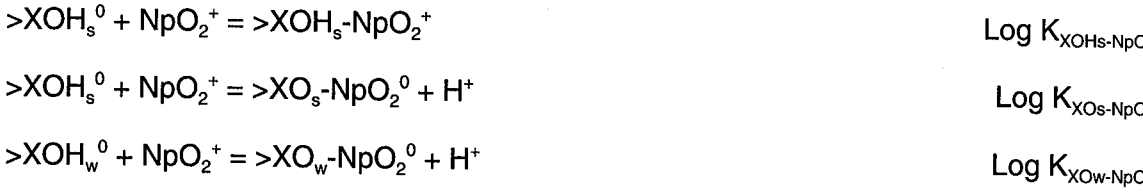
Potentiometric Titration Parameters using FITEQL, Version 2.0

Like the electrostatic DLM described previously, FITEQL, Version 2.0 (Westall, 1982a,b) was used to fit Log K⁺, Log K⁻, and T_{XOH} to the potentiometric titration data at all three ionic strengths. No electrostatic term was included in the reactions, and the results from the FITEQL runs were combined using the weighting scheme of Dzombak and Morel (1990).

Determining Np-Hematite NEM parameters using FITEQL, Version 2.0

Like the electrostatic DLM, a two-site model was selected for the NEM analysis and protonation and deprotonation constants for both site types were assumed to be equal and set at the weighted average values determined by the potentiometric titration data. The total site density (T_{XOHs} + T_{XOHw}) was assumed to be equal to the weighted average values determined from the potentiometric titration data (2.21 × 10⁻⁶ mol sites/m²).

As for the electrostatic DLM, the Np(V)-hematite sorption data for CO₂-free atmosphere, M/V = 0.1 g/L, I = 0.1 M NaClO₄, and Np_{total} = 1.24 × 10⁻⁶ M were selected for determining NEM parameters using FITEQL, Version 2.0. In the absence of the electrostatic term, it was necessary to invoke three mononuclear, monodentate sorption reactions, compared to two for the electrostatic DLM. Two surface complexes were postulated for Np sorption on the strong site, and a third reaction was invoked for Np sorption on the weak site.

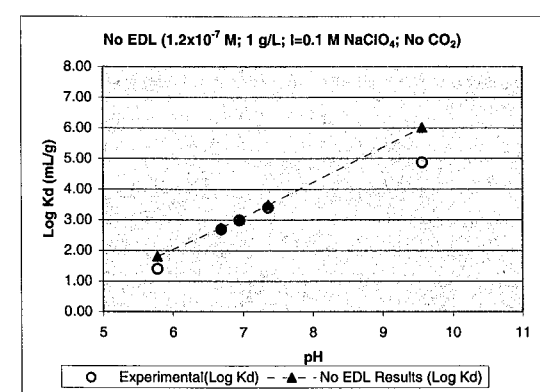
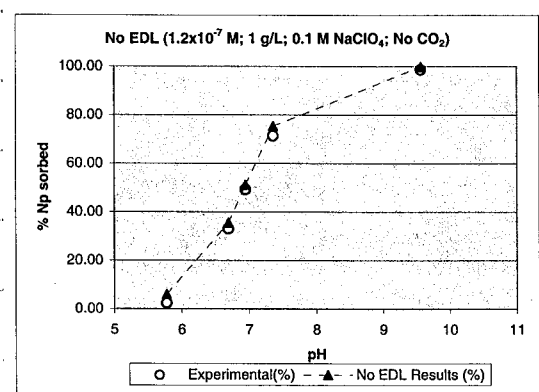
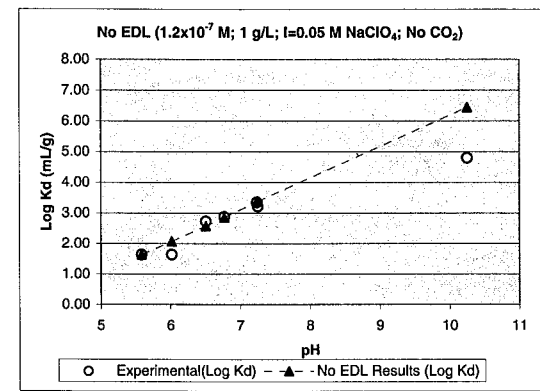
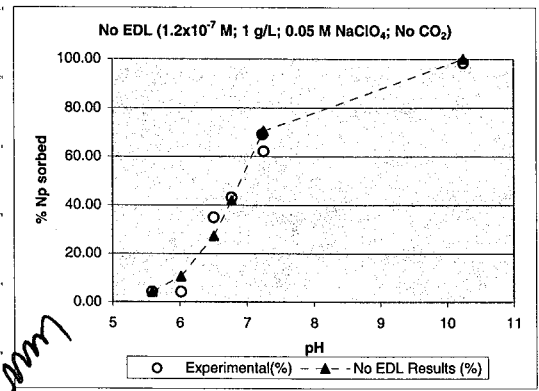
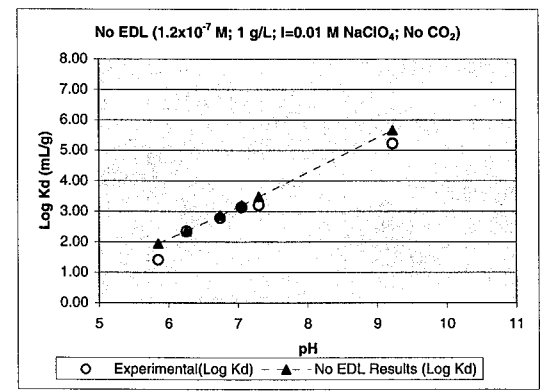
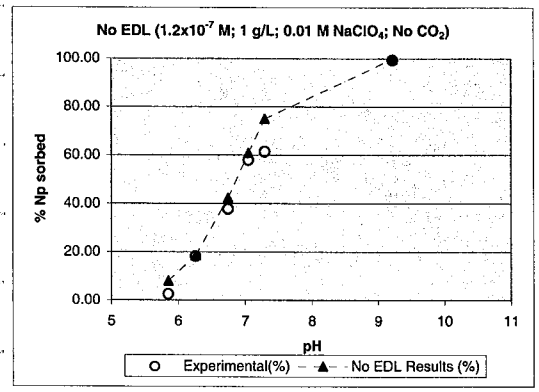
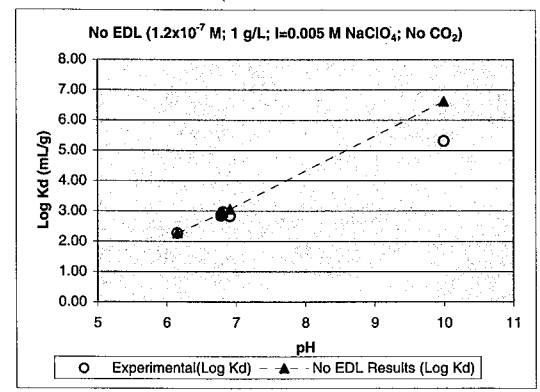
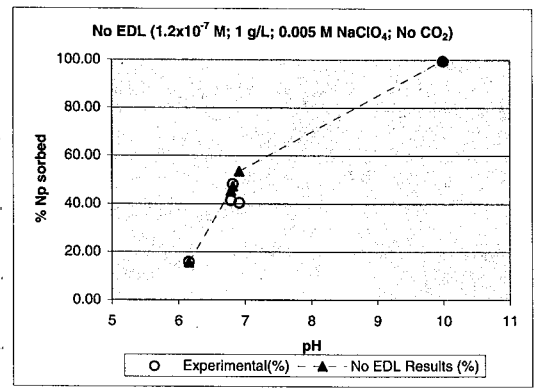


The >XOH_s-NpO₂⁺ was used to fit low pH sorption data. In the same way as described previously, FITEQL, Version 2.0 was used to solve for the binding constants for the postulated sorption reactions. An additional adjustable parameter (for a total of four) included the total concentration of the strong site type (T_{XOHs}).

Summary of Model Results

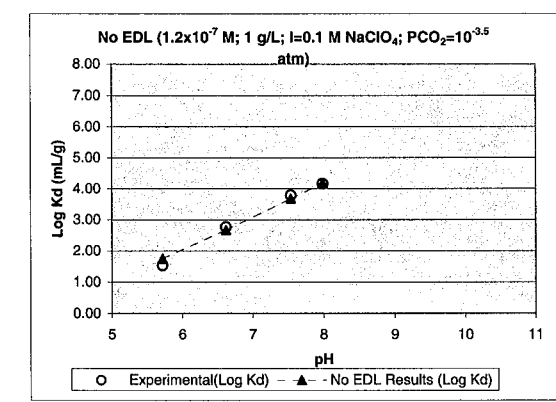
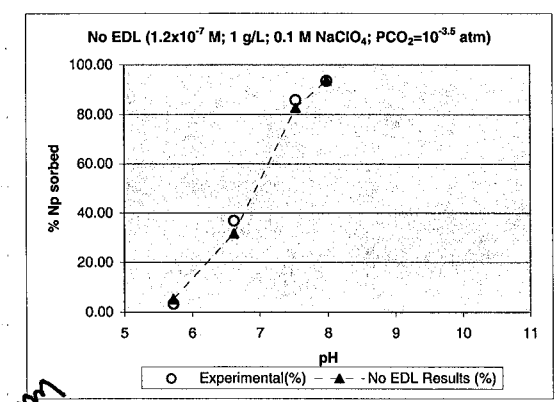
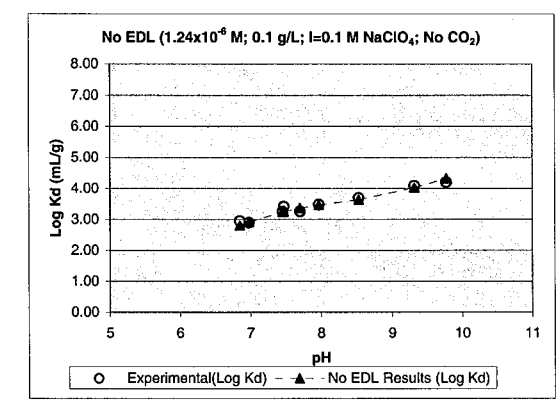
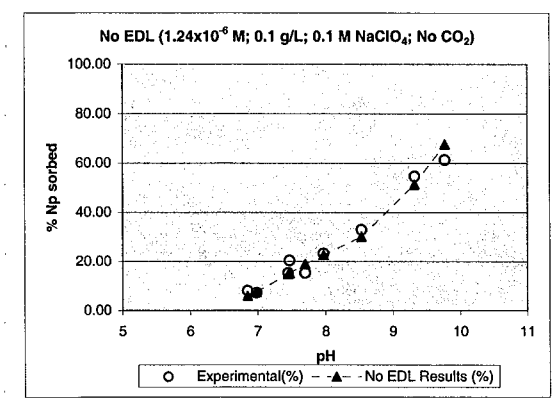
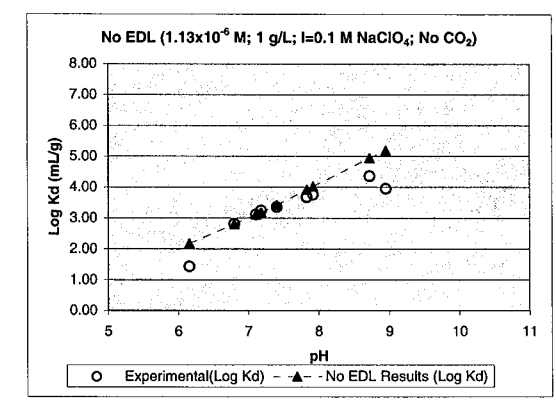
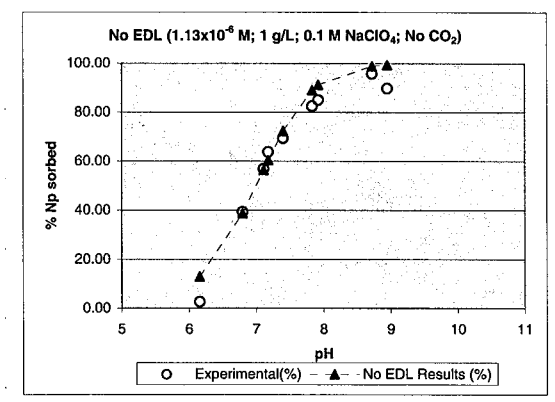
Like the electrostatic DLM, the NEM developed for this test case describes complex sorption behavior over a range in chemical conditions using a relatively simple postulated surface chemistry: NpO₂⁺ sorbed on two different sorption sites. The model required fitting potentiometric titration data to determine surface acidity constants and site concentration (three parameters). Once these are determined, the sorption data were described by an additional four fitted parameters, Log K_{XOHs-NpO2}, Log K_{XOs-NpO2}, Log K_{XOW-NpO2}, and strong site concentration (T_{XOHs}). Determining these four parameters requires a Np-sorption data set over a sufficiently wide pH range, with surface loadings high enough to achieve saturation of the strong sites.

7/5/2002
DRI

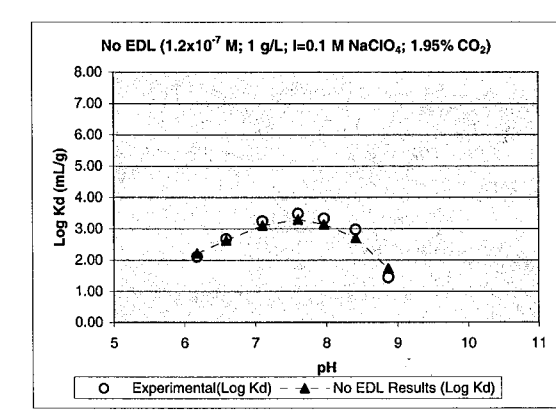
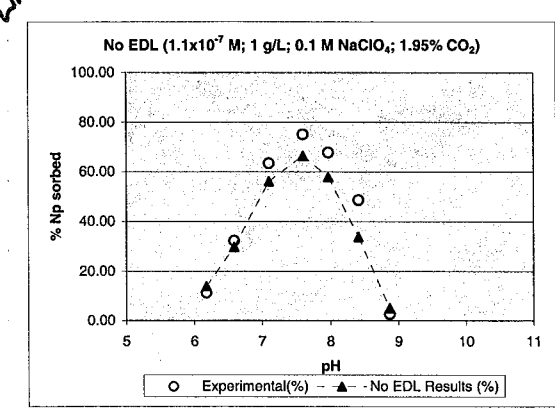


Dehmm

7/5/2002
DRI



Dehmm



7/15/2002
DJ

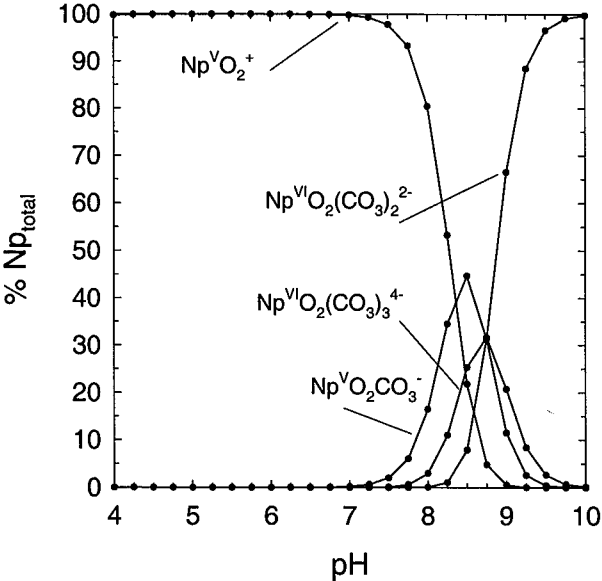
The model was applied using MINTEQA2, Version 4.02 (EPA, 1999a,b) with thermodynamic data from the NEA thermodynamic data base for neptunium (Lemire et al., 2001). Like the electrostatic DLM, the NEM does a good job of reproducing observed sorption data for CO₂-free systems over most of the observed pH range, especially when presented in terms of percent sorbed. It does an excellent job of predicting sorption under atmospheric P_{CO2} (10^{-3.5} atm), but tends to underpredict sorption at elevated CO₂ (1.95%). The quantitative goodness-of-fit described by Equation [1] ranges in most cases from 10⁻⁵ to 10⁻¹. Like the electrostatic DLM, the NEM tends to overpredict sorption under CO₂-free conditions at high pH values. The extent of overprediction, however, is somewhat less than that predicted with the electrostatic DLM.

The NEM predictions are more sensitive to ionic strength effects than the electrostatic DLM, and the NEM does a much better job of predicting sorption at ionic strength values lower than the fitted data set (0.1 M NaClO₄). As implemented in MINTEQA2, the NEM approach provides a more explicit treatment of sorption as a function of ionic strength. The surface complexes are treated like aqueous species through the use of dummy variables that represent 'surface sites'. Unlike the electrostatic DLM where the MINTEQA2 default is to assign surface complexes unity activity coefficients, the NEM approach in MINTEQA2 applies the Davies equation to determine activity coefficients for all species, including the surface complexes.

DLM

Based on the modeling results, the NEM developed here is applicable over a broad range in pH, surface loading, and P_{CO2}. Compared to the electrostatic DLM, results suggest that the NEM is better able to simulate ionic strength effects, but less effective at modeling the effects of elevated CO₂. The NEM called for as much fitting as the electrostatic DLM, and required an additional surface reaction to simulate the low pH sorption data. The chief advantage of the NEM would be in the absence of potentiometric titration data for a complex mineral assemblage, but its use as a predictive tool would be more limited (Davis et al., 1998)

7/15/2002
DJ



DLM

Neptunium speciation predicted by MINTEQA2, Version 4.02 (solid line, filled circles) as a function of pH. T = 25 °C, P_{CO2} = 10^{-3.5} atm, P_{O2} = 10^{-0.66} atm, Np_{total} = 10⁻⁷ m. Neptunium oxidation states change with pH and both Np(V)-species and Np(VI)-species are shown.

7/5/2002
DRJ

References For Test Case 1

Combes, J., C.J. Chisholm-Brause, G.E. Brown Jr., G.A. Parks, S.D. Conradson, P.G. Eller, I.R. Triay, D.E. Hobart, and A. Meijer. EXAFS spectroscopic study of neptunium(V) sorption at the α -FeOOH/Water Interface. *Environmental Science and Technology* 26: 376-382. 1992.

Davis, J.A., J.A. Coston, D.B. Kent, and C.C. Fuller. Application of the surface complexation concept to complex mineral assemblages. *Environmental Science and Technology* 32: 2,830-2,828. 1998.

Dzombak, D.A. and Morel, F.M.M. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons. 1990.

Kohler, M., B.D. Honeyman, and J.O. Leckie. Neptunium(V) sorption on hematite (α -Fe₂O₃) in aqueous suspension: The effect of CO₂. *Radiochimica Acta* 85: 33-48. 1999.

Lemire, R.J., J. Fuger, H. Nitsche, P. Potter, M.H. Rand, J. Rydberg, K. Spahiu, J.C. Sullivan, W.J. Ullman, P. Vitorge, and H. Wanner. *Chemical Thermodynamics Series, Volume 4: Chemical Thermodynamics of Neptunium and Plutonium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 2001.

Turner, D.R., R.T. Pabalan, and F.P. Bertetti. Neptunium(V) sorption on montmorillonite: An experimental and surface complexation modeling study. *Clays and Clay Minerals* 46: 256-269. 1998.

U.S. Environmental Protection Agency. "MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999a.

U.S. Environmental Protection Agency. "Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999b.

Westall, J.C. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 1.2*. Rpt. 82-01. Corvallis, Oregon: Department of Chemistry, Oregon State University. 1982a.

Westall, J.C. *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. 1982b.

DRJ

7/5/2002
DRJ

DRJ

Test Case 1: Np(V) sorption onto a laboratory preparation of pure hematite (α -Fe ₂ O ₃)	
Goal:	The goal of the test case is to determine whether the dependence of the K _d values for Np(V) sorption on chemical variables can be described with surface complexation models. In particular, the importance of fitting the selected data with and without an electrostatic correction term to the surface complexation reactions will be examined.
Modeling instructions:	See Worksheet 2
Data Source:	Kohler, M., Honeyman, B. D., and Leckie, J.O., 1999, <i>Radiochim. Acta</i> , v. 85, p. 33-48.
Solid adsorbent:	X-ray diffraction confirmed the material was crystalline hematite with no impurity Specific surface area (14.4 m ² /g) was measured by BET nitrogen gas adsorption
Electrolyte solution:	sodium perchlorate (NaClO ₄); varying concentrations used
Sorption experiments:	see data in Sheet 4 - Np sorption data
Temperature:	20-22°C
Batch equilibration:	reaction time of 12-14 hours
Additional data:	Surface charge data, carbonate adsorption data, and other experimental information are provided for use in developing the models, but it is not required that these data be used or simulated in the models.
	Acid-base titrations of the hematite suspension were conducted at 25°C (data in Sheet 5 - Surface Charge Data worksheet)
	point-of-zero charge (pH = 9.4)
	Other literature on Np adsorption may be relevant, e.g., Combes, et al., 1992, <i>Environmental Science and Technology</i> , v. 26, p. 376-382. EXAFS study of Np adsorption on goethite.
	Other literature on carbonate adsorption and ternary complex formation may be relevant, e.g., van Geen et al., 1994, <i>Geochimica et Cosmochimica Acta</i> , v. 58, p. 2073-2086 Adsorption of carbonate by goethite
	Villalobos and Leckie, 2001, <i>J. Colloid Interface Sci.</i> , v. 235, p. 15-32. Adsorption of carbonate by goethite
	Bargar et al., 2000, <i>Geochimica et Cosmochimica Acta</i> , v. 64, p. 2737-2749 EXAFS study of uranium-carbonate adsorption complexes on hematite

7/5/2002
DBA

Instructions to Modeling Teams

1. Develop two surface complexation models to describe the Np sorption data, one with electrostatic correction terms included in the mass law (Model 1) and one without such terms (Model 2). The modeling team can choose any model for electrostatic correction that it wishes (diffuse double-layer, triple layer, other), but it must be clear what model has been chosen. Assume that the Np(V) adsorption data provided were collected after the experimental systems achieved chemical equilibrium.

2. The objective is to obtain good fits to the Np(V) sorption data provided, with chemically reasonable (plausible) models, but with as few fitting parameters as possible. However, it is recognized that an increase in the number of fitting parameters in models can lead to a better fit of the adsorption data, and it is up to each Modeling Team to make the decision about how many and which parameters to include in their models.

3. For the development of these two models, use the thermodynamic data provided for the formation of aqueous species (see Sheet 3 - Thermodynamic Data worksheet). You may prepare additional model calculations with other thermodynamic data, but in that case, please submit these as additional modeling, providing the different data used, the reasons for substituting the different data, and the source of the data.

4. Additional data are provided, such as surface charge data, carbonate adsorption data, and other experimental information for use in developing the models, but it is not required that these data be used or simulated in the models. Other literature may be used in justifying modeling approaches or in assigning parameter values. Note that the surface area is given in Worksheet 1 - Information. If surface area is used as a parameter in the modeling, this experimental value for the surface area should be chosen.

5. Document the development of the model in a written format to submit to the TDT. Describe the sequence of model development decisions made and the rationale for the decisions. Describe how the values of model parameters were assigned, fitted, or assumed, such as the concentration of surface sites, the types of surface sites (if a multi-site model), the selection of surface species and the stability constants for their formation, all electrical double layer parameters, method for determining aqueous phase activity coefficients, etc. If a model parameter is assigned a value from an independent source, explain the source and reasoning. Make it clear which model parameters were determined by the fitting of experimental data. As for the selection of surface species, provide the reason that specific species were chosen, e.g., simplest reaction possible; dominant aqueous species, spectroscopic studies in the literature, best fit from trial-and-error, etc.

6. Document the data fitting procedure used, including any software packages and references. The documentation should make it clear what optimization routine was used (and version, e.g. FITEQL 4.0).

7. Enter the calculated values for %Np adsorbed and Kd (mL/g) in Worksheets 7 and 9, titled Model 1 output and Model 2 output. Model 1 is the model with electrostatic correction terms included in the mass law and Model 2 is the model without such terms. Add the concentrations of surface species and solution species for each experimental point to that row of the spreadsheet. Include all surface species and their concentrations, all Np aqueous species greater than 0.1% of the total Np concentration, calculated concentration of H+ (or calculated pH), and calculated total concentration of dissolved carbonate (sum of carbonate, bicarbonate, neptunyl carbonate, etc.).

8. Provide copies of input and output files that can be easily understood by members of the TDT. The output files should clearly show the calculated concentrations of surface and aqueous species corresponding to each experimental data point, the pH (or concentration of H+) the calculated concentrations of dissolved carbonate, etc. The TDT must be able to understand the identity of species in these files.

9. Provide a table of the formation constants for all surface species in Models 1 and 2 (Worksheets 8 and 10).

10. For each Model, provide graphs of calculated and experimental log Kd values versus pH, with the calculated value shown as an open circle and the experimental value as a filled (dark) triangle. Connect the symbols for the calculated values with a dotted line.

11. Provide written summary comments describing the modeling results and the Modeling Team's opinion of:
a) the strengths and weaknesses of the two modeling approaches (Models 1 and 2),
b) the goodness-of-fit for each approach,
c) the chemical plausibility of each Model,
d) numbers of fitting parameters required,
e) data requirements for each modeling approach,
f) the range of applicability of each modeling approach

12. Contact your TDT representative if you have questions about these instructions.

DBA

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Original Np sorption on hematite data

Experiment number	Hematite (grams)	Total Np concentration (moles/L)	Na2CO3 concentration (moles/L)	gas phase	Final pH	% Np adsorbed	Kd (mL/g)
1	1.00	1.00E-07	1.00E-07	equilibrated with 0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
2	2.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
3	3.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
4	4.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
5	5.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
6	6.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
7	7.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
8	8.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
9	9.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
10	10.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
11	11.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
12	12.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
13	13.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
14	14.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
15	15.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
16	16.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
17	17.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
18	18.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
19	19.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
20	20.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
21	21.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
22	22.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
23	23.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
24	24.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
25	25.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
26	26.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
27	27.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
28	28.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
29	29.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
30	30.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
31	31.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
32	32.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
33	33.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
34	34.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
35	35.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
36	36.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
37	37.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
38	38.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
39	39.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
40	40.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
41	41.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
42	42.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
43	43.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
44	44.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
45	45.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
46	46.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
47	47.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
48	48.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
49	49.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
50	50.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
51	51.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12
52	52.00	1.00E-07	1.00E-07	0.005 air with <5 ppm CO2	6.18	1.01E-07	188.12

The Kd (mL/g) values shown below were not in the original publication. The values were calculated by J. Davis (TDT) for this spreadsheet. Please contact TDT immediately if any errors are detected.

Raw hematite acid-base titration data at initial ionic strength of 0.01M NaClO4												
Hematite Titration 09-28-90 11:01:45					First Base/Acid leg							
Initial I =	0.01	Solids conc. =	15.6	g/L	14.4	m2/g						
Initial vol =	100.400	reagent : conc:	NaOH 0.049156	HClO4 0.051581								
reag. vol. [mL]	pH	eq [M] (Ca-Cb)	[H+] calc	[OH-] calc	Charge [M]	Solid conc. [g/L]	Sigma [Coul/m2]	Sigma [Coul/g]	Na [M]	ClO4 [M]	ionic strength [M]	
0.000	5.817	5.26E-04	2.68E-06	4.59E-09	5.23E-04	15.60	-0.225	3.234	1.00E-02	1.00E-02	1.00E-02	
0.050	5.724	5.01E-04	2.09E-06	5.87E-09	4.99E-04	15.59	0.214	3.087	1.00E-02	1.00E-02	1.00E-02	
0.130	5.994	4.62E-04	1.12E-06	1.09E-08	4.61E-04	15.58	0.198	2.852	1.01E-02	9.99E-03	1.00E-02	
0.210	6.256	4.22E-04	6.15E-07	2.00E-08	4.22E-04	15.57	0.182	2.615	1.01E-02	9.98E-03	1.00E-02	
0.240	6.354	4.08E-04	4.91E-07	2.51E-08	4.07E-04	15.56	0.175	2.525	1.01E-02	9.98E-03	1.00E-02	
0.290	6.520	3.83E-04	3.35E-07	3.67E-08	3.83E-04	15.56	0.165	2.376	1.01E-02	9.97E-03	1.00E-02	
0.340	6.683	3.59E-04	2.30E-07	5.34E-08	3.59E-04	15.55	0.155	2.226	1.01E-02	9.97E-03	1.00E-02	
0.390	6.944	3.35E-04	1.26E-07	9.75E-08	3.34E-04	15.54	0.144	2.077	1.02E-02	9.96E-03	1.01E-02	
0.440	6.991	3.10E-04	1.13E-07	1.09E-07	3.10E-04	15.53	0.134	1.926	1.02E-02	9.96E-03	1.01E-02	
0.490	7.142	2.86E-04	8.00E-08	1.54E-07	2.86E-04	15.52	0.123	1.777	1.02E-02	9.95E-03	1.01E-02	
0.510	7.201	2.76E-04	6.98E-08	1.76E-07	2.76E-04	15.52	0.119	1.717	1.02E-02	9.95E-03	1.01E-02	
0.530	7.259	2.66E-04	6.11E-08	2.01E-07	2.66E-04	15.52	0.115	1.657	1.02E-02	9.95E-03	1.01E-02	
0.550	7.322	2.57E-04	5.28E-08	2.33E-07	2.57E-04	15.52	0.111	1.597	1.02E-02	9.95E-03	1.01E-02	
0.585	7.433	2.40E-04	4.09E-08	3.00E-07	2.40E-04	15.51	0.104	1.492	1.02E-02	9.94E-03	1.01E-02	
0.630	7.576	2.18E-04	2.94E-08	4.18E-07	2.18E-04	15.50	0.094	1.357	1.02E-02	9.94E-03	1.01E-02	
0.675	7.730	1.96E-04	2.06E-08	5.95E-07	1.96E-04	15.50	0.085	1.223	1.03E-02	9.93E-03	1.01E-02	
0.720	7.891	1.74E-04	1.43E-08	8.63E-07	1.75E-04	15.49	0.076	1.089	1.03E-02	9.93E-03	1.01E-02	
0.765	8.061	1.52E-04	9.63E-09	1.28E-06	1.54E-04	15.48	0.066	0.957	1.03E-02	9.92E-03	1.01E-02	
0.785	8.129	1.43E-04	8.24E-09	1.49E-06	1.44E-04	15.48	0.062	0.898	1.03E-02	9.92E-03	1.01E-02	
0.815	8.241	1.28E-04	6.37E-09	1.93E-06	1.30E-04	15.47	0.056	0.810	1.03E-02	9.92E-03	1.01E-02	
0.845	8.357	1.14E-04	4.87E-09	2.52E-06	1.16E-04	15.47	0.050	0.724	1.03E-02	9.92E-03	1.01E-02	
0.875	8.476	9.90E-05	3.71E-09	3.32E-06	1.02E-04	15.47	0.044	0.638	1.03E-02	9.91E-03	1.01E-02	
0.905	8.600	8.45E-05	2.79E-09	4.41E-06	8.89E-05	15.46	0.039	0.555	1.03E-02	9.91E-03	1.01E-02	
0.935	8.722	7.01E-05	2.10E-09	5.85E-06	7.59E-05	15.46	0.033	0.474	1.04E-02	9.91E-03	1.01E-02	
0.965	8.844	5.58E-05	1.59E-09	7.74E-06	6.33E-05	15.45	0.027	0.395	1.04E-02	9.90E-03	1.01E-02	
0.995	8.960	4.11E-05	1.22E-09	1.01E-05	5.12E-05	15.45	0.022	0.320	1.04E-02	9.90E-03	1.01E-02	
1.025	9.072	2.67E-05	9.39E-10	1.31E-05	3.97E-05	15.44	0.017	0.248	1.04E-02	9.90E-03	1.02E-02	
1.070	9.231	4.99E-06	6.51E-10	1.89E-05	2.39E-05	15.44	0.010	0.149	1.04E-02	9.89E-03	1.02E-02	
1.115	9.374	-1.67E-05	4.69E-10	2.62E-05	9.57E-06	15.43	0.004	0.060	1.04E-02	9.89E-03	1.02E-02	
1.160	9.496	-3.83E-05	3.54E-10	3.47E-05	-3.56E-06	15.42	-0.002	-0.022	1.04E-02	9.89E-03	1.02E-02	
1.205	9.602	-5.99E-05	2.77E-10	4.43E-05	-1.56E-05	15.41	-0.007	-0.097	1.05E-02	9.88E-03	1.02E-02	
1.250	9.695	-8.15E-05	2.24E-10	5.49E-05	-2.66E-05	15.41	-0.012	-0.166	1.05E-02	9.88E-03	1.02E-02	
1.295	9.774	-1.03E-04	1.87E-10	6.59E-05	-3.72E-05	15.40	-0.016	-0.233	1.05E-02	9.87E-03	1.02E-02	
1.340	9.846	-1.25E-04	1.58E-10	7.78E-05	-4.69E-05	15.39	-0.020	-0.294	1.05E-02	9.87E-03	1.02E-02	
1.385	9.909	-1.46E-04	1.37E-10	8.99E-05	-5.62E-05	15.39	-0.024	-0.353	1.05E-02	9.86E-03	1.02E-02	
1.430	9.966	-1.68E-04	1.20E-10	1.03E-04	-6.52E-05	15.38	-0.028	-0.409	1.05E-02	9.86E-03	1.03E-02	
1.475	10.019	-1.89E-04	1.06E-10	1.16E-04	-7.33E-05	15.37	-0.032	-0.460	1.06E-02	9.86E-03	1.03E-02	
1.520	10.078	-2.65E-04	7.36E-11	1.67E-04	-8.61E-05	15.36	-0.038	-0.541	1.06E-02	9.85E-03	1.03E-02	
1.565	10.105	-2.27E-04	8.71E-11	1.41E-04	-9.84E-05	15.35	-0.043	-0.619	1.06E-02	9.84E-03	1.03E-02	
1.610	10.178	-3.04E-04	6.34E-11	1.94E-04	-1.09E-04	15.34	-0.048	-0.689	1.07E-02	9.83E-03	1.03E-02	
1.655	10.243	-3.42E-04	5.56E-11	2.21E-04	-1.20E-04	15.33	-0.053	-0.757	1.07E-02	9.82E-03	1.04E-02	
1.700	10.300	-3.79E-04	4.92E-11	2.50E-04	-1.29E-04	15.31	-0.057	-0.816	1.07E-02	9.82E-03	1.04E-02	
1.745	10.353	-4.17E-04	4.41E-11	2.79E-04	-1.39E-04	15.30	-0.061	-0.875	1.07E-02	9.81E-03	1.04E-02	
1.790	10.400	-4.55E-04	4.00E-11	3.07E-04	-1.48E-04	15.29	-0.065	-0.932	1.08E-02	9.80E-03	1.04E-02	
1.835	10.443	-4.93E-04	3.56E-11	3.46E-04	-1.47E-04	15.28	-0.064	-0.929	1.08E-02	9.79E-03	1.05E-02	
1.880	10.494	-5.31E-04	3.34E-11	3.68E-04	-1.63E-04	15.27	-0.071	-1.028	1.08E-02	9.79E-03	1.05E-02	
1.925	10.555	-5.68E-04	3.09E-11	3.98E-04	-1.70E-04	15.25	-0.075	-1.077	1.09E-02	9.78E-03	1.05E-02	
2.015	10.616	-6.39E-04	2.68E-11	4.58E-04	-1.81E-04	15.23	-0.079	-1.144	1.09E-02	9.76E-03	1.06E-02	
2.060	10.665	-7.09E-04	2.40E-11	5.13E-04	-1.96E-04	15.21	-0.086	-1.244	1.10E-02	9.75E-03	1.06E-02	
2.105	10.747	-8.25E-04	1.99E-11	6.19E-04	-2.06E-04	15.17	-0.091	-1.311	1.11E-02	9.73E-03	1.07E-02	
2.150	10.816	-9.41E-04	1.69E-11	7.28E-04	-2.16E-04	15.14	-0.095	-1.374	1.12E-02	9.70E-03	1.08E-02	
2.195	10.876	-1.06E-03	1.48E-11	8.33E-04	-2.23E-04	15.10	-0.099	-1.428	1.13E-02	9.68E-03	1.09E-02	
2.240	10.928	-1.17E-03	1.31E-11	9.39E-04	-2.32E-04	15.06	-0.103	-1.488	1.13E-02	9.66E-03	1.10E-02	
2.285	10.974	-1.29E-03	1.18E-11	1.04E-03	-2.42E-04	15.03	-0.108	-1.552	1.14E-02	9.63E-03	1.11E-02	
2.330	11.015	-1.40E-03	1.07E-11	1.15E-03	-2.52E-04	14.99	-0.113	-1.622	1.15E-02	9.61E-03	1.11E-02	
2.375	11.054	-1.51E-03	9.79E-12	1.26E-03	-2.57E-04	14.96	-0.115	-1.661	1.16E-02	9.59E-03	1.12E-02	
2.420	11.088	-1.63E-03	9.05E-12	1.36E-03	-2.68E-04	14.92	-0.120	-1.733	1.17E-02	9.56E-03	1.13E-02	
2.465	11.121	-1.74E-03	8.39E-12	1.47E-03	-2.73E-04	14.88	-0.123	-1.769	1.18E-02	9.54E-03	1.14E-02	
0.000	11.117	-1.74E-03	8.47E-12	1.45E-03	-2.86E-04	14.88	-0.129	-1.856	1.18E-02	9.54E-03	1.14E-02	
0.050	11.083	-1.61E-03	9.16E-12	1.34E-03	-2.69E-04	14.85	-0.121	-1.745	1.18E-02	9.64E-03	1.14E-02	
0.100	11.074	-1.59E-03	9.35E-12	1.31E-03	-2.73E-04	14.84	-0.123	-1.776	1.18E-02	9.66E-03	1.14E-02	
0.150	11.066	-1.57E-03	9.52E-12	1.29E-03	-2.74E-04	14.84	-0.124	-1.785	1.18E-02	9.68E-03	1.14E-02	
0.200	11.058	-1.54E-03	9.70E-12	1.27E-03	-2.75E-04	14.83	-0.124	-1.790	1.18E-02	9.69E-03	1.14E-02	
0.250	11.049	-1.52E-03	9.90E-12	1.24E-03	-2.78E-04	14.82	-0.126	-1.812	1.17E-02	9.71E-03	1.14E-02	
0.300	11.042	-1.50E-03	1.01E-11	1.22E-03	-2.76E-04	14.82	-0.125	-1.794	1.17E-02	9.73E-03	1.13E-02	
0.350	11.033	-1.47E-03	1.03E-11	1.20E-03	-2.78E-04	14.81	-0.126	-1.810	1.17E-02	9.75E-03	1.13E-02	
0.400	11.024	-1.45E-03	1.05E-11	1.17E-03	-2.80E-04	14.81	-0.127	-1.823	1.17E-02	9.77E-03	1.13E-02	
0.450	11.015	-1.43E-03	1.07E-11	1.15E-03	-2.81E-04	14.80	-0.127	-1.832	1.17E-02	9.78E-03	1.13E-02	
0.500	11.006	-1.41E-03	1.09E-11	1.12E-03	-2.82E-04	14.79	-0.128	-1.839	1.17E-02	9.80E-03	1.13E-02	
0.550	10.998	-1.38E-03	1.11E-11	1.10E-03	-2.80E-04	14.79	-0.127	-1.826	1.17E-02	9.82E-03	1.13E-02	
0.600	10.988	-1.36E-03	1.14E-11	1.08E-03	-2.82E-04	14.78	-0.128	-1.843	1.17E-02	9.84E-03	1.13E-02	
0.650	10.978	-1.34E-03	1.17E-11	1.05E-03	-2.84E-04	14.77	-0.129	-1.856	1.17E-02	9.85E-03	1.13E-02	
0.700	10.937	-1.24E-03	1.26E-11	9.59E-04	-2.79E-04	14.75	-0.127	-1.825	1.17E-02	9.93E-03	1.13E-02	
0.750	10.817	-9.89E-04	1.69E-11	7.28E-04	-2.61E-04	14.68	-0.119	-1.719	1.16E-02	1.01E-02	1.12E-02	
0.800	10.682	-7.42E-04	2.41E-11	5.09E-04	-2.33E-04	14.61	-0.107	-1.540	1.16E-02	1.03E-02	1.12E-02	
0.850	10.443	-4.98E-04	4.00E-11	3.07E-04	-1.90E-04	14.54	-0.088	-1.2.26				

7/5/2002
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These results were
not used in the
modeling approach described
on pp 118-130 of this SN.

CO_3^{2-} - Hematite

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Adsorption of carbonate by hematite		final dissolved carbonate (moles/L)		final pH		NaClO ₄ (moles/L)		Total carbonate in system (moles/L)		Hematite (grams/L)	
% carbonate adsorbed		3.08E-05		4		1.00E-01		5.10E-01		5.75	
40.16	2.048E-05	3.08E-05	5.75	4.02	10 ⁻⁰⁰⁰¹	5.10E-01	5.75	5.10E-01	5.75	5.75	5.75
47.04	2.493E-05	2.81E-05	5.75	4.31	10 ⁻⁰⁰⁰¹	5.30E-01	5.75	5.30E-01	5.75	5.75	5.75
58.30	3.177E-05	2.27E-05	5.75	4.64	10 ⁻⁰⁰⁰¹	5.45E-01	5.75	5.45E-01	5.75	5.75	5.75
70.72	4.031E-05	1.67E-05	5.75	4.74	10 ⁻⁰⁰⁰¹	5.70E-01	5.75	5.70E-01	5.75	5.75	5.75
77.45	4.531E-05	1.32E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	5.85E-01	5.75	5.85E-01	5.75	5.75	5.75
78.70	4.683E-05	1.27E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	5.95E-01	5.75	5.95E-01	5.75	5.75	5.75
81.41	4.966E-05	1.13E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	6.00E-01	5.75	6.00E-01	5.75	5.75	5.75
81.02	4.983E-05	1.17E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	6.00E-01	5.75	6.00E-01	5.75	5.75	5.75
81.23	5.036E-05	1.16E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	6.00E-01	5.75	6.00E-01	5.75	5.75	5.75
76.22	5.076E-05	1.16E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	6.00E-01	5.75	6.00E-01	5.75	5.75	5.75
65.94	5.121E-05	1.16E-05	5.75	4.79	10 ⁻⁰⁰⁰¹	6.00E-01	5.75	6.00E-01	5.75	5.75	5.75

7/5/2002

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Hm Potentiometric
titration data
I = 0.261 M

Raw hematite acid-base titration data at initial ionic strength of 0.261 M NaClO ₄											
Hematite Titration 09-28-90						Third Base leg (no acid leg)					
Initial I =	0.261	Solids conc. =	13.075	g/L	14.4	m2/g					
Initial vol. =	119.785	reagent: conc:	NaOH	-0.049156							
reag. vol. [mL]	pH	eq [M] (Ca-Cb)	[H ⁺] calc	[OH ⁻] calc	Charge [M]	Solid conc. [g/L]	Sigma [Coul/m2]	Sigma [Coul/g]	Na [M]	ClO ₄ [M]	Ionic strength [M]
0.000	5.700	5.94E-04	2.70E-06	6.77E-09	5.91E-04	13.08	0.303	4.362	2.610E-01	2.610E-01	2.61E-01
0.050	5.810	5.73E-04	2.09E-06	8.73E-09	5.71E-04	13.07	0.293	4.216	2.609E-01	2.609E-01	2.61E-01
0.100	5.983	5.53E-04	1.41E-06	1.30E-08	5.51E-04	13.06	0.283	4.071	2.608E-01	2.608E-01	2.61E-01
0.150	6.141	5.32E-04	9.77E-07	1.87E-08	5.31E-04	13.06	0.272	3.924	2.607E-01	2.607E-01	2.61E-01
0.200	6.285	5.11E-04	7.34E-07	2.48E-08	5.11E-04	13.05	0.262	3.775	2.606E-01	2.606E-01	2.61E-01
0.250	6.507	4.91E-04	4.21E-07	4.34E-08	4.91E-04	13.05	0.252	3.627	2.605E-01	2.605E-01	2.61E-01
0.300	6.734	4.58E-04	2.49E-07	7.32E-08	4.58E-04	13.04	0.235	3.388	2.604E-01	2.603E-01	2.60E-01
0.410	7.044	4.25E-04	1.22E-07	1.50E-07	4.25E-04	13.03	0.219	3.149	2.603E-01	2.601E-01	2.60E-01
0.455	7.087	4.07E-04	1.11E-07	1.66E-07	4.07E-04	13.03	0.209	3.014	2.602E-01	2.600E-01	2.60E-01
0.515	7.240	3.82E-04	7.78E-08	2.33E-07	3.82E-04	13.02	0.197	2.834	2.601E-01	2.599E-01	2.60E-01
0.615	7.523	3.41E-04	4.05E-08	4.51E-07	3.42E-04	13.01	0.176	2.535	2.599E-01	2.597E-01	2.60E-01
0.715	7.827	3.01E-04	2.01E-08	9.07E-07	3.01E-04	13.00	0.155	2.238	2.597E-01	2.595E-01	2.60E-01
0.815	8.127	2.60E-04	1.01E-08	1.81E-06	2.62E-04	12.99	0.135	1.944	2.596E-01	2.592E-01	2.59E-01
0.875	8.265	2.35E-04	7.34E-09	2.48E-06	2.38E-04	12.98	0.123	1.768	2.595E-01	2.591E-01	2.59E-01
0.935	8.398	2.11E-04	5.40E-09	3.39E-06	2.14E-04	12.97	0.111	1.594	2.594E-01	2.590E-01	2.59E-01
0.995	8.527	1.87E-04	4.02E-09	4.55E-06	1.91E-04	12.97	0.089	1.423	2.592E-01	2.588E-01	2.59E-01
1.055	8.649	1.62E-04	3.03E-09	6.02E-06	1.68E-04	12.96	0.087	1.253	2.592E-01	2.587E-01	2.59E-01
1.115	8.753	1.38E-04	2.39E-09	7.66E-06	1.46E-04	12.95	0.075	1.085	2.590E-01	2.586E-01	2.59E-01
1.175	8.857	1.14E-04	1.88E-09	9.72E-06	1.23E-04	12.95	0.064	0.920	2.589E-01	2.585E-01	2.59E-01
1.235	8.961	8.94E-05	1.48E-09	1.24E-05	1.02E-04	12.94	0.053	0.759	2.588E-01	2.583E-01	2.59E-01
1.295	9.052	6.52E-05	1.20E-09	1.52E-05	8.04E-05	12.94	0.042	0.600	2.587E-01	2.582E-01	2.59E-01
1.795	9.610	-1.36E-04	3.32E-10	5.51E-05	-8.09E-05	12.88	-0.042	-0.606	2.579E-01	2.571E-01	2.58E-01
2.295	9.919	-3.35E-04	1.63E-10	1.12E-04	-2.23E-04	12.83	-0.117	-1.679	2.570E-01	2.561E-01	2.57E-01

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For Test Case 6 of the Nuclear Energy Agency (NEA) sorption exercise, the objective is to simulate the U(VI)-schist sorption data of Payne (1999) using: (1) a surface complexation modeling approach calibrated using the entire available pH range of data for sample W2, and (2) a surface complexation modeling approach calibrated using a restricted set of sorption data for sample W2 between a pH of 4.75 and 8.75. Detailed model results are provided in the accompanying electronic files in the folder at the end of this scientific notebook.

Mineral-Radioelement System

U(VI) sorption on schist (Payne, 1999). Full data set (pH from 2.14 to 9.64).

Model Selected

- Diffuse Layer Model (DLM) with electrostatic corrections. Models A, C, D, and E in the supporting electronic files.

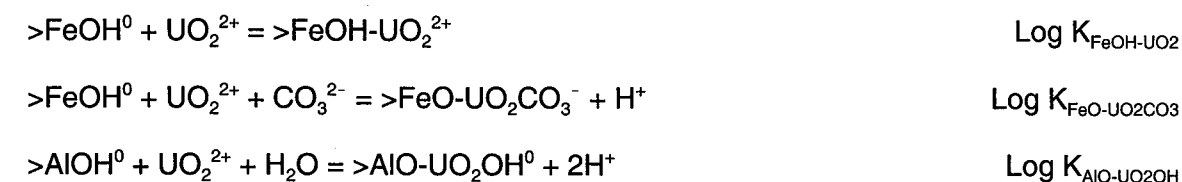
Describing Surface Protonation/Deprotonation

There are no potentiometric titration data available for the complex mineral assemblage represented by the Koongaara schist. The modeling approach adopted here assumes that sorption sites are represented by ferrinol ($>\text{FeOH}^0$) and aluminol ($>\text{AlOH}^0$) sites. To describe the surface acidity behavior, protonation/deprotonation constants for ferrihydrite and γ -alumina were taken from Turner and Sassman (1996). A starting point for site concentrations is assuming a total site density of 3.84×10^{-6} mol sites/m² and assuming that 20 percent of the total elemental content of Fe and Al, as determined by multi-step extraction, is available as $>\text{FeOH}^0$ and $>\text{AlOH}^0$. Because these site concentrations are poorly constrained, however, the site concentrations were ultimately treated as fitting parameters in interpreting the U(VI) sorption data using the nonlinear parameter optimization code FITEQL, Version 2.0 (Westall, 1982a,b).

Determining U(VI)-schist DLM parameters using FITEQL, Version 2.0

As instructed by the technical direction team, the U(VI)-schist sorption data for atmospheric CO₂ (P_{CO2} = 10^{-3.5} atm), M/V = 4 g/L, I = 0.1 M NaNO₃, and U_{total} = 3.882 × 10⁻⁶ M was selected for fitting over the entire available pH range from 2.14 to 9.64.

A simplified modeling approach was used. Three mononuclear, monodentate surface complexes were postulated to fit the available data:



FITEQL, Version 2.0 (Westall, 1982a,b) was used to solve for the binding constants for the postulated sorption reactions. Additional input data include the surface protonation/deprotonation constants and total site concentration determined from the

Diffuse Layer Model using LogK+, LogK-, and T(XOH) as fitting parameters												
Mineral	Reference	Electrolyte	I.S.	LogK+	sigK+	LogK-	sigK-	T(XOH)	sigT(XOH)	Ns	signs	SOS/DF
Hematite (14.4 m2/g)	Table 5A	NaClO4	0.0100	10.14	0.0388	-10.39	0.0566	5.13E-04	4.98E-06	1.38	1.34E-02	45.3
	Table 5B	NaClO4	0.1000	9.37	0.0199	-10.17	0.0377	5.48E-04	3.16E-06	1.61	8.47E-03	56.7
	Table 5C	NaClO4	0.2610	9.42	0.0243	-10.19	0.0522	5.57E-04	3.20E-06	1.78	8.58E-03	68.1
Mineral	sum 1/sigK+	w.f.	wfLog K+	LogK+	sum 1/sigK-	w.f.	wfLogK-	LogK-	sum 1/sigNs	w.f.	wfLogNs	LogNs
Hematite	117.18	0.219951513	2.23	9.56	63.35	0.278891994	-2.90	-10.24	309.48	0.242001876	0.332989971	1.62
		0.428850186	4.02			0.418707874	4.26			0.381382704	0.612759006	
		0.351198301	3.31			0.302400132	-3.08			0.57661542	0.671422382	
	LogK+	LogK+	LogK+	LogK-	LogK-	LogK-	Ns	Ns	Ns	Ns	Ns	
	sum wf diff/2	Sx^2	conf lim (95%)	sum wf diff	Sx^2	conf lim (95%)	sum wf diff	Sx^2	conf lim (95%)			
	0.074778957	0.048173598	0.54	0.00649413	0.004538	0.17	0.01407793	0.012224524	0.27			
	0.0714984047			0.001902329			4.19983E-05					
	0.006584193			0.000679542			0.010329119					

WITH EDL / Potentiometric titration
with $\text{Ti}(\text{XOH})_4$ as fitting parameters

NO EDL/Potentiometric titration and T/VOH as fitting parameters

Diffuse Layer Model using LogK+, LogK-, and T(XOH) as fitting parameters													
Mineral	Reference	Electrolyte	I.S.	LogK+	LogK-	LogK+	LogK-	T(XOH)	LogK+	LogK-	LogK+	LogK-	SOS/DF
Hematite (14.4 m2/g)	Table 5A	NaClO4	0.0100	7.82	-10.89	0.0083	0.0216	4.11E-04	1.71E-06	1.10	4.57E-03	62.4	
	Table 5B	NaClO4	0.1000	8.03	-10.66	0.0081	0.0199	4.54E-04	1.42E-06	1.33	3.82E-03	100.6	
	Table 5C	NaClO4	0.2610	8.24	-10.35	0.0098	0.0332	4.90E-04	1.73E-06	1.57	4.63E-03	94.1	
Mineral	sum 1/sigK+	w.f.	wfLog K+	LogK+	LogK-	sum 1/sigK-	w.f.	wfLogK-	LogK+	sum 1/sigNs	w.f.	wfLogNs	NS
Hematite	346.28	0.34987353	2.74	8.02	-10.67	126.76	0.365917312	-3.98	-10.67	696.94	0.313872603	0.346044768	1.33
		0.354512168	2.85				0.396241951	-4.22			0.376073639	0.500914704	
		0.295614302	2.44				0.237840797	-2.46			0.310053759	0.486303693	
	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+	LogK+
	sum wf*diff/2	Sx/2	conf lim (95%)	sum wf*diff	Sx/2	conf lim (95%)	sum wf*diff	Sx/2	conf lim (95%)	sum wf*diff	Sx/2	conf lim (95%)	sum wf*diff
	0.013800471	0.01416809	0.30	0.017641177	0.021052364	0.36	0.016714127	0.016932332	0.32	0.016714127	0.016932332	0.32	
	4.60275E-05			4.31081E-05			6.39549E-07			6.39549E-07			
	0.014489682			0.024420443			0.017149897			0.017149897			

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potentiometric titration data, and thermodynamic data for U(VI) from the NEA thermodynamic database (Grenthe et al., 1992). Ionic strength activity coefficients were determined using the Davies Equation as identified in Table 2.13 of Dzombak and Morel (1990). Additional fitting parameters included the total concentration of ferrinol (T_{FeOH}) and aluminol (T_{AlOH}). It should be noted that the T_{AlOH} determined by FITEQL was very similar to the starting concentration assuming that 20 percent of the total elemental content of Al was available as $>AlOH^0$.

Table 3. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 6 (U-Schist). Electrostatic Diffuse Layer surface complexation model for entire pH range (2.14 to 9.64)

Surface Reaction/Fitted Parameter	Log K (I=0)	Site Concentration (mol/m ²)	Comment
$>FeOH^0 + H^+ = >FeOH_2^+$	7.29	-	From Turner and Sassman (1996).
$>FeOH^0 = >FeO^- + H^+$	-8.93	-	From Turner and Sassman (1996).
$>FeOH^0 + UO_2^{2+} = >FeOH-UO_2^{2+}$	11.90	-	Determined using $PCO_2=10^{-3.5}$, $M/V = 4$ g/L, $I = 0.1$ M $NaNO_3$, $U_{total} = 3.882 \times 10^{-6}$ M, pH 2.14 to 9.64, with FITEQL 2.0
$>FeOH^0 + UO_2^{2+} + CO_3^{2-} = >FeO-UO_2CO_3^- + H^+$	11.15	-	Determined using $PCO_2=10^{-3.5}$, $M/V = 4$ g/L, $I = 0.1$ M $NaNO_3$, $U_{total} = 3.882 \times 10^{-6}$ M, pH 2.14 to 9.64, with FITEQL 2.0
$>AlOH^0 + H^+ = >AlOH_2^+$	6.85	-	From Turner and Sassman (1996).
$>AlOH^0 = >AlO^- + H^+$	-9.05	-	From Turner and Sassman (1996).
$>AlOH^0 + UO_2^{2+} + H_2O = >AlO-UO_2OH^0 + 2H^+$	-5.60	-	Determined using $PCO_2=10^{-3.5}$, $M/V = 4$ g/L, $I = 0.1$ M $NaNO_3$, $U_{total} = 3.882 \times 10^{-6}$ M, pH 2.14 to 9.64, with FITEQL 2.0
T_{FeOH}	-	1.57×10^{-8}	Determined using $PCO_2=10^{-3.5}$, $M/V = 4$ g/L, $I = 0.1$ M $NaNO_3$, $U_{total} = 3.882 \times 10^{-6}$ M, pH 2.14 to 9.64, with FITEQL 2.0
T_{AlOH}	-	1.67×10^{-8}	Determined using $PCO_2=10^{-3.5}$, $M/V = 4$ g/L, $I = 0.1$ M $NaNO_3$, $U_{total} = 3.882 \times 10^{-6}$ M, pH 2.14 to 9.64, with FITEQL 2.0

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Summary of Model Results

The electrostatic DLM developed here describes complex sorption behavior over a range in chemical conditions using a relatively simple postulated surface chemistry with at total of five fitted parameters, $Log K_{FeOH-UO_2}$, $Log K_{FeO-UO_2CO_3}$, $Log K_{AlO-UO_2OH}$, T_{FeOH} , and T_{AlOH} . Determining these parameters requires a U-sorption data set over a broad pH range.

The model was applied using MINTQA2, Version 4.02 (EPA, 1999a,b) with thermodynamic data from the NEA thermodynamic data base for uranium (Grenthe et al., 1992). The electrostatic DLM, fitted to the full data set for W2, does a reasonable job of fitting the sorption data for W2 over changing ionic strengths and U(VI)-concentrations, and provides an excellent prediction of the effects of increased CO_2 .

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Example MINTQA2 Input File (Model A DLM with EDL, fit to full pH range):

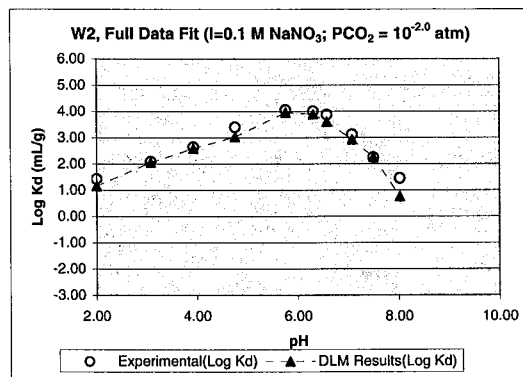
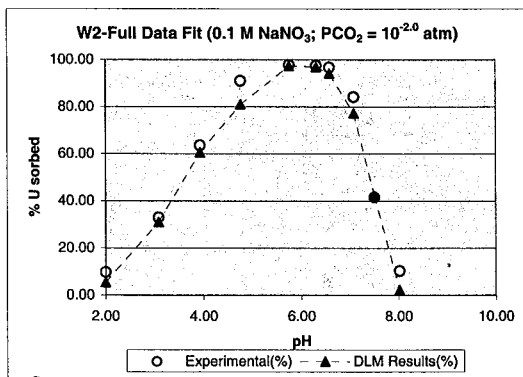
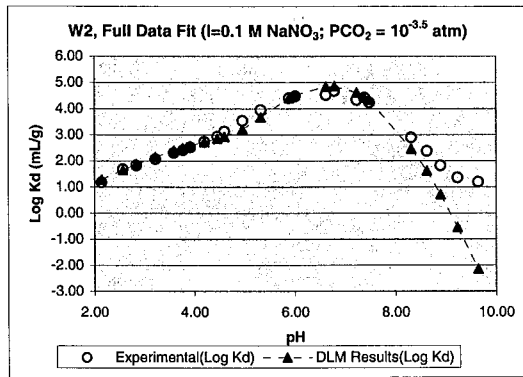
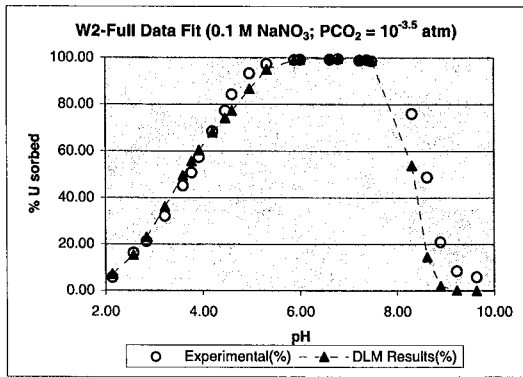
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NEA Test Case 6, Fit to Full Data, U-schist sorption, W2 (sheet 6)
PCO2=1e-3.5M, U=3.88e-6 M, M/V=4g/L, I=0.1 M NaNO3
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 6 3
24 H+1
1 330 1.000
ACTIVITY mol/L
2.14 2.57 2.84 3.22 3.59 3.77
3.92 4.20 4.46 4.60 4.96 5.32
5.89 6.01 6.62 6.79 7.23 7.38
7.48 8.31 8.62 8.89 9.23 9.64
W2_air.123 8118930 8118931 8128930 893 8934920 8933300
4 1 7
4.000E+00 52.30 0.000 0.000 81
330 0.000E+00 -7.00 y /H+1
500 1.000E-01 -1.00 y /Na+1
492 1.000E-01 -1.00 y /NO3-1
893 3.882E-06 -5.41 y /UO2+2
140 0.000E+00 -7.00 y /CO3-2
813 0.000E+00 0.00 y /ADS1PSIo
811 3.279E-06 -5.42 y /ADS1TYP1
812 3.502E-04 -3.45 y /ADS1TYP2

2 1
8933301 -11.7000 75.7100 /uo2 (oh) 2 (aq)
3 2
3301403 21.6470 -4.0600 /CO2 (g)
330 7.0000 0.0000 /H+1
6 1
813 0.0000 0.0000 /ADS1PSIo

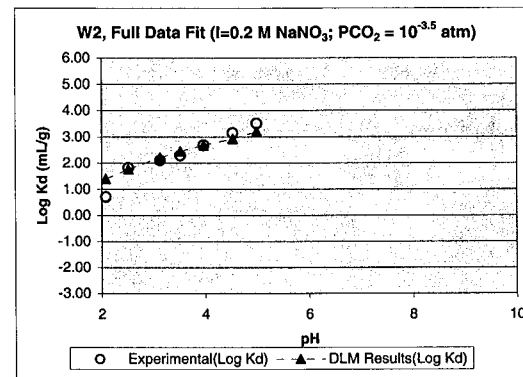
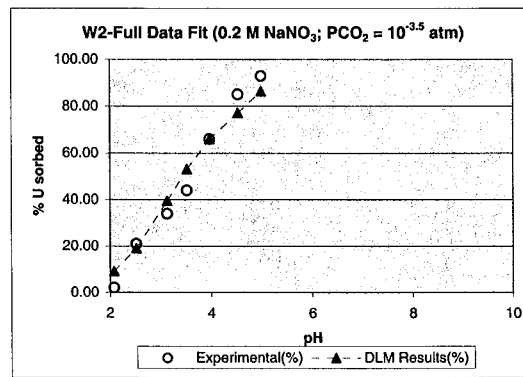
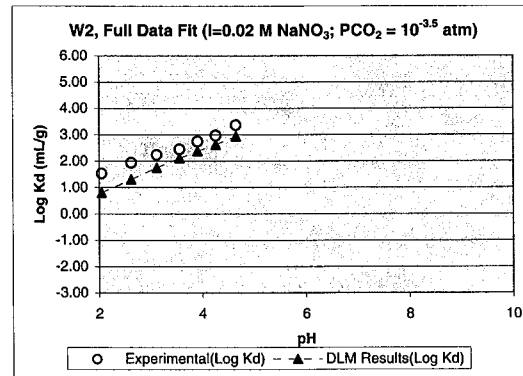
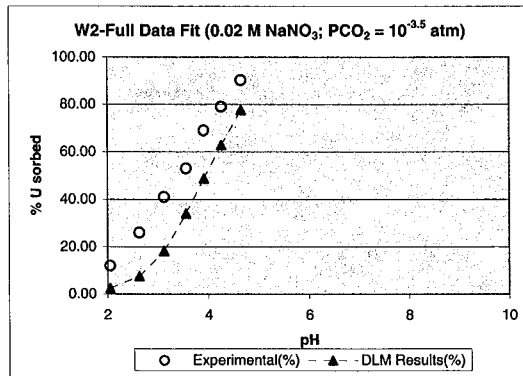
2 7
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0.00 3 1.000 811 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113301 >feo- 0.0000 -8.9300 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118930 >feohuo2+2 0.0000 11.9000 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 893 2.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8118931 >feouo2co3 0.0000 11.1500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 5 1.000 811 1.000 893 1.000 140 -1.000 330 -1.000 813 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8123300 >aloh2+ 0.0000 6.8500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 812 1.000 330 1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8123301 >alo- 0.0000 -9.0500 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 812 -1.000 330 -1.000 813 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8128930 >alouo2oh 0.0000 -5.6000 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 4 1.000 812 1.000 893 1.000 2 -2.000 330 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
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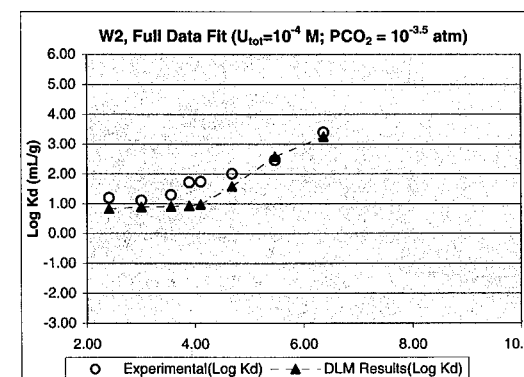
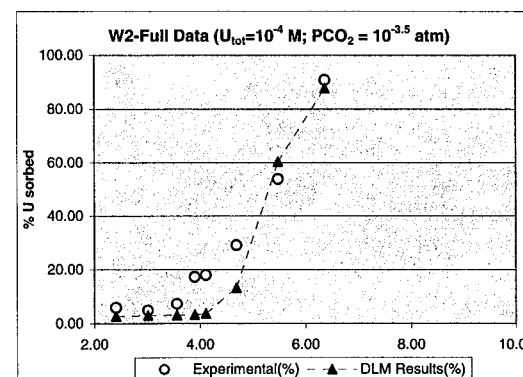
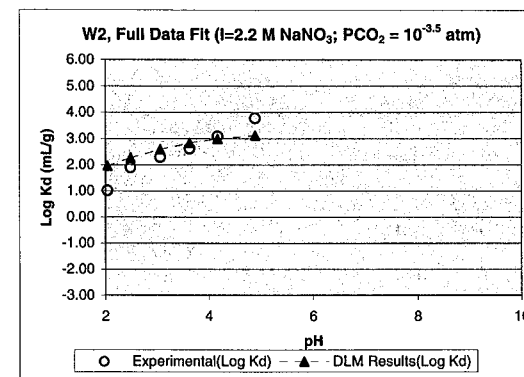
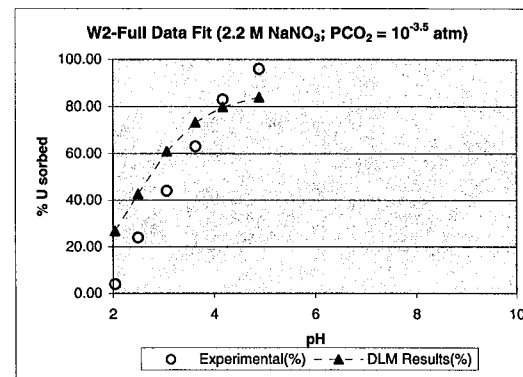
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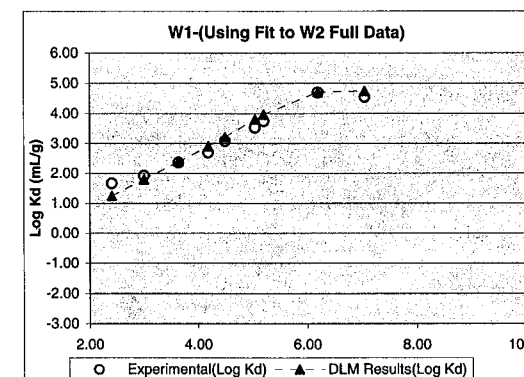
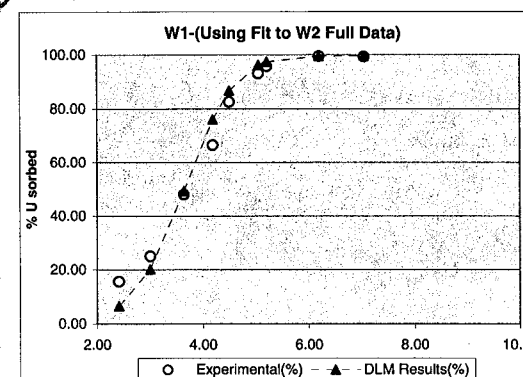


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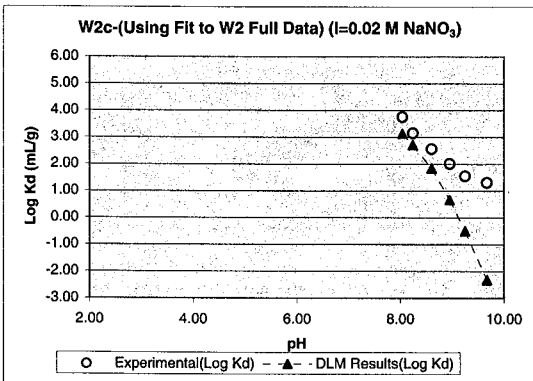
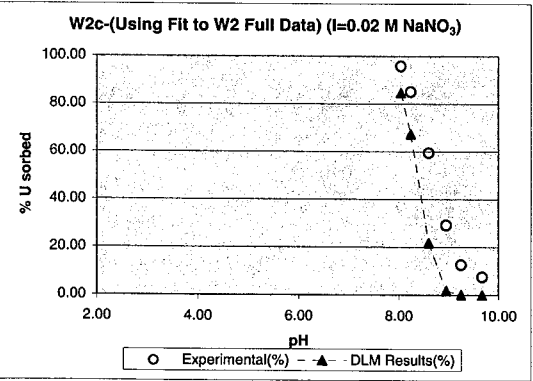
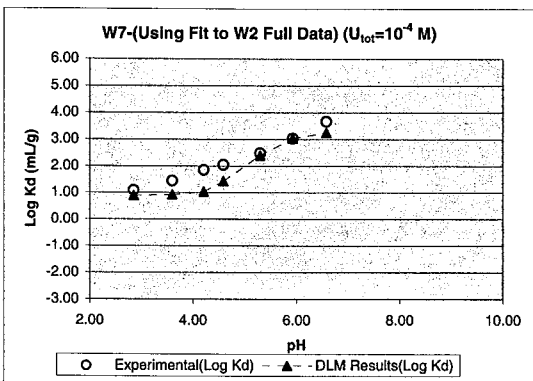
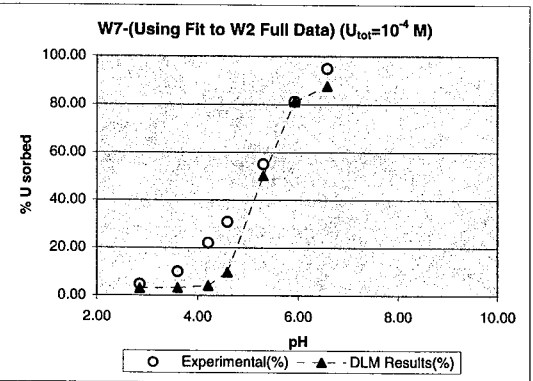
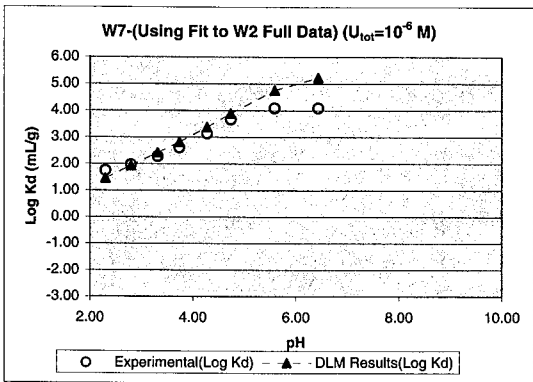
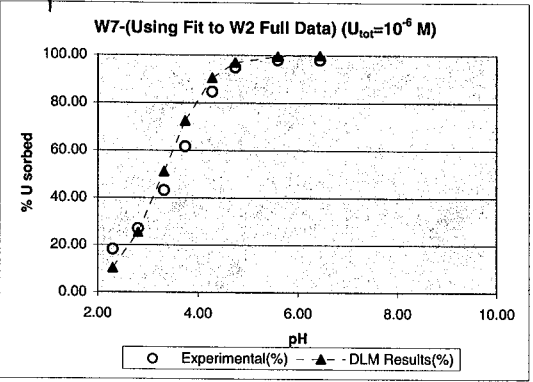
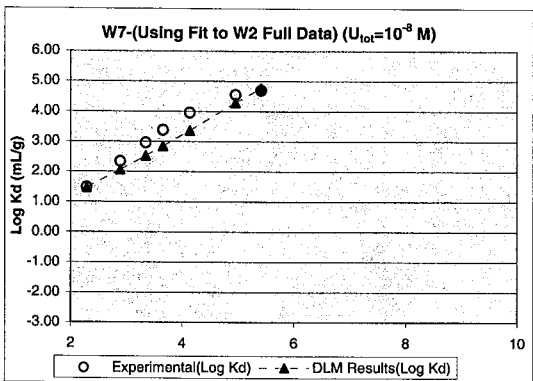
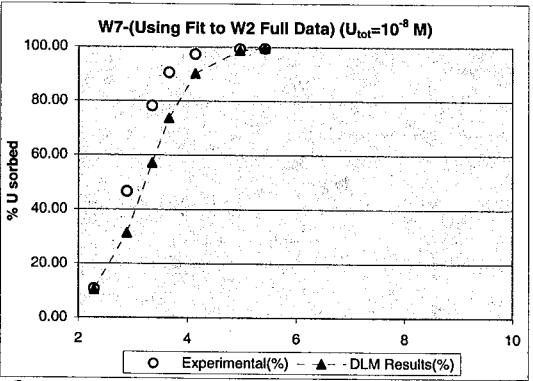
In applying the model to sorption data for other samples (W1, W7, and W2c), we only scaled the site concentrations for the N₂-BET surface area of the composite samples. All site densities and binding constants remained the same. The predicted sorption for sample W1 (Labeled Model C in the supporting electronic files) is excellent over the entire pH range from 2.4 to 7.1. The model also does a good job of predicting the effects of variable U(VI) concentration for sample W7 (Model D in the supporting electronic files).



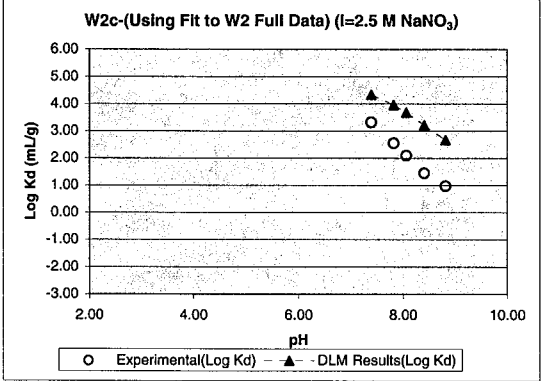
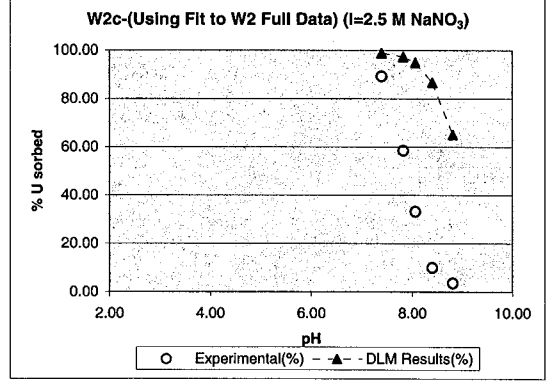
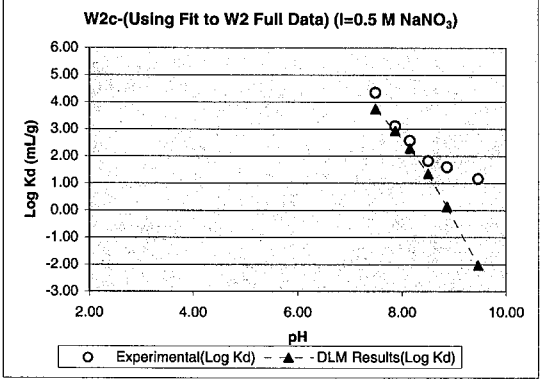
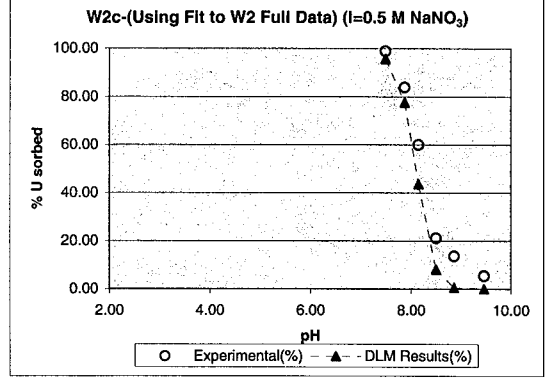
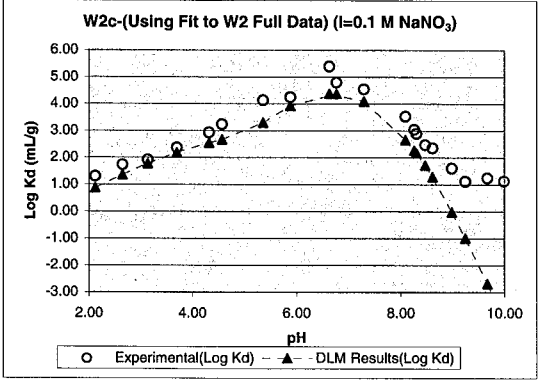
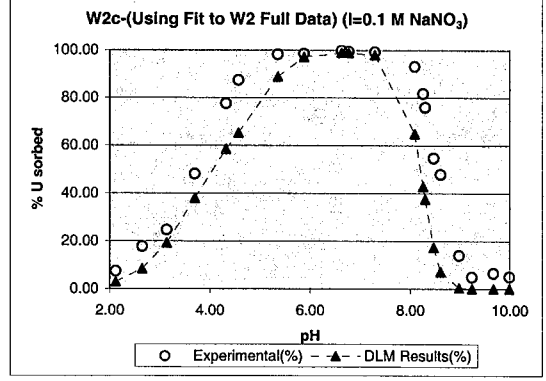
For sample W2c (Model E), the surface area-scaled model consistently underpredicts sorption, except at the highest ionic strengths. One reason for this may be due to the presence of an additional >TiOH⁰ site (Payne, 1999). Elemental analysis of W2c provided by the technical direction team indicate higher concentrations of Ti. Modifying the model to include U(VI) sorption on >TiOH⁰ would likely improve the model prediction, but would require at least four additional parameters (Log K_{TiOH2+}, Log K_{TiO-}, T_{TiOH}, and a binding constant such as Log K_{TiO-UO2}).

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The goodness-of-fit calculated using the definition of the technical direction team is typically small, in most cases ranging from 10^{-4} to 10^{-1} for all samples. The goodness-of-fit tends to degrade, however, at the highest pH values ($\text{pH} > 9$) where the model consistently underpredicts sorption, and at high ionic strengths ($>2 \text{ M NaNO}_3$).

The model predictions are relatively insensitive to ionic strength (Samples W2 and W2c), tending to underpredict sorption at ionic strength values lower than the fitted data set (0.1 M NaNO_3). This may be due to ion exchange on clay minerals in the schist that is not accounted for in the model. Although the model results are consistent with general trends in the sorption data, the prediction for high ionic strength solutions ($>2 \text{ M NaNO}_3$) is not very accurate, particularly at high pH values. This is likely due to the breakdown of the Davies equation at high ionic strength, especially for highly charged aqueous species like $\text{UO}_2(\text{CO}_3)_3^{4-}$. The use of a high ionic strength activity coefficient correction such as the Pitzer approach might correct some of the model results. Ionic strength is included in the electrostatic term of the DLM, but unlike multilayer models like the Triple-Layer Model, the DLM does not explicitly consider the sorption

of background electrolytes. The DLM also does not allow the treatment of inner and outer layer complexes. A model like the Triple-Layer Model might better simulate sorption at different ionic strengths, but the number of adjustable parameters and data requirements would increase.

The model is chemically plausible with regard to U(VI) speciation. The equivalent aqueous species (UO_2^{2+} , UO_2OH^+ , and UO_2CO_3^0) are all present in the experimental pH range covered for the model (Pabalan et al., 1998). Postulating formation of the surface complex $>\text{FeOH}-\text{UO}_2^{2+}$ was necessary to fit the sorption data in the low pH ($\text{pH} < 4$), while invoking $>\text{FeOH}-\text{UO}_2\text{CO}_3^-$ provided a better fit to the high pH ($\text{pH} > 8$) data. The electrostatic DLM does not consider sorption of background electrolytes, and other than $>\text{FeOH}-\text{UO}_2\text{CO}_3^-$, the model presented here does not invoke sorption of carbonate species such as CO_3^{2-} , or HCO_3^- . The model accurately predicts decreasing UO_2^{2+} sorption under increasing CO_2 by increasing competition of aqueous uranyl carbonate species for available UO_2^{2+} . One question is the plausibility of different surface complexes on the $>\text{FeOH}^0$ and $>\text{AlOH}^0$ sites. There is no strong evidence for this type of segregation. The model could be modified to include the same type of surface complexes on both sites, but the number of adjustable parameters would increase with the need to provide additional binding constants for the surface reactions.

Although the two-site modeling approach of Dzombak and Morel (1990) was not used for the individual ferrinol and aluminol sites, the final model was, in effect, a two-site 'strong/weak' model. In the initial FITEQL effort, we found that using T_{FeOH} as a fitting parameter provided an improved prediction of the observed data. The final site concentration for T_{FeOH} (1.567×10^{-8} mol sites/ m^2) was about two orders of magnitude less than that determined for T_{AlOH} (1.674×10^{-6} mol sites/ m^2). This produces, in effect, a two-site model with 'strong' sites represented by $>\text{FeOH}^0$ and 'weak' sites represented by $>\text{AlOH}^0$. Although there is no evidence for this type of site arrangement in the data provided for the Koongarra materials, high-resolution transmission electron microscopy characterization of aquifer sands from Virginia (Penn et al., 2001) suggest that iron oxide coatings may be encapsulated and passivated by Al- and Si-coatings. If this is also the case for the Koongarra samples, then this may support an assumption of a limited number of $>\text{FeOH}^0$ sites.

ELECTROSTATIC MODEL USING PARTIAL DATA: MODELING DECISIONS

Mineral-Radioelement System

U(VI) sorption on schist (Payne, 1999). Partial data set (pH from 4.75 to 8.75)

Model Selected

Diffuse Layer Model (DLM) with electrostatic corrections. Model B in the supporting electronic files.

Describing Surface Protonation/Deprotonation

The surface was modeled using the same approach as described previously for fitting the full W2 data set. The best fits for concentration of the ferrinol ($>\text{FeOH}^0$) and aluminol ($>\text{AlOH}^0$) sites is slightly different from that determined for the full W2 data set.

Determining U(VI)-schist DLM parameters using FITEQL, Version 2.0

As instructed by the technical direction team, the U(VI)-schist sorption data for atmospheric CO_2 ($P_{\text{CO}_2} = 10^{-3.5}$ atm) -free atmosphere, M/V = 4 g/L, I = 0.1 M NaNO_3 , and $U_{\text{total}} = 3.882 \times 10^{-6}$ M

was selected for fitting over a restricted pH range from 4.75 to 8.75.

A simple modeling approach was used. Three mononuclear, monodentate surface complexes were postulated to fit the available data:

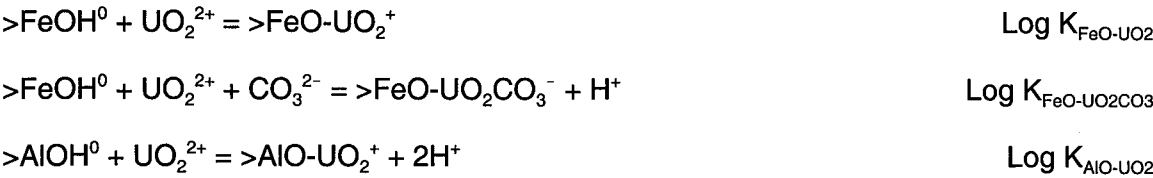


Table 4. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 6 (U-Schist). Electrostatic Diffuse Layer surface complexation model for partial pH range (4.75 to 8.75)

Surface Reaction/Fitted Parameter	Log K (I=0)	Site Concentration (mol/m ²)	Comment
$>\text{FeOH}^0 + \text{H}^+ = >\text{FeOH}_2^+$	7.29	-	From Turner and Sassman (1996).
$>\text{FeOH}^0 = >\text{FeO}^- + \text{H}^+$	-8.93	-	From Turner and Sassman (1996).
$>\text{FeOH}^0 + \text{UO}_2^{2+} = >\text{FeO}-\text{UO}_2^{2+} + \text{H}^+$	6.04	-	Determined using $\text{PCO}_2=10^{-3.5}$, M/V = 4 g/L, I = 0.1 M NaNO_3 , $U_{\text{total}} = 3.882 \times 10^{-6}$ M, pH 4.75 to 8.75, with FITEQL 2.0
$>\text{FeOH}^0 + \text{UO}_2^{2+} + \text{CO}_3^{2-} = >\text{FeO}-\text{UO}_2\text{CO}_3^- + \text{H}^+$	12.10	-	Determined using $\text{PCO}_2=10^{-3.5}$, M/V = 4 g/L, I = 0.1 M NaNO_3 , $U_{\text{total}} = 3.882 \times 10^{-6}$ M, pH 4.75 to 8.75, with trial-and-error.
$>\text{AlOH}^0 + \text{H}^+ = >\text{AlOH}_2^+$	6.85	-	From Turner and Sassman (1996).
$>\text{AlOH}^0 = >\text{AlO}^- + \text{H}^+$	-9.05	-	From Turner and Sassman (1996).
$>\text{AlOH}^0 + \text{UO}_2^{2+} = >\text{AlO}-\text{UO}_2^+ + \text{H}^+$	1.87	-	Determined using $\text{PCO}_2=10^{-3.5}$, M/V = 4 g/L, I = 0.1 M NaNO_3 , $U_{\text{total}} = 3.882 \times 10^{-6}$ M, pH 4.75 to 8.75, with FITEQL 2.0
T_{FeOH}	-	1.05×10^{-8}	Determined using $\text{PCO}_2=10^{-3.5}$, M/V = 4 g/L, I = 0.1 M NaNO_3 , $U_{\text{total}} = 3.882 \times 10^{-6}$ M, pH 4.75 to 8.75, with FITEQL 2.0
T_{AlOH}	-	1.61×10^{-6}	Determined using $\text{PCO}_2=10^{-3.5}$, M/V = 4 g/L, I = 0.1 M NaNO_3 , $U_{\text{total}} = 3.882 \times 10^{-6}$ M, pH 4.75 to 8.75, with FITEQL 2.0

Different surface reactions are postulated from those used to describe the full W2 data set. In particular, we did not use the $>\text{FeOH}-\text{UO}_2^{2+}$ surface complex to describe the restricted data set. When this complex was invoked, FITEQL tended to converge on a high binding constant that did not accurately predict the sharp sorption edge observed for W2. During the optimization process, the formation of $>\text{FeO}-\text{UO}_2^+$ and $>\text{AlO}-\text{UO}_2^+$ provided an excellent fit to the partial W2 data set such that the fit was not improved by addition of a $>\text{FeO}-\text{UO}_2\text{CO}_3^-$ surface complex. The binding constant for this surface species was determined by trial-and-error to fit the high pH data. Additional adjustable parameters included the total concentration of ferrinol (T_{FeOH}) and aluminol (T_{AlOH}).

Summary of Model Results

As developed for this test case, the electrostatic DLM describes complex sorption behavior over a range in chemical conditions using a relatively simple postulated surface chemistry. The sorption data were described by five adjustable parameters, Log $K_{\text{FeO}-\text{UO}_2}$, Log $K_{\text{FeO}-\text{UO}_2\text{CO}_3^-}$, Log $K_{\text{AlO}-\text{UO}_2}$, T_{FeOH} , and T_{AlOH} . These parameters were determined using U-sorption data set over a restricted pH range from 4.75 to 8.75.

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Example MINTEQA2 Input File (Model A DLM with EDL, fit to partial pH range):

NEA Test Case 6, Fit to Partial Data, U-schist sorption, W2 (sheet 6)
PCO2=1e-3.5M, U=3.88e-6 M, M/V=4g/L, I=0.1 M NaNO3
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 6 3

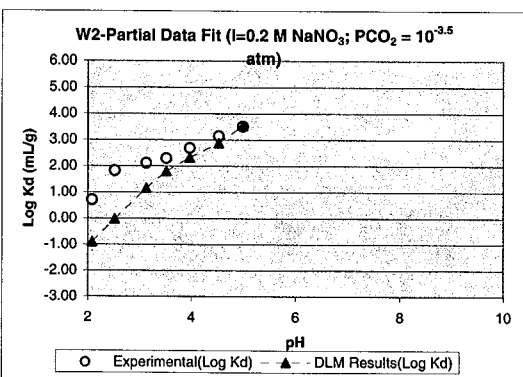
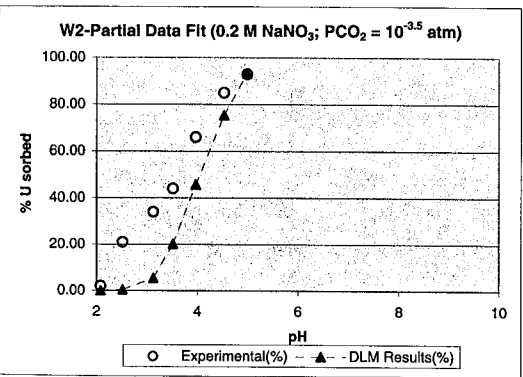
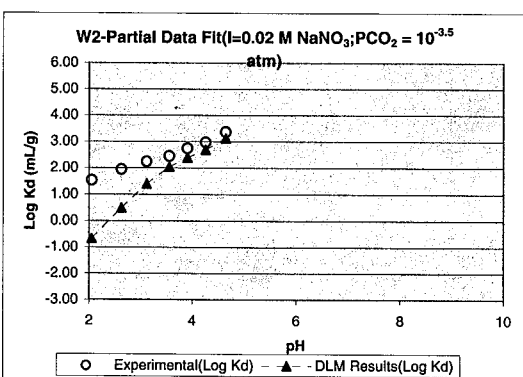
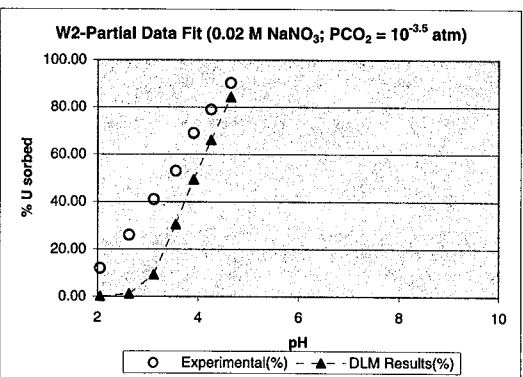
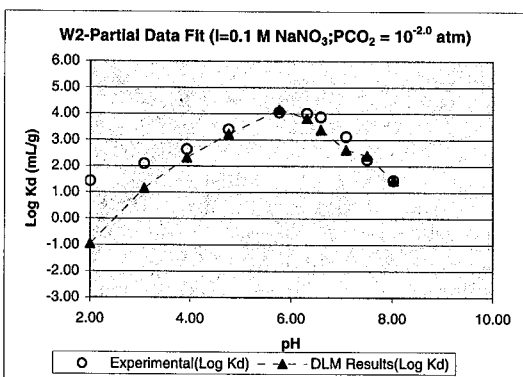
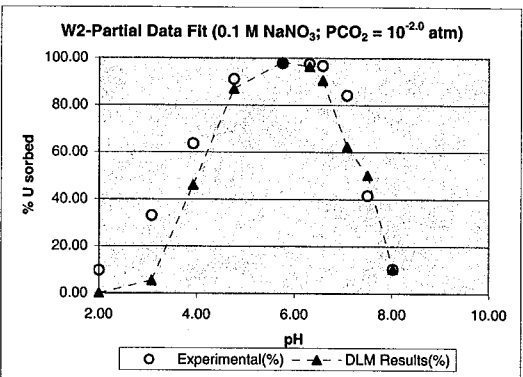
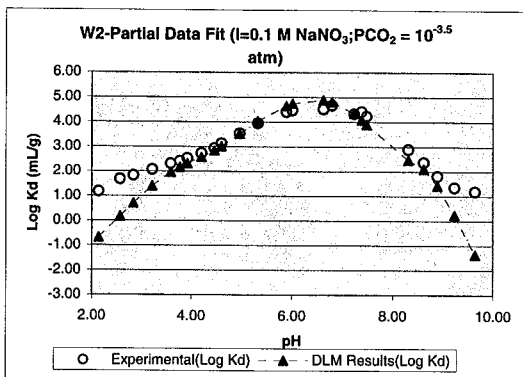
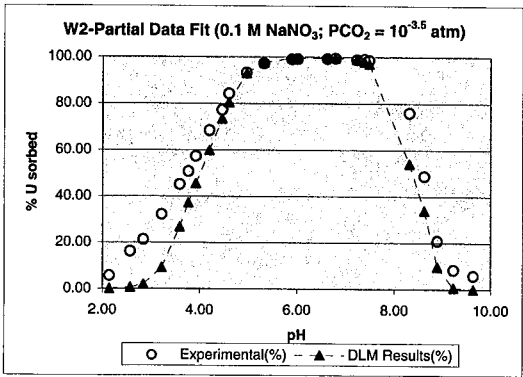
24 H+1		ACTIVITY		mol/L	
1	330	1.000			
		2.14	2.57	2.84	3.22
		3.92	4.20	4.46	4.60
		5.89	6.01	6.62	6.79
		7.48	8.31	8.62	8.89
				9.23	9.64
W2	air.123	8118930	8118931	8128930	893 8934920 8933300
4	1	7			
		4.000E+00	52.30	0.000	0.000 81
	330	0.000E+00	-7.00	y	/H+1
	500	1.000E-01	-1.00	y	/Na+1
	492	1.000E-01	-1.00	y	/NO3-1
	893	3.882E-06	-5.41	y	/UO2+2
	140	0.000E+00	-7.00	y	/CO3-2
	813	0.000E+00	0.00	y	/ADS1PSIo
	811	2.194E-06	-5.66	y	/ADS1TYP1
	812	3.374E-04	-3.47	y	/ADS1TYP2

2	1				
8933301	-11.7000	75.7100			/uo2 (oh) 2 (aq)
3	2				
3301403	21.6470	-4.0600			/CO2 (g)
330	7.0000	0.0000			/H+1
6	1				
813	0.0000	0.0000			/ADS1PSIo

LogK recommended by Technical Direction Team (vs upper limit of -10.3 in NEA TDB).

8113300	>feoh2+	0.0000	7.2900	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 3	1.000 811	1.000 330	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8113301	>feo-	0.0000	-8.9300	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 3	1.000 811	-1.000 330	-1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8118930	>feuo2+	0.0000	6.0400	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 4	1.000 811	1.000 893	-1.000 330	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8118931	>feuo2co3	0.0000	12.1000	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 5	1.000 811	1.000 893	1.000 140	-1.000 330	-1.000 813	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8123300	>aloh2+	0.0000	6.8500	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 3	1.000 812	1.000 330	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8123301	>alo-	0.0000	-9.0500	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 3	1.000 812	-1.000 330	-1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
8128930	>alouo2+	0.0000	1.8700	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 4	1.000 812	1.000 893	-1.000 330	1.000 813	0.000 0	0.000 0	0.000 0	0.000 0	
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	

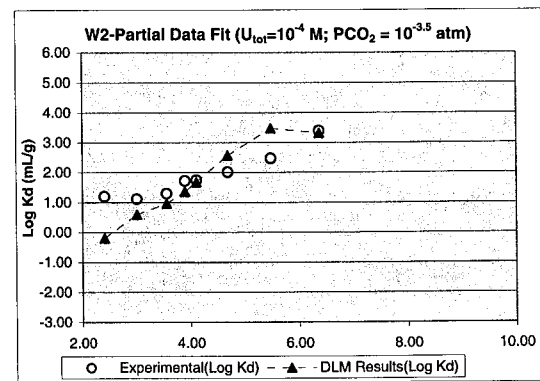
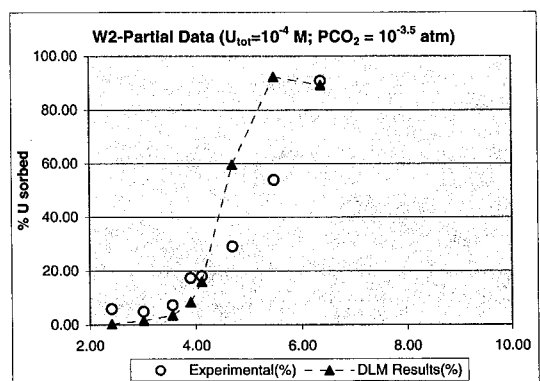
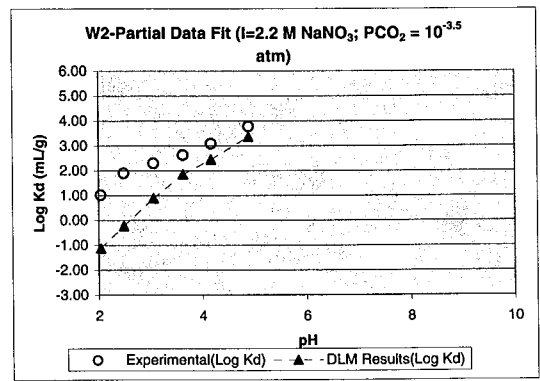
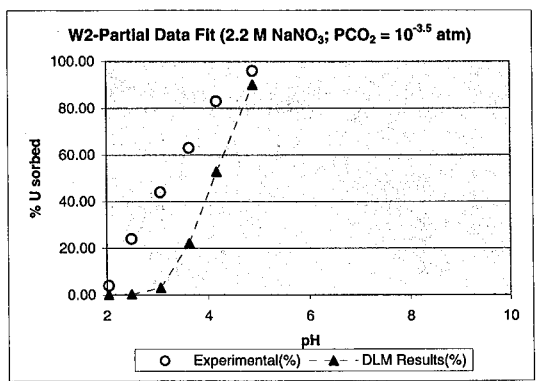
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The electrostatic DLM, fitted to the partial data set for W2, does not do as good a job of fitting the sorption data for W2 over changing ionic strengths and U(VI)-concentrations as the model determined using the full data set. In particular, it tends to under predict sorption at a low pH. It

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determined using the full data set. In particular, it tends to under predict sorption at a low pH. It does, however, provide a reasonable prediction of the effects of increased CO₂.

The quantitative goodness-of-fit (Equation [1]) is larger than that predicted using the full data set, especially at lower pH values (pH < 5). Like the results fit to the full W2 data set, the goodness-of-fit tends to degrade at the highest pH values (pH > 9).

The model predictions are relatively insensitive to ionic strength, underpredicting sorption in all cases for pH < 6. As discussed previously, this may be due to ion exchange on clay minerals in the schist that is not accounted for in the model.

Like the model fitted to the full W2 data set, the model determined for the partial W2 data set is chemically plausible with regard to U(VI) speciation. The equivalent aqueous species (UO₂²⁺ and UO₂CO₃⁰) are present in the experimental pH range covered for the model (Figure 1) (Pabalan et al., 1998). Although >FeO-UO₂⁺ and >AlO-UO₂⁺ are the same type of surface complex, there are still questions on the plausibility of invoking the >FeO-UO₂CO₃⁻ surface complex only for the ferrinol site. As discussed previously, there is no strong evidence for this type of segregation. The >AlO-UO₂CO₃⁻ surface complex could be added to the model, but FITEQL indicates that the goodness-of-fit to the partial W2 data set is not sensitive to this complex, and the additional binding constant would need to be provided through trial and error.

References for Test Case 6

Dzombak, D.A. and Morel, F.M.M. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons. 1990.

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Grenthe, I., J. Fuger, R. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, and H. Wanner. *Chemical Thermodynamics Series, Volume 1: Chemical Thermodynamics of Uranium*. Nuclear Energy Agency, Organization for Economic Cooperation and Development. New York: Elsevier. 1992.

Pabalan, R.T., D.R. Turner, F.P. Bertetti, and J.D. Prikryl. Uranium^{VI} sorption onto selected mineral surfaces. E.A. Jenne, ed. *Adsorption of Metals by Geomedia*. New York, NY: Academic Press, Inc.: 99-130. 1998.

Payne, T.E. *Uranium(VI) Interactions with Mineral Surfaces: Controlling Factors and Surface Complexation Modelling*. Ph.D Dissertation. University of New South Wales. 1999.

Turner, D.R. and S.A. Sassman. Approaches to sorption modeling for high-level waste performance assessment. *Journal of Contaminant Hydrology* 21: 311-332. 1996.

U.S. Environmental Protection Agency. "MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999a.

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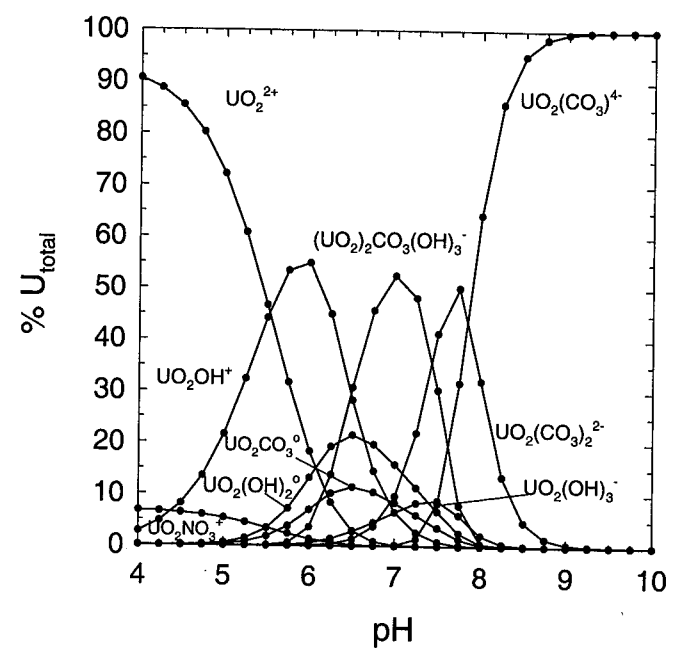
U.S. Environmental Protection Agency. "Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999b.

Westall, J.C. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 1.2*. Rpt. 82-01. Corvallis, Oregon: Department of Chemistry, Oregon State University. 1982a.

Westall, J.C. *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. 1982b.

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Aqueous speciation predicted by MINTEQA2, Version 4.02 as a function of pH. T = 25 °C, PCO2 = 10^{-3.5} atm, PO2 = 10^{-0.66} atm. Uranium speciation with U_{total} = 10⁻⁷ m.

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Test case 6		Uranium sorption on weathered schist									
Limited version											
List of worksheets											
1	Information										
2	Index and modelling outline										
3	Detailed instructions										
4	Thermodynamic data										
5	Solid characterisation data										
6 to 12	Adsorption data and model output										
	Substrate	Mass loading	Gas phase	U added	NaNO3						
6	W2	4 g/L	air	trace	0.1 M	Insert model output on this sheet					
7	W2	4 g/L	1 % CO2	trace	0.1 M	Insert model output on this sheet					
8	W2	4 g/L	air	trace	0.02, 0.2, 2.2M	Insert model output on this sheet					
9	W2	4 g/L	air	100 umol/L	0.1 M	Insert model output on this sheet					
10	W1	4 g/L	air	trace	0.1 M	Insert model output on this sheet					
11	W7	4 g/L	Air	Trace, 1uM, 100uM	0.1 M	Insert model output on this sheet					
12	W2c	4 g/L	Air	Trace	0.02,0.1,0.5,2.5	Insert model output on this sheet					
13	Model constants					Insert model constants on this sheet					

- 15 Contact your TDT representative if you have questions about these instructions.

SOLID CHARACTERISATION DATA									
sample	depth	total U ug/g	labile U content ug/g	BET surface m2/g					
W1	13.0 - 13.2	356	42.6	24.6					
W2	14.0 - 14.2	426	225	52.3					
W2c	12.0 - 12.2	213.5	97.3	20.3					
W7	13.0 - 13.2	10.4	1.0	51.9					
Labile U determined by TAO extraction									
TOTAL ELEMENTAL CONTENT									
1)	By multi-step extraction analysis				Totals in mg/g				
	Fe	Al	Mn	Mg	Ca	Ti	K		
W1	80.6	173.8	0.04	5.2	0.2	3	12.3		
W2	108.4	128.1	0.3	17.5	0.4	0.9	9.1		
W2c	80.9	98.2	0.2	19.3	1.23	4.66	5.03		
W2c (rpt)	87.6	107.5	0.22	20.6	1.19	5.46	5.47		
W7	53.1	85.9	0.3	7.3	<0.15	1.5	6.3		
2)	By PIXE/PIGME				Totals in mg/g				
	Fe	Al	Mn	Mg	Ca	Ti	K	Si	
W1	86.5	158.3	<0.015	6.14	0.338	4.37	27.2	216	
W2	115	133	0.391	21.4	0.383	1.49	7.45	195	
W7	89.9	143	0.503	27.3	0.196	2.7	13.9	206	
Qualitative XRD and SEM/EDX information indicated the materials are weathered schist with main mineral components being quartz, kaolinite, crystalline Fe-oxides and amorphous Fe-oxides.									

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Model output			
List all surface reactions in the sorption model and their log K values			
Supplementary data means model input data, such as BET surface area, site density, etc			
Please add sufficient lines to fully describe each model.			
All models are based on DLM with electrostatics, assuming ferric (<leoh) and aluminum (<aloh) bridging sites.			
Model A			
Surface reaction		Log K	
>leoh + H+ =>leoh2+		7.29	Describe how log K was determined (fitting data, other source, etc.) Ferrythite acidity constants (Dzombak and Morel, 1990) Ferrythite acidity constants (Dzombak and Morel, 1990) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Gamma alumina acidity constants (Turner and Sassen, 1996) Gamma alumina acidity constants (Turner and Sassen, 1996) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Describe source of supplementary data (fitting data, other source, etc.) Provided by TDT with input data FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L)
>leoh = feo + H+		-8.93	
>leoh + uo2+2 =>leohuo2+2		11.90	
>leoh + uo2+2 + co3-2 =>leoh-uo2co3 + H+		11.15	
>leoh + H+ =>leoh2+		6.85	
>leoh = alc + H+		-9.05	
>leoh + uo2+2 + H2O =>leohuo2oh + 2H+		-5.60	
Supplementary data used		4	
MV (g/L)		52.3	
SA (m2/g) (BET)		1.567E-08	
X<leoh (mol sites/m2)		1.674E-06	
X<aloh (mol sites/m2)			
Model B (Note: Only pH data from 4.75 to 8.75 used in FITEQL fitting)			
Surface reaction		Log K	
>leoh + H+ =>leoh2+		7.29	Describe how log K was determined (fitting data, other source, etc.) Ferrythite acidity constants (Dzombak and Morel, 1990) Ferrythite acidity constants (Dzombak and Morel, 1990) FITEQL, Version 2.0 Fit to partial data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 indicates that fit to partial data is not sensitive to >leohuo2co3-. Trial-and-error fit to match high pH data. Gamma alumina acidity constants (Turner and Sassen, 1996) Gamma alumina acidity constants (Turner and Sassen, 1996) FITEQL, Version 2.0 Fit to partial data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Describe source of supplementary data (fitting data, other source, etc.) Provided by TDT with input data FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to partial data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L)
>leoh = feo + H+		-8.93	
>leoh + uo2+2 =>leohuo2+2 + H+		6.04	
>leoh + uo2+2 + co3-2 =>leoh-uo2co3- + H+		12.10	
>leoh + H+ =>leoh2+		6.85	
>leoh = alc + H+		-9.05	
>leoh + uo2+2 =>leohuo2+2 + H+		1.87	
Supplementary data used		4	
MV (g/L)		52.3	
SA (m2/g) (BET)		1.049E-08	
X<leoh (mol sites/m2)		1.673E-06	
X<aloh (mol sites/m2)			
Model C (Same parameters as Model A, surface area scaled to TDT data for W1)			
Surface reaction		Log K	
>leoh + H+ =>leoh2+		7.29	Describe how log K was determined (fitting data, other source, etc.) Ferrythite acidity constants (Dzombak and Morel, 1990) Ferrythite acidity constants (Dzombak and Morel, 1990) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Gamma alumina acidity constants (Turner and Sassen, 1996) Gamma alumina acidity constants (Turner and Sassen, 1996) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Describe source of supplementary data (fitting data, other source, etc.) Provided by TDT with input data FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L)
>leoh = feo + H+		-8.93	
>leoh + uo2+2 =>leohuo2+2		11.90	
>leoh + uo2+2 + co3-2 =>leoh-uo2co3- + H+		11.15	
>leoh + H+ =>leoh2+		6.85	
>leoh = alc + H+		-9.05	
>leoh + uo2+2 + H2O =>leohuo2oh + 2H+		-5.60	
Supplementary data used		4	
MV (g/L)		24.6	
SA (m2/g) (BET)		1.567E-08	
X<leoh (mol sites/m2)		1.674E-06	
X<aloh (mol sites/m2)			
Model D (Same parameters as Model A, surface area scaled to TDT data for W1)			
Surface reaction		Log K	
>leoh + H+ =>leoh2+		7.29	Describe how log K was determined (fitting data, other source, etc.) Ferrythite acidity constants (Dzombak and Morel, 1990) Ferrythite acidity constants (Dzombak and Morel, 1990) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Gamma alumina acidity constants (Turner and Sassen, 1996) Gamma alumina acidity constants (Turner and Sassen, 1996) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Describe source of supplementary data (fitting data, other source, etc.) Provided by TDT with input data FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L)
>leoh = feo + H+		-8.93	
>leoh + uo2+2 =>leohuo2+2		11.90	
>leoh + uo2+2 + co3-2 =>leoh-uo2co3- + H+		11.15	
>leoh + H+ =>leoh2+		6.85	
>leoh = alc + H+		-9.05	
>leoh + uo2+2 + H2O =>leohuo2oh + 2H+		-5.60	
Supplementary data used		4	
MV (g/L)		51.9	
SA (m2/g) (BET)		1.567E-08	
X<leoh (mol sites/m2)		1.674E-06	
X<aloh (mol sites/m2)			
Model E (Same parameters as Model A, surface area scaled to TDT data for W2)			
Surface reaction		Log K	
>leoh + H+ =>leoh2+		7.29	Describe how log K was determined (fitting data, other source, etc.) Ferrythite acidity constants (Dzombak and Morel, 1990) Ferrythite acidity constants (Dzombak and Morel, 1990) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Gamma alumina acidity constants (Turner and Sassen, 1996) Gamma alumina acidity constants (Turner and Sassen, 1996) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) Describe source of supplementary data (fitting data, other source, etc.) Provided by TDT with input data FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L) FITEQL, Version 2.0 Fit to full data set for W2 (U(IV)=3.882E-6 M, I=0.1 M NaNO3, PCO2=1E-3.5 atm, MV=4 g/L)
>leoh = feo + H+		-8.93	
>leoh + uo2+2 =>leohuo2+2		11.90	
>leoh + uo2+2 + co3-2 =>leoh-uo2co3- + H+		11.15	
>leoh + H+ =>leoh2+		6.85	
>leoh = alc + H+		-9.05	
>leoh + uo2+2 + H2O =>leohuo2oh + 2H+		-5.60	
Supplementary data used		4	
MV (g/L)		20.3	
SA (m2/g) (BET)		1.567E-08	
X<leoh (mol sites/m2)		1.674E-06	
X<aloh (mol sites/m2)			

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NEA SORPTION EXERCISE TEST CASE 7: Co(II) SORPTION ONTO A SOIL AND ITS MINERALOGICAL COMPONENTS

As described by the technical direction team for the Nuclear Energy Agency (NEA) sorption exercise, the model teams are to simulate the Co sorption data of Zachara et al. (1994) using: (1) a general composite model, and (2) an additive surface complexation modeling approach based on Co sorption on the component minerals of the soil. Both modeling approaches are to be used to simulate sorption with and without the addition of humic acid (HA) to the Co-solution-sorbent systems. Data provided by the technical data direction team includes sorption as a function of pH between about 4 to 8. Two different NaClO₄ concentrations (0.01 and 0.1 M) are used to investigate the effects of ionic strength on sorption behavior. Sorption data are available for both soil composites (CP isolate) and the individual minerals of Al-goethite (5.9 mass percent), gibbsite (10 mass percent), and kaolinite (70 mass percent). The remainder of the soil is made up of an unspecified 2:1 layer silicate (14.1 mass percent), for which no sorption data are available. The modeling assumptions used in Test Case 7 by the Center for Nuclear Waste Regulatory Analyses (CNWRA) modeling team are summarized below. Detailed model results are provided in the accompanying electronic files.

COMPOSITE NON-ELECTROSTATIC MODEL, NO HUMIC ACID: MODELING DECISIONS

Mineral-Radioelement System

Co(II) sorption on soil, kaolinite, gibbsite, and Al-goethite (Zachara et al., 1994).

Model Selected

Surface Complexation Model (SCM) without electrostatic corrections. The surface is represented as a composite with a generic site type (>XOH⁰) that is not specific to a given mineral surface. Model parameters to be determined by fitting Co-soil sorption data using FITEQL, Version 2.0 (Westall, 1982a,b).

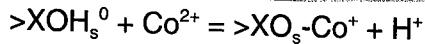
Describing Surface Protonation/Deprotonation

There are no potentiometric titration data available for the complex mineral assemblage represented by the soil. Therefore, the modeling approach adopted here includes no reactions for protonation or deprotonation of surface sites. A similar approach was described for Zn(II) sorption on soil in Davis et al. (1998). A starting point for total site concentrations is assuming a total site density of 3.84 × 10⁻⁶ mol sites/m² and using the N₂-BET measured surface area of 68.2 m²/g for the soil. We assumed a two-site model for the soil material, but because site concentrations are not constrained for the soil composite, we ultimately used the strong site concentration as an adjustable parameter in interpreting the Co sorption data using the nonlinear parameter optimization code FITEQL, Version 2.0 (Westall, 1982a,b).

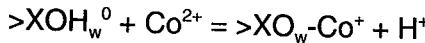
Determining Co-soil sorption parameters using FITEQL, Version 2.0

In the optimization, we used the Co-soil sorption data for atmospheric CO₂ (P_{CO2} = 10^{-3.5} atm), M/V = 1.29 g/L and Co_{total} = 1.0 × 10⁻⁶ M over the entire available pH range from about 4 to 8. We fit data for both ionic strengths (0.01 and 0.1 M NaClO₄).

A simplified modeling approach was used. Because aqueous speciation of Co is dominated by free Co²⁺ over the pH range considered, two mononuclear, monodentate surface complexes were postulated to fit the available data:



Log K_{XOs-Co}



Log K_{XOw-Co}

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FITEQL, Version 2.0 (Westall, 1982a,b) was used to solve for the binding constants for the postulated sorption reactions. Additional input data include the thermodynamic data for Co provided by the technical direction team. Ionic strength activity coefficients were determined using the Davies Equation as identified in Table 2.13 of Dzombak and Morel (1990). An additional adjustable parameter (for a total of three) included the total concentration of strong sites (T_{XOHs}). These were fit simultaneously for each data set (I = 0.01 and 0.1 M) and the results combined using a weighting scheme outlined in Dzombak and Morel (1990).

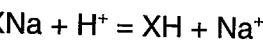
Table 5. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 7 (Co-sorption on CP isolate, no humic acid). Non electrostatic surface complexation composite model with ion exchange

Surface Reaction/Fitted Parameter	Log K (I=0)	Site Concentration (mol/m ²)	Comment
>XOH _s ⁰ + Co ²⁺ = >XO _s -Co ⁺ + H ⁺	1.56	-	Determined using Co-soil sorption data for P _{CO2} = 10 ^{-3.5} atm, M/V = 1.29 g/L and Co _{total} = 1.0 x 10 ⁻⁶ M over the entire available pH range (4 to 8). Data for both ionic strengths (0.01 and 0.1 M NaClO ₄) with FITEQL 2.0 and combined using Dzombak and Morel (1990) weighting scheme.
>XOH _w ⁰ + Co ²⁺ = >XO _w -Co ⁺ + H ⁺	-3.20	-	Determined using Co-soil sorption data for P _{CO2} = 10 ^{-3.5} atm, M/V = 1.29 g/L and Co _{total} = 1.0 x 10 ⁻⁶ M over the entire available pH range (4 to 8). Data for both ionic strengths (0.01 and 0.1 M NaClO ₄) with FITEQL 2.0 and combined using Dzombak and Morel (1990) weighting scheme.
XNa + H ⁺ = XH + Na ⁺	2.90		Log K from Zachara et al. (1994)
2XNa + Co ²⁺ = X ₂ Co + 2Na ⁺	4.37		Log K from Zachara et al. (1994)
T _{XOHs}	-	8.68x10 ⁻¹⁰	Determined using Co-soil sorption data for P _{CO2} = 10 ^{-3.5} atm, M/V = 1.29 g/L and Co _{total} = 1.0 x 10 ⁻⁶ M over the entire available pH range (4 to 8). Data for both ionic strengths (0.01 and 0.1 M NaClO ₄) with FITEQL 2.0 and combined using Dzombak and Morel (1990) weighting scheme.
T _{XOHw}	-	3.83x10 ⁻⁶	Determined using total site concentration of 3.84 x 10 ⁻⁶ mol sites/m ² and subtracting the value of TXOHs determined by FITEQL
T _{XNa}	-	8.67x10 ⁻⁷	Determined using Co-soil sorption data for P _{CO2} = 10 ^{-3.5} atm, M/V = 1.29 g/L and Co _{total} = 1.0 x 10 ⁻⁶ M over the entire available pH range (4 to 8). Data for I=0.01 M NaClO ₄ with FITEQL 2.0 and the ion exchange constants provided from Zachara et al. (1994).

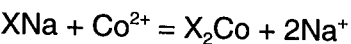
Summary of Model Results

The modeling was carried out using the weighted parameters in MINTEQA2, Version 4.02 (EPA, 1999a,b) with thermodynamic data provided by the technical direction team. We assumed that only Co(II) was present in the system, and neglected the possible effects of redox on the sorption results. In the composite modeling approach adopted here, the nonelectrostatic SCM using weighted parameters provided a good fit to the I = 0.1 M data, but significantly underpredicted sorption observed under low ionic strength (I=0.01 M) conditions. This suggests that an additional sorption reaction is necessary to reflect the effects of ionic strength, particularly one that boosts calculated sorption at low ionic strength.

As reported by Zachara et al. (1994), one likely candidate for this type of reaction is ion exchange with a fixed charge site. Zachara et al (1994) proposed two exchange reactions in a Na-system:



Log K_{XH}



Log K_{X2Co}

In simple terms, at low background NaClO₄ conditions, competition by Na+ is reduced, and Co sorption by ion exchange is enhanced (i.e., the forward direction of the second ion exchange reaction is favored). At the higher background electrolyte concentrations, however, Na+

competition increases, and Co ion exchange is suppressed (i.e., the second ion exchange reaction is pushed to the left).

The two ion exchange reactions were added to interpret the Co-soil sorption data at I = 0.01 M. The values for Log K_{XH} (2.9) and Log K_{X2Co} (4.37) reported by Zachara et al. (1994) were used to describe ion exchange for the Co-soil sorption at different ionic strengths. Again, because the availability of ion exchange sites in the composite soil is poorly constrained, we used T_{XNa} as an adjustable parameter. The ion exchange option on MINTEQA2, Version 4.02 was used with the resulting site concentration and ion exchange coefficients to reinterpret the sorption data.

Example MINTEQA2 Input File (Model 1, NEM for composite model, no Humic Acid):

```
Co-sorption on soil; I=0.01 M NaClO4; PCO2=1e-3.5 atm
SCM, no EDL, no surface acidity, wtd Log K, IE(Zach94) fit TXna
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 6 3
18 H+1
1 330 1.000
4.86 4.83 5.32 5.32 6.08 6.07
6.67 6.71 7.08 7.13 7.44 7.41
7.73 7.79 7.84 7.86 8.06 8.09
co_noHA2 .123 32000 42000 8112000 200 2003300 2001400
1 1 4
0.000E+00 0.00 0.000 0.000 81
330 0.000E+00 -7.00 y /H+1
200 1.010E-06 -6.00 y /Co+2
500 1.000E-02 -2.00 y /Na+1
181 1.000E-02 -2.00 y /ClO4-
140 0.000E+00 -7.00 y /CO3-2
3 7.636E-08 -7.19 y /noedlstr
4 3.373E-04 -3.47 y /noedlwk
811 7.626E-05 -4.12 /ADS1TYP1

2 8
2003300 -9.6500 0.0000 /cooh+
2003301 -18.1800 0.0000 /co(oh)2 (aq)
2003302 -31.5000 0.0000 /co(oh)3-
2003303 -46.3000 0.0000 /co(oh)4-2
2003304 -11.2000 0.0000 /co2oh+3
2003306 -30.5300 0.0000 /co4(oh)4+4
2001400 4.2200 0.0000 /coco3 (aq)
2001401 11.7200 0.0000 /cohco3+

3 2
3301403 21.6470 -4.0600 /CO2 (g)
330 7.0000 0.0000 /H+1

6 2
2003305 -32.0915 260.4540 /coooh-
2000023 -11.2000 0.0000 /co2(oh)3 +1
```

2 4	32000 >xos-co+	0.0000	1.5600	0.000	0.000	0.00	0.00	0.00	0.0000
0.00 3	1.000 3	1.000 200	-1.000 330	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
42000 >xow-co+	0.0000	-3.2000	0.000	0.000	0.00	0.00	0.00	0.0000	0
0.00 3	1.000 4	1.000 200	-1.000 330	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
8113300 XH	0.0000	2.9000	0.000	0.000	0.00	0.00	0.00	0.0000	0
0.00 3	1.000 811	1.000 330	-1.000 500	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0
0 0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0.000 0	0

Model predictions were greatly improved. The ion exchange increased Co sorption for the low ionic strength conditions. As expected, the ion exchange component of total sorption is greatly reduced at the higher ionic strength. There is some underprediction of observed sorption at the upper end of the pH range. This may indicate that there is sorption of a Co(OH)_n²⁻ⁿ species at the surface or a need to include surface protonation/deprotonation reactions in the model.

The quantitative measure of goodness-of-fit defined by the technical direction team is typically small, in most cases ranging from 10⁻⁷ to 10⁰ for all samples. The goodness-of-fit tends to degrade at the highest pH values (pH > 8) where the model consistently underpredicts sorption.

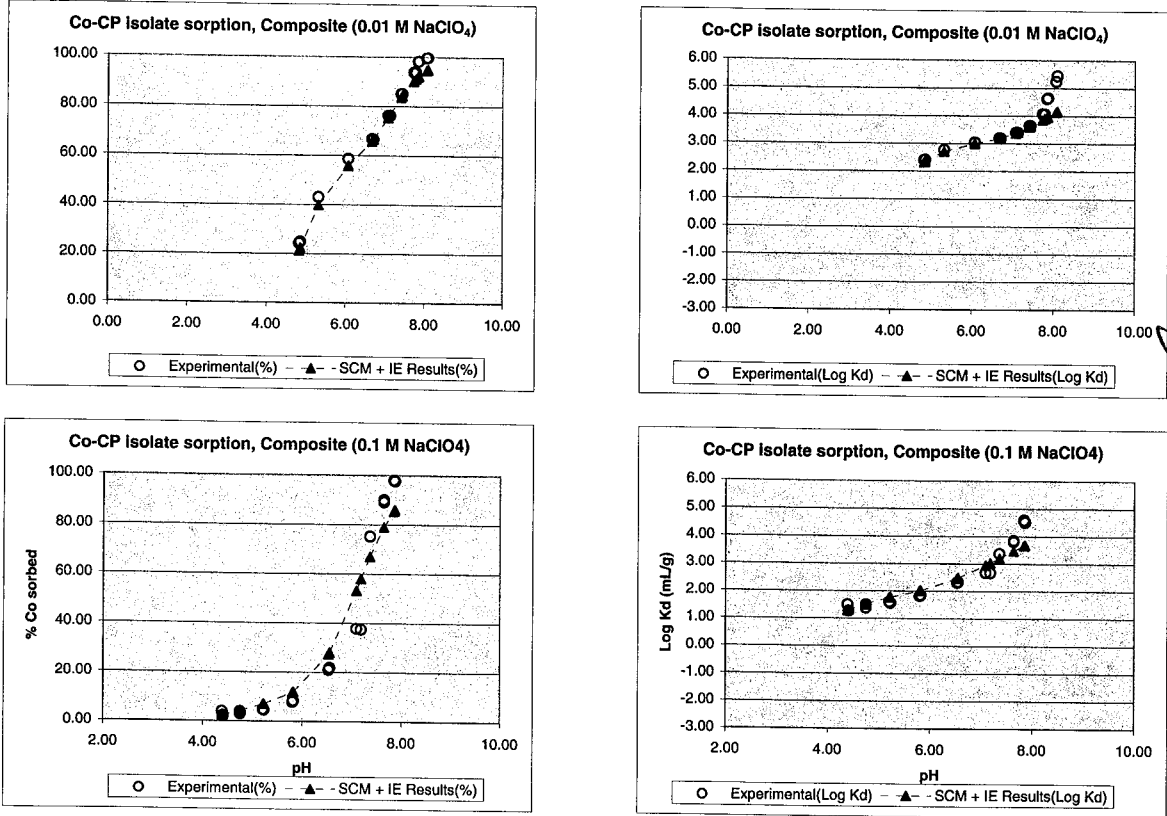
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Based on the modeling results, the simple (four adjustable parameters) nonelectrostatic SCM and ion exchange approach developed here does a good job at predicting sorption over a broad range in pH, at least for the two ionic strengths considered. The model has not been tested to determine the effects of P_{CO_2} . More surface reactions involving $Co(OH)_n^{2-n}$ species are likely to improve model results at the higher pH, but will require additional parameters. Protonation/deprotonation reactions might also improve the fit at the upper end of the pH range, but given the lack of data on the acid/base behavior of the soil, we elected to leave these reactions out for simplicity. As with most sorption modeling, the parameters are model dependent. This is especially true in the composite modeling approach, and makes extrapolation of model results to other systems more uncertain.

ADDITIVE NON-ELECTROSTATIC MODEL, NO HUMIC ACID: MODELING DECISIONS

Mineral-Radioelement System

Co(II) sorption on soil, kaolinite, gibbsite, and Al-goethite (Zachara et al., 1994).



DZ

Model Selected

Surface Complexation Model (SCM) without electrostatic corrections and ion exchange.

Describing Surface Protonation/Deprotonation

The Co-mineral sorption data includes sorption to kaolinite, gibbsite, and Al-goethite at two ionic strengths (0.01 and 0.1 M $NaClO_4$). The data also includes sorption data for kaolinite at two separate Co concentrations (10^{-6} and 10^{-7} M). The modeling approach developed here includes no electrostatic terms and no protonation/deprotonation constants for the mineral surfaces. Data for goethite and gibbsite sorption data ($I = 0.01$ M $NaClO_4$ and 10^{-6} M Co) were simulated using a simplified single-site nonelectrostatic model. Site concentration was based on an assumed total site density of 3.84×10^{-6} mol sites/ m^2 (Davis and Kent, 1990), and binding constant values were

determined using FITEQL, Version 2.0 (Westall, 1982a,b). Assuming that ion exchange in the soil is dominated by fixed charged sites on kaolinite, the Co-kaolinite sorption data was modeled using XNa as a component species. For the FITEQL optimization of the kaolinite sorption data, the concentration of the exchange sites was set at a constant value equal to the CEC at pH = 6 (Zachara et al., 1994).

DZ

Determining Co-soil sorption parameters using FITEQL, Version 2.0

In the parameter optimization, we used binding constants derived for the Co-mineral systems. For gibbsite and goethite, single site, monodentate sorption reactions of the form:



were assumed. For kaolinite, the same ion exchange reactions as in the composite model were assumed to be the only sorption mechanism. This is probably not realistic since kaolinite has variably charged edge sites (Payne et al., 1999), but it does provide a simplified way of obtaining ion exchange constants for the composite soil.

The Co-mineral sorption parameters in the pure mineral assemblages were assumed to be the same for the complex soil assemblage. Site concentration for the gibbsite and goethite components of the soil were calculated using the mass percent from Zachara et al. (1994), N_2 -BET surface areas for the two minerals, and an assumed site density of 3.84×10^{-6} mol sites/ m^2 (Davis and Kent, 1990). The concentration of ion exchange sites was used as an adjustable parameter. Using FITEQL to determine T_{XNa} through nonlinear optimization tended to provide a higher concentration of exchange sites that matched the sorption results at the pH extremes, but tended to overestimate sorption in the middle pH range. We used trial and error to reduce T_{XNa} and provide a better fit to the entire pH range.

Table 6. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 7 (Co-sorption on CP isolate, no humic acid). Non electrostatic surface complexation additive model with ion exchange

Surface Reaction/Fitted Parameter	Log K (I=0)	Site Concentration (mol/m ²)	Comment
$>FeOH_s^0 + Co^{2+} = >FeO_s-Co^+ + H^+$	-2.70	-	Determined using Co-Al goethite data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 0.16 g/L, $Co_{total} = 1.0 \times 10^{-6}$ M, and $I = 0.01$ M $NaClO_4$ with FITEQL 2.0. SA=186 m ² /g
$>AlOH_w^0 + Co^{2+} = >AlO_w-Co^+ + H^+$	-2.80	-	Determined using Co-gibbsite data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 7.5 g/L, $Co_{total} = 1.0 \times 10^{-6}$ M, and $I = 0.01$ M $NaClO_4$ with FITEQL 2.0. SA=4 m ² /g
$XNa + H^+ = XH + Na^+$	3.62		Determined using Co-kaolinite data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 1.57 g/L, $Co_{total} = 1.0 \times 10^{-6}$ M, and $I = 0.01$ M $NaClO_4$ with FITEQL 2.0. SA=11.4 m ² /g
$2XNa + Co^{2+} = X_2Co + 2Na^+$	5.88		Determined using Co-kaolinite data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 1.57 g/L, $Co_{total} = 1.0 \times 10^{-6}$ M, and $I = 0.01$ M $NaClO_4$ with FITEQL 2.0. SA=11.4 m ² /g
T_{XOHs}	-	6.1810^{-7}	Determined using Co-soil sorption data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 1.29 g/L and $Co_{total} = 1.0 \times 10^{-6}$ M over the entire available pH range (4 to 8). Data for both ionic strengths (0.01 and 0.1 M $NaClO_4$) with FITEQL 2.0 and combined using Dzombak and Morel (1990) weighting scheme.
T_{XOHw}	-	2.25×10^{-8}	Determined using total site concentration of 3.84×10^{-6} mol sites/ m^2 and subtracting the value of $TXOHs$ determined by FITEQL
T_{XNa}	-	3.13×10^{-7}	Determined using Co-soil sorption data for $P_{CO_2} = 10^{-3.5}$ atm, M/V = 1.29 g/L and $Co_{total} = 1.0 \times 10^{-6}$ M over the entire available pH range (4 to 8). Data for $I=0.01$ M $NaClO_4$ with FITEQL 2.0 and the ion exchange constants provided from Zachara et al. (1994).

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Example MINTEQA2 Input File (Model 1, NEM for additive model, no Humic Acid):

```
Co-sorption on soil; I=0.01 M NaClO4; PCO2=1e-3.5 atm
SCM, no EDL, no surface acidity, Co-gibb,goet,kaol parameters
25.00 MOLAL 0.000 0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 6 3
18 H+1 ACTIVITY mol/L
1 330 1.000
4.86 4.83 5.32 5.32 6.08 6.07
6.67 6.71 7.08 7.13 7.44 7.41
7.73 7.79 7.84 7.86 8.06 8.09
co_soil1.123 32000 42000 8112000 200 2003300 2001400
1 1 4
0.000E+00 0.00 0.000 0.000 81
330 0.000E+00 -7.00 y /H+1
200 1.010E-06 -6.00 y /Co+2
500 1.000E-02 -2.00 y /Na+1
181 1.000E-02 -2.00 y /ClO4-
140 0.000E+00 -7.00 y /CO3-2
3 5.440E-05 -4.41 y /noedlstr
4 1.980E-06 -5.70 y /noedlwk
811 2.750E-05 -4.60 y /ADS1TYP1

2 8
2003300 -9.6500 0.0000 /cooh+
2003301 -18.1800 0.0000 /co(oh)2 (aq)
2003302 -31.5000 0.0000 /co(oh)3-
2003303 -46.3000 0.0000 /co(oh)4-2
2003304 -11.2000 0.0000 /co2oh+3
2003306 -30.5300 0.0000 /co4(oh)4+4
2001400 4.2200 0.0000 /coco3 (aq)
2001401 11.7200 0.0000 /cohco3+

3 2
3301403 21.6470 -4.0600 /CO2 (g)
330 7.0000 0.0000 /H+1

6 2
2003305 -32.0915 260.4540 /cooh-
2000023 -11.2000 0.0000 /co2(oh)3 +1

2 4
32000 >feo-co+ 0.0000 -2.7000 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 3 1.000 200 -1.000 330 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
42000 >alo-co+ 0.0000 -2.8000 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 4 1.000 200 -1.000 330 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8113300 XH 0.0000 3.6190 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 1.000 811 1.000 330 -1.000 500 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
8112000 X2Co 0.0000 5.8770 0.000 0.000 0.00 0.00 0.00 0.0000
0.00 3 2.000 811 1.000 200 -2.000 500 0.000 0 0.000 0 0.000 0
0.000 0 0.000 0 0.000 0 0.000 0 0.000 0
0 0.000 0 0.000 0 0.000 0
```

Summary of Model Results

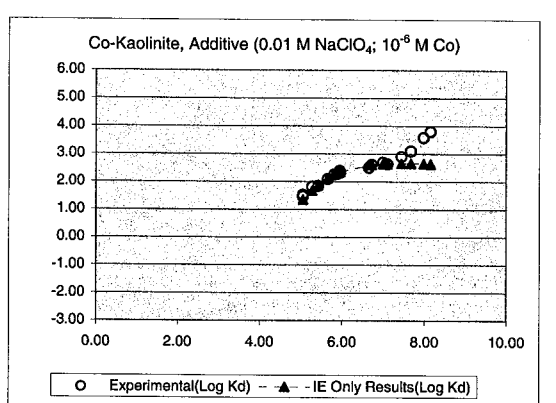
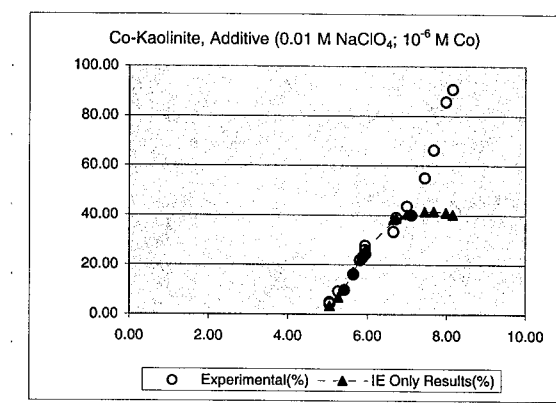
The modeling was carried out using the additive modeling approach in MINTEQA2, Version 4.02 (EPA, 1999a,b) with thermodynamic data provided by the technical direction team. The ion exchange option on MINTEQA2, Version 4.02 was used with the resulting site concentration and ion exchange coefficients derived from the Co-kaolinite sorption data. The nonelectrostatic surface complexation was represented using the parameters determined for the Co-gibbsite and Co-goethite systems. In general, the model predictions were reasonable.

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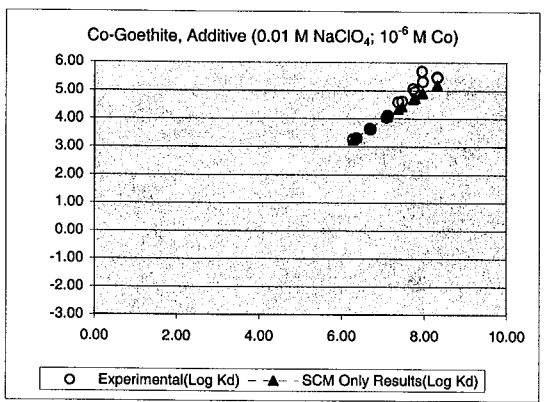
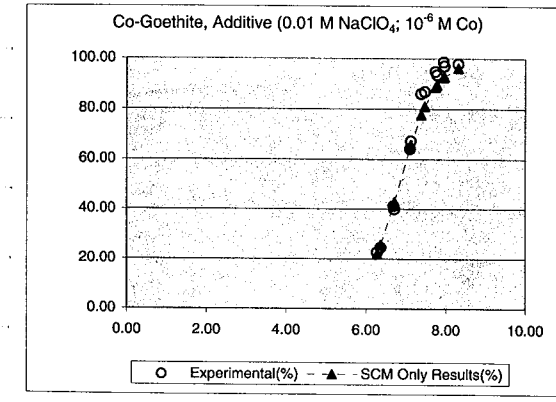
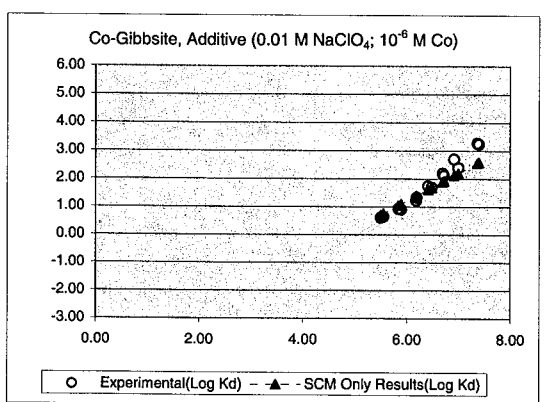
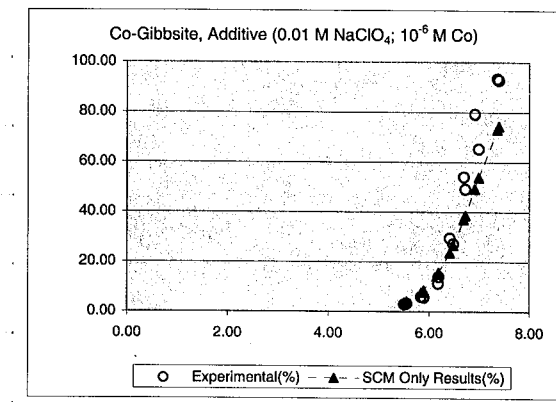
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As implemented here, the additive approach tends to provide the best prediction for the pH range from 5 to 7, and underestimates sorption at the pH extremes. For the high ionic strength ($I = 0.1$ M) Co-soil system, the ion exchange is suppressed and the shape of the sorption curve is matched very well by the nonelectrostatic sorption reactions. For the lower ionic strength, however, even though the match to the observed data is reasonable in the middle pH range, the shape of the predicted curve does not match the sorption data. Additional surface complexes like $\text{Co}(\text{OH})_n^{2-n}$ might improve the predictions at higher pH, but this was not investigated.

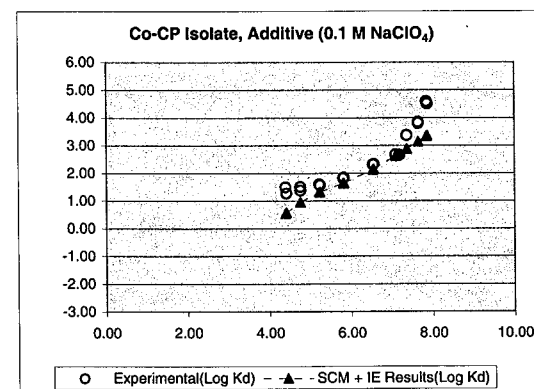
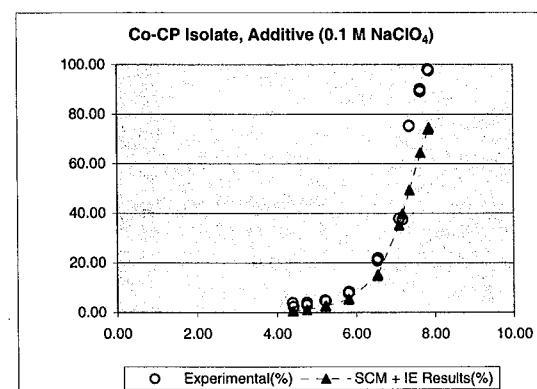
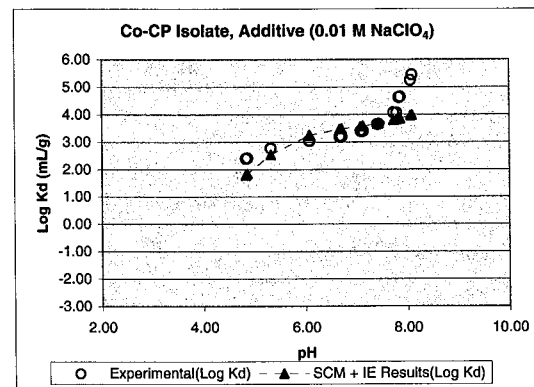
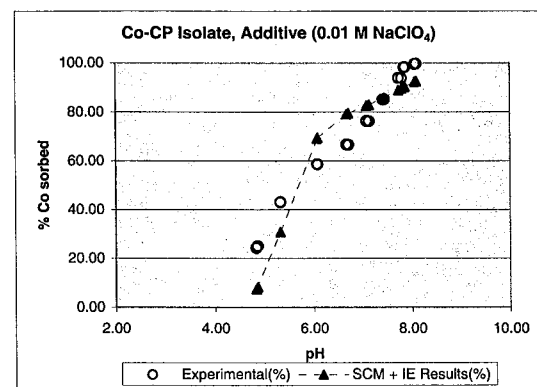
The quantitative measure of goodness-of-fit is generally larger (i.e., the fit is not as good) than that predicted using the composite model, but is still small, ranging from 10^{-4} to 10^0 for all samples. Like the composite model, the goodness-of-fit tends to degrade at the highest pH values ($\text{pH} > 9$) where the model consistently underpredicts sorption.



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Based on the modeling results, the simple additive nonelectrostatic/ion exchange additive model developed here does a reasonable job predicting the observed sorption behavior for the two ionic strengths considered. A very simple single-site model was effective at reproducing the observed sorption behavior for the pure mineral systems (goethite, gibbsite, kaolinite). For the pH range considered the shape of the predicted sorption curve at the lower ionic strength does not match the observed data, but it does reproduce the data in the middle pH range. The model has not been tested to determine the effects of P_{CO_2} . Results suggest that there is some underprediction at the high end of the pH range considered. More surface reactions involving $Co(OH)_n^{2-n}$ species or protonation/deprotonation of the individual minerals are likely to improve model results at the



higher pH, but will require additional parameters. Significant uncertainty remains in determining sorption site concentration for the individual minerals that make up the soil, and the concentration of ion exchange sites was used as an adjustable parameter to interpret the Co-soil sorption data.

References Test Case 7 (no HA only)

Davis, J.A., and D.B. Kent. 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, D.C.: Mineralogical Society of America: 177-260. 1990.

Davis, J.A., J.A. Coston, D.B. Kent, and C.C. Fuller. Application of the surface complexation concept to complex mineral assemblages. *Environmental Science and Technology* 32: 2,820-2,828. 1998.

Dzombak, D.A. and Morel, F.M.M. *Surface Complexation Modeling: Hydrous Ferric Oxide*. New York: John Wiley and Sons. 1990.

Payne, T.E. *Uranium(VI) Interactions with Mineral Surfaces: Controlling Factors and Surface Complexation Modelling*. Ph.D Dissertation. University of New South Wales. 1999.

Turner, D.R. and S.A. Sassman. Approaches to sorption modeling for high-level waste performance assessment. *Journal of Contaminant Hydrology* 21: 311-332. 1996.

U.S. Environmental Protection Agency. "MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999a.

U.S. Environmental Protection Agency. "Diffuse-Layer Sorption Reactions for use in MINTEQA2 for HWIR Metals and Metalloids." Athens, Georgia: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. 1999b.

Westall, J.C. *FITEQL: A Computer Program for Determination of Chemical Equilibrium Constants From Experimental Data, Version 1.2*. Rpt. 82-01. Corvallis, Oregon: Department of Chemistry, Oregon State University. 1982a.

Westall, J.C. *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. 1982b.

Zachara, J.M., C.T. Resch, and S.C. Smith. Influence of humic substances on Co^{2+} sorption by a subsurface mineral separate and its mineralogic components. *Geochimica et Cosmochimica Acta* 58: 553-566. 1994.

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Test Case 7: Co(II) sorption onto a soil and its mineralogical components	
Goal:	The goal of the test case is to determine whether the Kd values for Co(II) sorption on a soil fraction, as a function of pH, ionic strength, and humic acid concentration, can be described with surface complexation models. Two different modeling approaches will be tested: 1) building a model directly from Co(II) sorption data on the soil, and 2) predicting sorption from the knowledge of Co(II) sorption on the major minerals that are present in the soil. Each of these modeling approaches will be tested for the soil without (Part A) and with (Part B) humic acid addition.
Data Source: Zachara, J.M., Resch, C.T., and Smith, S.C., 1994. <i>Geochimica Cosmochimica Acta</i> , v. 58, p. 553-566.	
Solid adsorbents:	1) A <2 micron size fraction of an ultisol saprolite, collected from beneath the Cecil soil series (Typic Hapludult) in South Carolina (USA) Separated from Na-saturated saprolite by sedimentation, dialyzed against deionized water, and freeze-dried (referred to as CP isolate in original data source) Amounts of Fe, Al, Si, and Mn in hydroxylamine hydrochloride and DCB extractions determined (see original data source) Mineralogical composition by weight: goethite and hematite (5.9%), gibbsite (10%), kaolinite (70%), and 2:1 layer silicates (14.1%) pH-dependent cation exchange capacity determined (see original data source) Specific surface area: (68.2 m ² /g) measured by BET nitrogen gas adsorption (118 m ² /g) measured by EGMIE 2) Kaolinite, <2 micron isolate of sample KGa-1, from the Clay Minerals Society Specific surface area: (11.4 m ² /g) measured by BET nitrogen gas adsorption 3) Gibbsite, commercially prepared, Alcan SF-4 Specific surface area: (4 m ² /g) measured by BET nitrogen gas adsorption Crystallite length of 1.5 micron 4) Al-substituted goethite, 20% Al substitution, synthetic preparation Specific surface area: (186 m ² /g) measured by BET nitrogen gas adsorption
Electrolyte solution: sodium perchlorate (NaClO ₄); varying concentrations used	
Complexing ligand added to certain sorption experiments:	Leonardite humic acid, sample obtained from the International Humic Substances Society 15% of carbon is carboxylate carbon 58% aromatic, high molecular weight
Sorption experiments: see data in Sheets 4, 5, 6, 7, and 8	Temperature: 25°C Batch equilibration: reaction time of approx. 24 hours, maintained under a nitrogen gas phase
Additional data:	Cobalt complexation by the humic acid (Sheet 9), humic acid adsorption data (Sheet 10), humic acid desorption data (Sheet 11), and other experimental information are provided for use in developing the models, but it is not required that these data be used or accurately simulated in the models. Two types of original data are also available from the TDT if a Modeling Team wishes to have it. These data are: 1. Electrophoretic mobilities of the soil after with and without humic acid adsorption (Figure 6 in Zachara et al. reference). 2. Cobalt sorption on the soil after DCB extraction, an extraction that dissolves iron oxides, with and without humic acid sorption (Figures 2 and 8b in Zachara et al. reference).
Additional references:	Westall et al., 1995. Models for association of metal ions with heterogeneous environmental sorbents. 1. Complexation of Co(II) by Leonardite humic acid as a function of pH and NaClO ₄ concentration. <i>Environ. Sci. Technol.</i> 29:951-959. Davis et al. (1998). Application of the surface complexation concept to complex mineral assemblages, <i>Environ Sci Technol.</i> 32: 2820-2828.

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Instructions to Modeling Teams	
Part A:	
1. Develop two surface complexation models to describe the Co sorption data on the soil without humic acids added (data in Sheet 4), one from fitting the experimental data (Model 1) and one from prediction based on separate models for the mineralogical components: kaolinite, gibbsite, and Al-goethite, without humic acid present (Model 2). The modeling team can choose to have models that include electrostatic correction terms or models without such terms. Assume that the Co(II) sorption data provided were collected after the experimental systems achieved chemical equilibrium. Note that Sheets 6, 7, and 8 contain Co sorption data for the mineral components for developing the Model 2 prediction. Sheets 6, 7, and 8 also contain Co sorption data for the mineral components with humic acid added, but these data are not needed for Model 2.	
2. The objective is to obtain good fits to the Co(II) sorption data provided, with chemically reasonable (plausible) models, but with as few fitting parameters as possible. However, it is recognized that an increase in the number of fitting parameters in models can lead to a better fit of the adsorption data, and it is up to each Modeling Team to make the decision about how many and which parameters to include in their models.	
3. For the development of these two models, use the thermodynamic data provided for the formation of aqueous species (see Sheet 3 - Thermodynamic Data worksheet). You may prepare additional model calculations with other thermodynamic data, but in that case, please submit these as additional modeling, providing the the different data used, the reasons for substituting the different data, and the source of the data.	
4. Additional data are available in the original reference (Zachara et al., 1994), for use in developing the models, but it is not required that these data be used or simulated in the models. Other literature may be used in justifying modeling approaches or in assigning parameter values. Note that the surface areas of the soil, kaolinite, gibbsite, and Al-goethite are given in Sheet 1 - Information.	
5. Document the development of the models in a written format to submit to the TDT. Describe the sequence of model development decisions made and the rationale for the decisions. Describe how the values of model parameters were assigned, fitted, or assumed, such as the concentration of surface sites, the types of surface sites (if a multi-site model), the surface area used, the selection of surface species and the stability constants for their formation, all electrical double layer parameters, method for determining aqueous phase activity coefficients, etc. If a model parameter is assigned a value from an independent source, explain the source and reasoning. Make it clear which model parameters were determined by the fitting of experimental data. As for the selection of surface species, provide the reason that specific species were chosen, e.g., simplest reaction possible; dominant aqueous species, spectroscopic studies in the literature, best fit from trial-and-error, etc.	
6. Document the data fitting procedure used, including any software packages and references. The documentation should make it clear what optimization routine was used (and version, e.g. FITEQL 4.0).	
7. Enter the calculated values for %Co adsorbed and Kd (mL/g) in Worksheets 12 and 14, titled Model 1 output and Model 2 output. Model 1 is the model developed by fitting the Co soil sorption data directly. Model 2 is the prediction of Co sorption on the soil based on separate models for Co sorption on the mineralogical components. Add the concentrations of surface species and solution species for each experimental point to that row of the spreadsheet. Include all surface species and their concentrations, all Co aqueous species greater than 0.1% of the total Co concentration and the calculated concentration of H ⁺ (or calculated pH).	
8. Provide copies of input and output files that can be easily understood by members of the TDT. The output files should clearly show the calculated concentrations of surface and aqueous species corresponding to each experimental data point and the pH (or concentration of H ⁺), etc. The TDT must be able to understand the identity of species in these files.	
9. Provide a table of the formation constants for all surface species in Models 1 and 2 (Worksheets 13 and 15).	
10. For each Model, provide graphs of calculated and experimental log Kd values versus pH, with the calculated value shown as a open circle and the experimental value as a filled (dark) triangle. Connect the symbols for the calculated values with a dotted line.	
11. Provide written summary comments describing the modeling results and the Modeling Team's opinion of:	a) the strengths and weaknesses of the two modeling approaches (Models 1 and 2), b) the goodness-of-fit for each approach, c) the chemical plausibility of each Model, d) numbers of fitting parameters required, e) data requirements for each modeling approach, f) the range of applicability of each modeling approach

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12. Contact your TDT representative if you have questions about these instructions.

Part B:

13. Repeat the exercise, this time describing the Co sorption data with humic acids added (data in Sheet 5). Develop two surface complexation models to describe the Co sorption data on the soil with humic acids added, one from fitting the experimental data (Model 3) and one from prediction based on separate models for the mineralogical and organic components: kaolinite, gibbsite, Al-goethite, and humic acids (Model 4). Again, the modeling team can choose to have models that include electrostatic correction terms or models without such terms. Assume that the Co(II) sorption data provided were collected after the experimental systems achieved chemical equilibrium.

14. Same as 2 above.

15. Same as 3 above.

16. Additional data are given in Sheets 6, 7, 8, 9, 10, and 11 (minerals with humic acid present) and are available in the original reference (Zachara et al., 1994), for use in developing the models, but it is not required that these data be used or simulated in the models. Other literature may be used in justifying modeling approaches or in assigning parameter values.

17. Same as 5 above.

18. Same as 6 above.

19. Enter the calculated values for %Co adsorbed and Kd (mL/g) in Worksheets 16 and 18, titled Model 3 output and Model 4 output. Model 3 is the model developed by fitting the Co sorption data directly on the humic-amended soil. Model 4 is the prediction of Co sorption on the humic-amended soil based on separate models for Co sorption on the mineralogical and humic acid components. Add the concentrations of surface species and solution species for each experimental point to that row of the spreadsheet. Include all surface species and their concentrations, all Co aqueous species greater than 0.1% of the total Co concentration and the calculated concentration of H+ (or calculated pH).

20. Provide copies of input and output files that can be easily understood by members of the TDT. The output files should clearly show the calculated concentrations of surface and aqueous species corresponding to each experimental data point and the pH (or concentration of H+), etc. The TDT must be able to understand the identity of species in these files.

21. Provide a table of the formation constants for all surface species in Models 3 and 4 (Worksheets 17 and 19).

22. For each Model, provide graphs of calculated and experimental log Kd values versus pH, with the calculated value shown as a open circle and the experimental value as a filled (dark) triangle. Connect the symbols for the calculated values with a dotted line.

23. Provide written summary comments describing the modeling results and the Modeling Team's opinion of:

a) the strengths and weaknesses of the two modeling approaches (Models 3 and 4),

b) the goodness-of-fit for each approach,

c) the chemical plausibility of each Model,

d) numbers of fitting parameters required,

e) data requirements for each modeling approach,

f) the range of applicability of the each modeling approach

g) the range of applicability outside the conditions used for calibration (pH, humic acid concentration, etc.)


24. Contact your TDT representative if you have questions about these instructions.

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Thermodynamic data at zero ionic strength			
Species	Formation reaction	Log K	Source
Co+2		0	Defined as master species
CoOH+1	Co+2 + H2O - H+ -> CoOH+1	-9.65	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Co(OH)2	Co+2 + 2H2O - 2H+ -> Co(OH)2	-18.8	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Co(OH)3-1	Co+2 + 3H2O - 3H+ -> Co(OH)3-1	-31.5	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Co(OH)4-2	Co+2 + 4H2O - 4H+ -> Co(OH)4-2	-46.3	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Co2OH+3	2Co+2 + H2O - H+ -> Co2OH+3	-11.2	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Co4(OH)4+4	4Co+2 + 4H2O - 4H+ -> Co4(OH)4+4	-30.53	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
CoHCO3+	Co+2 + HCO3- -> CoHCO3+	1.39	Critical Stability Constants Volume 4: Inorganic Complexes
CoCO3	Co+2 + CO3-2 -> CoCO3	4.22	Critical Stability Constants Volume 6: Second Supplement
CoCl+	Co+2 + Cl- -> CoCl+	0.48	Critical Stability Constants Volume 4: Inorganic Complexes
CoSO4	Co+2 + SO4-2 -> CoSO4	2.36	Critical Stability Constants Volume 4: Inorganic Complexes
CoNO3+	Co+2 + NO3- -> CoNO3+	0.2	Critical Stability Constants Volume 4: Inorganic Complexes
Co(NO3)2	Co+2 + 2NO3- -> Co(NO3)2	0.5	Critical Stability Constants Volume 4: Inorganic Complexes
Co+3	Co+2 - e- -> Co+3		NBS Tables of Chemical Thermodynamic Properties. D D Wagman et al. American Chemical Society, 1982. J. Physical Chemical Ref. i Data 11, 1982, Suppl.2.
Solid phases			
	Co(OH)2 -> Co+2 + 2H2O - 2H+	12.3	The Hydrolysis of Cations' C F Baes and R E Mesmer 1986
Auxiliary data			
Dissolution of CO2	CO2(g) + H2O -> H2CO3	-1.47	NEA, 2001
H2CO3	CO3-2 + 2H+ -> H2CO3	16.68	NEA, 2001
HCO3-	CO3-2 + H+ -> HCO3-	10.33	NEA, 2001
Water dissociation	H2O - H+ -> OH-	-14.00	NEA, 2001
Partial pressure of CO2 in atmospheric air		10E-3.5	

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Handsheet: Please contact TDI if

DATE RECEIVED: 11/11/2011

The log Kd (L/g) values shown below were given in the original publication. The Kd values (mL/g) and log Kd values (mL/g) were calculated by J. Daw

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Original Co supplier data on Algalithia, both with and without humic acid added									
Algalithia (g/L)	Total Co concentration (mol/L)	NaOCl concentration (mol/L)	Humic acid present in experiment	final pH	final dissolved Co (mole/L)	% Co dissolved	Kd values (mL/g) and log Kd values (mL/g)	The Kd values (mL/g) and log Kd values (mL/g) were calculated by J. Davis (TDI) for this spreadsheet. Please contact TDI immediately if any errors are detected.	
0.16	1.0E-06	1.0E-02	none	6.27	25.64	2.56	1.92E+03	3.262	
0.16	1.0E-06	1.0E-02	none	6.36	7.62E-07	7.62E-07	2.01E+03	3.303	
0.16	1.0E-06	1.0E-02	none	6.58	5.92E-07	5.92E-07	4.39E+03	3.643	
0.16	1.0E-06	1.0E-02	none	6.70	6.08E-07	6.08E-07	4.15E+03	3.618	
0.16	1.0E-06	1.0E-02	none	7.11	3.31E-07	3.31E-07	1.28E+04	4.107	
0.16	1.0E-06	1.0E-02	none	7.29	3.82E-07	3.82E-07	1.17E+04	4.069	
0.16	1.0E-06	1.0E-02	none	7.46	1.33E-07	1.33E-07	4.15E+04	4.615	
0.16	1.0E-06	1.0E-02	none	7.73	5.17E-08	5.17E-08	1.58E+05	5.064	
0.16	1.0E-06	1.0E-02	none	7.77	6.45E-08	6.45E-08	9.15E+04	4.962	
0.16	1.0E-06	1.0E-02	none	7.96	2.89E-08	2.89E-08	2.03E+05	5.321	
0.16	1.0E-06	1.0E-02	none	7.94	1.30E-08	1.30E-08	4.78E+05	5.680	
0.16	1.0E-06	1.0E-02	none	8.31	2.13E-08	2.13E-08	2.90E+05	5.462	
0.16	1.0E-06	1.0E-02	none	8.31	1.30E-08	1.30E-08	1.30E+05	5.113	
0.16	1.0E-06	1.0E-02	none	8.40	6.89E-07	6.89E-07	1.30E+05	5.113	
0.16	1.0E-06	1.0E-01	none	5.32	9.84E-07	9.84E-07	1.48E+02	2.175	
0.16	1.0E-06	1.0E-01	none	5.59	9.04E-07	9.04E-07	7.32E+02	2.865	
0.16	1.0E-06	1.0E-01	none	5.99	8.92E-07	8.92E-07	8.01E+02	2.904	
0.16	1.0E-06	1.0E-01	none	6.63	5.70E-07	5.70E-07	4.82E+03	3.683	
0.16	1.0E-06	1.0E-01	none	6.54	5.83E-07	5.83E-07	4.57E+03	3.661	
0.16	1.0E-06	1.0E-01	none	7.04	3.40E-07	3.40E-07	1.27E+04	4.089	
0.16	1.0E-06	1.0E-01	none	7.46	1.56E-07	1.56E-07	3.40E+04	4.532	
0.16	1.0E-06	1.0E-01	none	7.46	1.53E-07	1.53E-07	3.47E+04	4.541	
0.16	1.0E-06	1.0E-01	none	7.67	7.29E-08	7.29E-08	6.07E+04	4.907	
0.16	1.0E-06	1.0E-01	none	7.69	7.29E-08	7.29E-08	6.05E+04	4.905	
0.16	1.0E-06	1.0E-01	none	7.84	3.77E-08	3.77E-08	1.50E+05	5.205	
0.16	1.0E-06	1.0E-01	none	7.84	3.77E-08	3.77E-08	1.50E+05	5.205	
0.16	1.0E-06	1.0E-01	none	8.04	1.00E-06	1.00E-06	4.49E+02	2.652	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	5.67	6.71E-07	6.71E-07	3.79E+03	3.580	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	5.50	8.25E-07	8.25E-07	1.94E+03	3.284	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	5.79	5.98E-07	5.98E-07	5.03E+03	3.702	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	5.78	6.14E-07	6.14E-07	4.79E+03	3.675	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.13	3.02E-07	3.02E-07	1.03E+04	4.025	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.43	1.90E-07	1.90E-07	2.89E+04	4.461	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.43	1.84E-07	1.84E-07	3.03E+04	4.481	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.62	1.49E-07	1.49E-07	3.90E+04	4.591	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.73	1.79E-07	1.79E-07	5.40E+04	4.737	
0.16	1.0E-06	1.0E-02	11.92 mg carbon/1	6.83	1.79E-07	1.79E-07	5.40E+04	4.737	
0.16	1.0E-06	1.0E-02	11.92 mg						

07/12/2002
DJS

Original data for Co complexation with humic acids									
NaClO4 concentration (moles/L)	Humic acid present in experiment	final pH	% Co complexed with humic acid	log Kd (L/g)	log Kd (L/g)	log Kd (L/g)	log Kd (L/g)	log Kd (L/g)	log Kd (L/g)
1.00E-06	50 mg carbon/liter	4.82	20.25	2.507E-04	4.351	1.351	4.351	1.351	4.351
1.00E-06	50 mg carbon/liter	4.55	34.79	5.184E-04	4.773	1.773	4.773	1.773	4.773
1.00E-06	50 mg carbon/liter	5.88	55.85	1.317E-05	5.118	2.118	5.118	2.118	5.118
1.00E-06	50 mg carbon/liter	5.78	57.27	1.417E-05	5.151	2.151	5.151	2.151	5.151
1.00E-06	50 mg carbon/liter	6.12	48.12	8.348E-04	4.970	1.970	4.970	1.970	4.970
1.00E-06	50 mg carbon/liter	6.11	63.55	2.103E-05	5.323	2.323	5.323	2.323	5.323
1.00E-06	50 mg carbon/liter	6.39	72.40	3.221E-05	5.598	2.598	5.598	2.598	5.598
1.00E-06	50 mg carbon/liter	6.42	71.94	3.173E-05	5.591	2.591	5.591	2.591	5.591
1.00E-06	50 mg carbon/liter	6.64	77.30	3.767E-05	5.576	2.576	5.576	2.576	5.576
1.00E-06	50 mg carbon/liter	6.81	75.05	3.500E-05	5.544	2.544	5.544	2.544	5.544
1.00E-06	50 mg carbon/liter	6.82	78.30	3.848E-05	5.585	2.585	5.585	2.585	5.585
1.00E-06	50 mg carbon/liter	6.81	71.63	3.592E-05	5.555	2.555	5.555	2.555	5.555
1.00E-06	50 mg carbon/liter	4.91	11.97	1.184E-04	4.073	1.073	4.073	1.073	4.073
1.00E-06	50 mg carbon/liter	4.93	10.59	1.045E-04	4.018	1.018	4.018	1.018	4.018
1.00E-06	50 mg carbon/liter	5.39	18.59	2.050E-04	4.312	1.312	4.312	1.312	4.312
1.00E-06	50 mg carbon/liter	5.72	31.96	2.142E-04	4.331	1.331	4.331	1.331	4.331
1.00E-06	50 mg carbon/liter	5.78	31.96	4.302E-04	4.634	1.634	4.634	1.634	4.634
1.00E-06	50 mg carbon/liter	6.04	29.71	3.871E-04	4.588	1.588	4.588	1.588	4.588
1.00E-06	50 mg carbon/liter	6.04	38.79	5.781E-04	4.762	1.762	4.762	1.762	4.762
1.00E-06	50 mg carbon/liter	6.09	41.00	6.388E-04	4.804	1.804	4.804	1.804	4.804
1.00E-06	50 mg carbon/liter	6.36	36.05	5.170E-04	4.713	1.713	4.713	1.713	4.713
1.00E-06	50 mg carbon/liter	6.36	50.07	9.242E-04	4.965	1.965	4.965	1.965	4.965
1.00E-06	50 mg carbon/liter	6.36	44.85	7.917E-04	4.888	1.888	4.888	1.888	4.888
1.00E-06	50 mg carbon/liter	6.36	50.43	9.835E-04	4.983	1.983	4.983	1.983	4.983
1.00E-06	50 mg carbon/liter	6.36	50.69	1.015E-05	5.006	2.006	5.006	2.006	5.006
1.00E-06	50 mg carbon/liter	6.39	55.36	1.058E-05	5.025	2.025	5.025	2.025	5.025

DJS

Original data for humic acid sorption by the soil (CP isolate)

CP soil (grams/L)	NaClO4 concentration (moles/L)	Humic acid present in experiment	final pH	% humic acid sorbed
1.3	1.00E-01	12.12 mg carbon/liter	7.78	86.8
1.3	1.00E-01	12.12 mg carbon/liter	7.93	85.2
1.3	1.00E-01	12.12 mg carbon/liter	7.83	85.3
1.3	1.00E-01	12.12 mg carbon/liter	7.83	86.5
1.3	1.00E-01	12.12 mg carbon/liter	7.57	87.1
1.3	1.00E-01	12.12 mg carbon/liter	7.55	87.8
1.3	1.00E-01	12.12 mg carbon/liter	7.30	88.0
1.3	1.00E-01	12.12 mg carbon/liter	7.23	89.3
1.3	1.00E-01	12.12 mg carbon/liter	6.79	90.4
1.3	1.00E-01	12.12 mg carbon/liter	6.64	90.5
1.3	1.00E-01	12.12 mg carbon/liter	6.35	91.0
1.3	1.00E-01	12.12 mg carbon/liter	6.27	89.6
1.3	1.00E-01	12.12 mg carbon/liter	5.49	89.2
1.3	1.00E-01	12.12 mg carbon/liter	5.72	91.1
1.3	1.00E-01	12.12 mg carbon/liter	4.98	90.1
1.3	1.00E-01	12.12 mg carbon/liter	4.99	92.0
1.3	1.00E-01	12.12 mg carbon/liter	4.50	90.1
1.3	1.00E-01	12.12 mg carbon/liter	4.47	92.9

Note to Modeling Teams:

Kd values for humic acid sorption by the soil (CP isolate), kaolinite, gibbsite, and Al-substituted goethite are presented in Table 6 of the original source publication (Zachara et al., 1994 - see Sheet 1 for full reference)

DJS

Original data for humic acid desorption by the soil (CP isolate)				
CP soil (grams/L)	NaClO4 concentration (moles/L)	Humic acid present in experiment	final pH	% humic acid desorbed
1.27	1.00E-02	11.3 mg carbon/liter	4.40	0.00
1.27	1.00E-02	11.3 mg carbon/liter	4.97	4.85
1.27	1.00E-02	11.3 mg carbon/liter	5.35	3.97
1.27	1.00E-02	11.3 mg carbon/liter	5.89	4.14
1.27	1.00E-02	11.3 mg carbon/liter	6.39	4.32
1.27	1.00E-02	11.3 mg carbon/liter	6.69	7.40
1.27	1.00E-02	11.3 mg carbon/liter	7.19	8.64
1.27	1.00E-02	11.3 mg carbon/liter	7.43	8.20
1.27	1.00E-02	11.3 mg carbon/liter	7.50	19.39
1.27	1.00E-02	11.3 mg carbon/liter	7.94	29.61

DJS

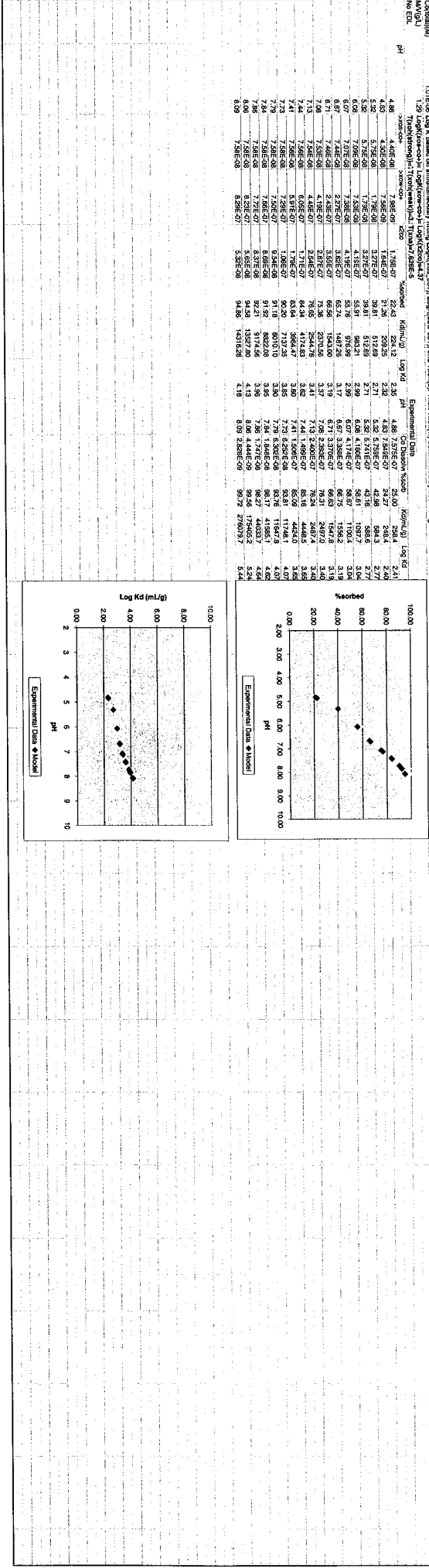
07/12/2002
DJS

07/12/2002
JBL

JBLmm

Co-CP, no HA, 0.01 M, with IE

No HA
SCM/NDEM with ion exchange
I=0.01 M

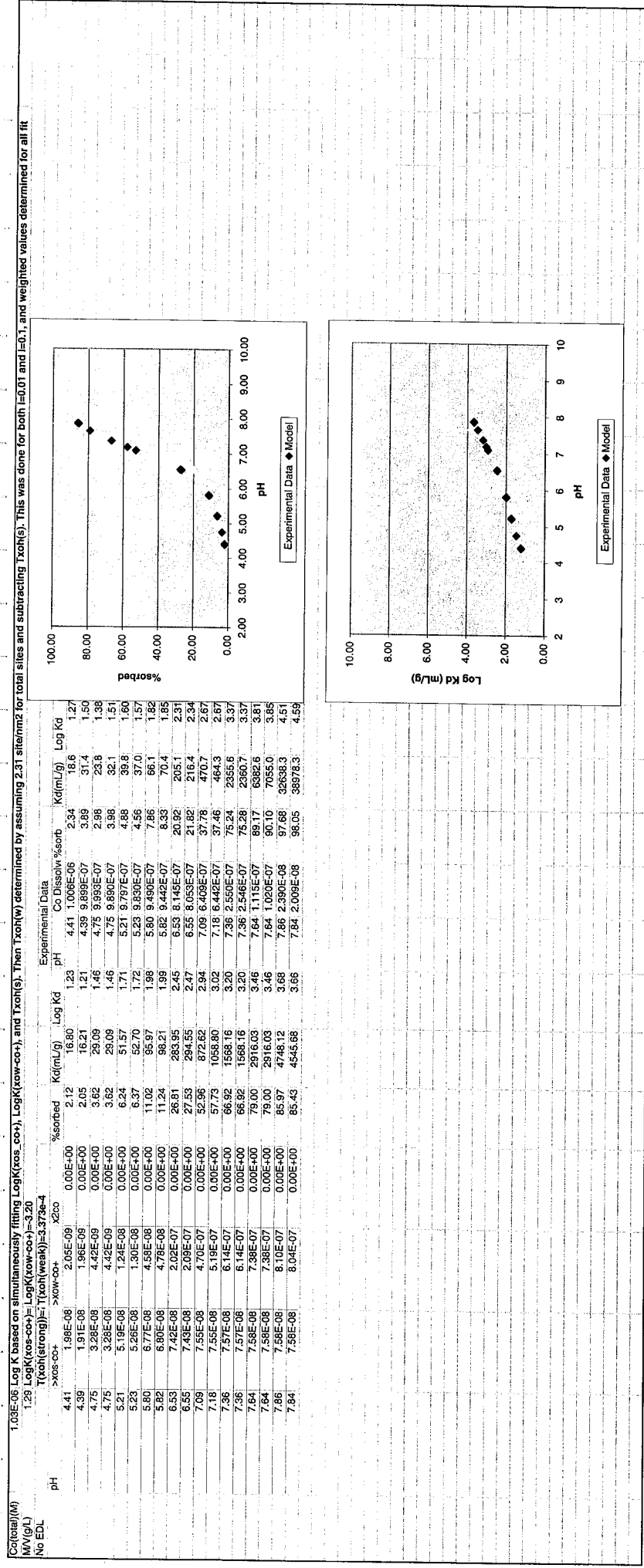


07/12/2002
JBL

JBLmm

No HA
SCM/NDEM only (no ion exchange)
I=0.1 M

Co-CP, no HA, 0.1 M, no IE



Signature: _____

Co-CP, no HA, 0.1 M, with IE

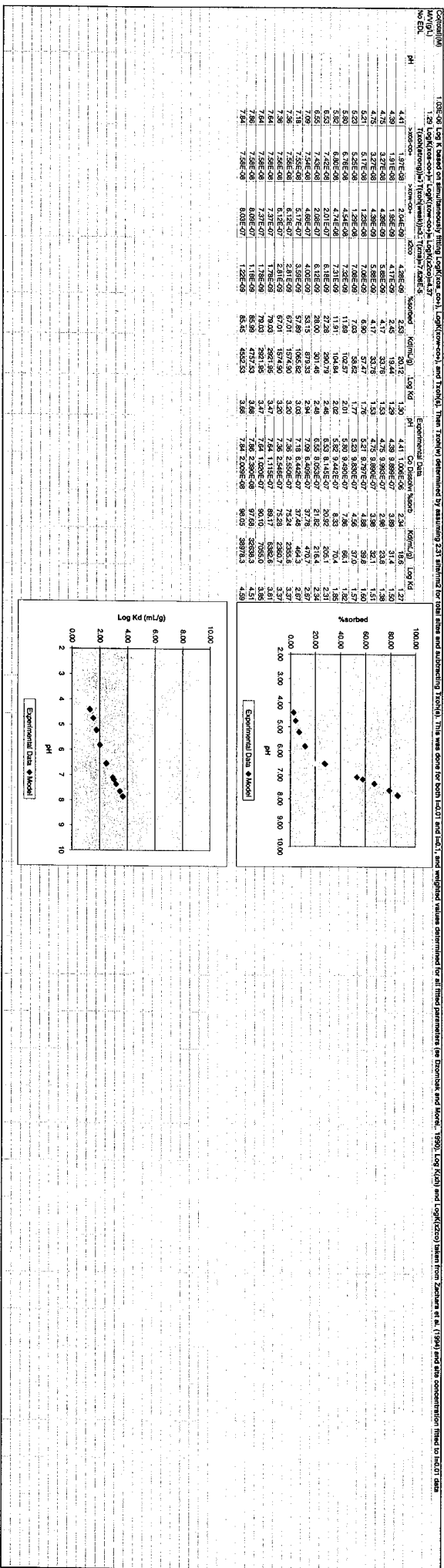
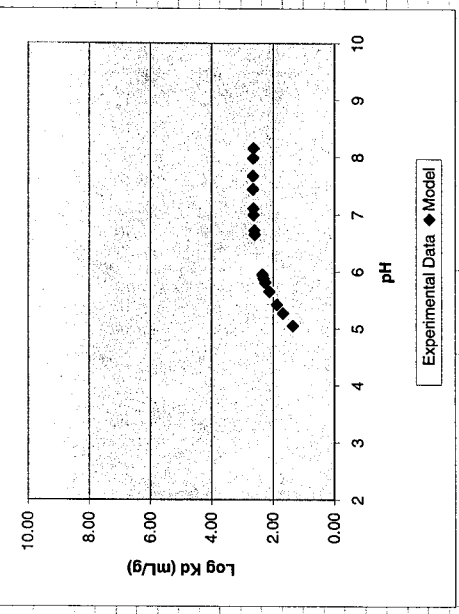


Figure 1 consists of two side-by-side scatter plots. The left plot has 'Log Kd (mL/g)' on the y-axis, ranging from 0.00 to 10.00 in increments of 2.00, and 'pH' on the x-axis, ranging from 2 to 10 in increments of 1. The right plot has '% sorbed' on the y-axis, ranging from 0.00 to 100.00 in increments of 20.00, and 'pH' on the x-axis, ranging from 2.00 to 10.00 in increments of 1.00. Both plots contain two data series: 'Experimental Data' represented by solid black circles and 'Model' represented by open circles. In the left plot, the experimental data points are clustered between pH 4 and 8, with Log Kd values ranging from approximately 2.0 to 4.0. The model data points are scattered across the pH range from 2 to 10, with Log Kd values ranging from approximately 0.5 to 4.0. In the right plot, the experimental data points are clustered between pH 4 and 8, with % sorbed values ranging from approximately 20% to 60%. The model data points are scattered across the pH range from 2 to 10, with % sorbed values ranging from approximately 10% to 60%.



Co-kao, no HA, 0.01 M, IE

07/12/2002

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[illegible]

Pahute Mesa Wells

These 3 wells
are on Palmito Mesa

SA (m²/L)

UE19C

 $0.27 \text{ m}^2/\text{L}$

Water Well 20

 $0.23 \text{ m}^2/\text{L}$

Well 8

 $0.34 \text{ m}^2/\text{L}$

Calculated from data reported
in Kingston & Whitbeck (1991)
Max colloid loading

moles/sites (2.31 sites/nm²) $\text{mol s}^{-1} / \text{L}$

$$\frac{(0.27 \text{ m}^2/\text{L})(2.31 \text{ s}^2/\text{m}^2)(10^{18} \text{ nm}^2/\text{m}^2)}{6.023 \times 10^{23}} = 1.036 \times 10^{-6}$$

$$\frac{(0.23 \text{ m}^2/\text{L})(2.315 \text{ s} / (\text{s} \cdot \text{nm}^2)) (10^8 \text{ nm}^2/\text{m}^2)}{6.023 \times 10^{23}} = 8.812 \times 10^{-7}$$

$$\frac{(0.34 \text{ m}^2/\text{L})(2.31 \text{ s} \cdot \text{m}^2/\text{nm}^2)(10^8 \text{ nm}^2/\text{m}^2)}{6.023 \times 10^{23}} = 1.304 \times 10^{-6}$$

22/10/2020

Assuming total surface loading with mononuclear, monodentate Pu complexes

Absolute maximum: ~~1.038~~ $(8.8 \times 10^{-7}) + (1.3 \times 10^{-6})$ mol/L

for GFW = 239 (Pu isotope of concern)

$$\begin{aligned} \text{Max Pu} & (1.0 \times 10^{-4} \text{ mol/L})(239 \text{ g/mol}) = 2.39 \times 10^{-4} \text{ g/L} \\ & (8.8 \times 10^{-7} \text{ mol/L})(239 \text{ g/mol}) = 2.11 \times 10^{-4} \text{ g/L} \\ & (1.3 \times 10^{-6} \text{ mol/L})(239 \text{ g/mol}) = 3.12 \times 10^{-4} \text{ g/L} \end{aligned}$$

Based on $Pu(V)$ calculations (see next page)

Kd from 5,000 (UEAC) + 14750 (LW20) mL/g

$(5000 \text{ mL/g}) \times \left(\frac{0.64 \times 10^{-3} \text{ g}}{1000 \text{ mL}} \right) (0.12 \times 10^{-3} \text{ g Pu/L}) = 4.1 \times 10^{-7} \text{ g Pu/L (sorbed)}$

$(14750 \text{ mL/g}) \times \left(\frac{0.48 \times 10^{-3} \text{ g}}{1000 \text{ mL}} \right) (0.12 \times 10^{-3} \text{ g Pu/L}) = 8.5 \times 10^{-7} \text{ g Pu/L (sorbed)}$

Based on Th (IV)

K_d from 4250 (UE14C) to 4500 (Well 8) mL/g

07/12/2002

DD

$$K_d = \frac{S}{C} = \left(\frac{\frac{g}{g}}{\frac{g}{mL}} \right) \left(\frac{m}{V} \right)$$

$$= \left(\frac{\text{amt sorbed}}{\text{amt dissolved}} \right) \left(\frac{V}{m} \right)$$

DLM

$$K_d = \left(\frac{\text{amt sorbed}}{\text{amt dissolved}} \right) \left(\frac{1000 \text{ mL}}{0.69 \times 10^{-3} \text{ g}} \right)$$

$$(5,000 \text{ mL/g}) \left(\frac{0.69 \times 10^{-3} \text{ g}}{1000 \text{ mL}} \right) (0.12 \times 10^{-3} \text{ g/L}) = \text{amt sorbed} = 4.1 \times 10^{-7} \text{ g/L}$$

$$(14,750 \text{ mL/g}) \left(\frac{0.48 \times 10^{-3} \text{ g}}{1000 \text{ mL}} \right) (0.12 \times 10^{-3} \text{ g/L}) = \text{amt sorbed} = 8.5 \times 10^{-7} \text{ g/L}$$

MINTEQA2, v.3.11

Sorption parameters calculated using MINTEQA2 and DLM method described in Turner and Pabalan (1999), with DLM parameters from Turner (1995).				
Site Name	ArcID	density g/cc	Colloid Conc (g/L)	Kd-Pu (mL/g)
UE19c NTS	SamplD=1-Wel	2.65	0.69	4998
Water Well 20 NTS	SamplD=2-Wel	2.65	0.48	14731
Well 8 NTS	SamplD=3-Wel	2.65	0.73	9564

For DLM, Pu(V) A'(alumina)=13 m2/g

in mg/L as

reported in Kingston & Whitbeck (1991)

Test Case 5 contained in SN #547

SE 9/10/02

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