CNWRA
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20.01402.871
Radionuclide Transport KTI

20.01402.871
KTI on Radionuclide Transport

Objectives (20.01402.871) - KTI on Radionuclide Transport (09/10/2002)

This scientific notebook (CNWRA Controlled Copy 547) is to be used to document the results of experiments and modeling studies conducted to examine radionuclide transport. These studies may be designed to examine different geochemical processes that lead to the retardation of radionuclide transport, including sorption, ion exchange, and coprecipitation. Different geochemical conditions will be investigated to determine the effects of geochemical variability on these retardation processes. The procedures used in these experiments and modeling studies will either be documented in this notebook, or incorporated by reference to other CNWRA notebooks. Computer codes that may be used include the most recent versions of the 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. To the extent possible, electronic copies of experimental results will be included in the back of this notebook.

David R. Turner CNWRA/Principal Scientist

9/10/2002

9/10/2002

NEA SORPTION EXERCISE
TEST CASE 5: Np(V) SORPTION ON MONTMORILLONITE

As described by the technical direction team for the NEA Phase II sorption exercise, the model teams were asked to simulate the Np-montmorillonite sorption data obtained at the CNWRA and reported in Turner et al. (1998) using a surface complexation model. The model developed to describe the CNWRA data was then to be used to predict the Np-montmorillonite sorption data of Gorgeon (unpublished). The modeling assumptions used in Test Case 5 by the CNWRA modeling team and modeling results are summarized below. Detailed model results are provided in the accompanying electronic files.

CNWRA Np-MONTMORILLONITE DATA: MODELING DECISIONS

Mineral-Radioelement System

Np(V) sorption on montmorillonite (Turner et al., 1998).

Model Selected

Combined DLM with electrostatic corrections and ion exchange. The sorption site types and concentrations were described using a generic surface model developed by Wanner et al. (1994) to describe montmorillonite potentiometric titration data.

Determining Np-Hematite DLM parameters using FITEQL, Version 2.0

Based on the DLM of Dzombak and Morel (1990), Wanner et al. (1994) described the electrostatic behavior of the montmorillonite surface with a combination of a generic surface complexation site to represent sorption on variably charged crystallite edges, and ion exchange to represent sorption on constant charge planar sites. In a simple electrolyte solution, the electrostatic behavior of montmorillonite is therefore described using the following three reactions:

Surface Complexation:	$>XOH^0 + H^+ = >XOH_2^+$	Log K^+
	$>XOH^0 = >XO^- + H^+$	Log K^-
Ion Exchange:	$XNa + H^+ = XH + Na^+$	Log K_{XH}

The values determined by Wanner et al. (1994) for Log K^+, Log K^-, Log K_{XH}, and site concentrations T_{XOH} and T_{XNa} (Table 3) were used to model the CNWRA Np-montmorillonite sorption data.

Depending on the mineral source, preparation techniques, and solution chemistry, montmorillonite may have a wide range in surface areas and reported cation exchange capacities (CEC). For example, the Arizona Cheto (SAz-1) Na-montmorillonite used by Turner et al. (1998) has a reported CEC of 120 meq/100 g, the Wyoming bentonite used by Gorgeon (unpublished) has a CEC of 109 meq/100 g, and Wanner et al. (1994) report a CEC of 108 meq/100 g for pretreated MX-80 bentonite. To normalize site concentrations (T_{XOH} and T_{XNa}) to the minerals and experimental conditions considered in this exercise, we scaled the values reported by Wanner et al. (1994) (Table 3) using solid-mass to solution-volume (M/V) for each experiment, and the ratio of reported CEC. For example, for the CNWRA NpM3 (no CO_2) experiment:

$$T_{XOH} = (2.84 \times 10^{-5}\ \text{mol/g}) \times (4.20\ \text{g/L}) \times [(120\ \text{meq/100 g})/108\ \text{meq/100 g})] = 1.33 \times 10^{-5}\ \text{mol/L}$$

The Np(V)-montmorillonite sorption data for CNWRA experiments NpM1 (M/V = 3.97 g/L, Trace CO_2, I = 0.1 M $NaNO_3$, Np_{total} = 8.79 × 10^{-7} M) and NpM3 (M/V = 4.20 g/L, CO_2-free atmosphere, I = 0.1 M $NaNO_3$, Np_{total} = 9.46 × 10^{-7} M) were selected for interpretation using the combined DLM and ion exchange model. As implemented in FITEQL, the electrostatic DLM requires an estimate of mineral surface area to calculate surface charge. Based on Wanner et al. (1994), the edge sites were assumed to comprise about 10 percent of the total surface area measured by N_2/BET [e.g., about 9.7 m^2/g of the total N_2/BET = 97 m^2/g reported by Turner et al. (1998)].

A simplified modeling approach was used. Two mononuclear, monodentate sorption reactions were assumed to form on the generic edge sites:

$$>XOH^0 + NpO_2^+ = >XOH\text{-}NpO_2^+ + H^+ \qquad \text{Log } K_{XOH\text{-}NpO2}$$

$$>XOH^0 + NpO_2^+ + H_2O = >XO\text{-}NpO_2OH^0 + 2H^+ \qquad \text{Log } K_{XO\text{-}NpO2OH}$$

along with a single ion exchange reaction on the planar constant charge sites:

$$XNa + NpO_2^+ = XNpO_2 + Na^+ \qquad \text{Log } K_{XNpO2}$$

FITEQL, Version 2.0 (Westall, 1982a,b) was used to solve for the Log K constants for the postulated sorption reactions. The sorption results were entered in the FITEQL input file as serial data. Additional input data include the surface protonation/deprotonation constants and total site concentrations of Wanner et al. (1994), scaled to the CNWRA experimental conditions as described previously. Thermodynamic data for Np(V)-CO_2-H_2O system was taken from the NEA thermodynamic database (Lemire et al., 2001). Ionic strength activity coefficients were determined using the Davies Equation. All three adjustable parameters (Log $K_{XOH\text{-}NpO2}$, Log $K_{XO\text{-}NpO2OH}$, and Log K_{XNpO2}) were solved simultaneously for each of the two data sets, and the results were combined using the weighted averaging scheme developed in Dzombak and Morel (1990).

Table 3. Model Parameters for NEA Sorption Exercise, Phase II, Test Case 5 (Np-Montmorillonite). DLM with Electrostatic Double Layer and Ion Exchange

Surface Reaction	Log K (I=0)	Site Concentration	Source
$>XOH^0 + H^+ = >XOH_2^+$	5.39	—	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
$>XOH^0 = >XO^- + H^+$	-6.68	—	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
$XNa + H^+ = XH + Na^+$	4.57[a]	—	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
$>XOH^0 + NpO_2^+ = >XOH\text{-}NpO_2^+$	2.20	—	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously, weighted average.
$>XOH^0 + NpO_2^+ + H_2O = >XOH\text{-}NpO_2OH^- + 2H^+$	-12.70	—	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously, weighted average.
$XNa + NpO_2^+ = XNpO_2 + Na^+$	1.82[a]	—	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously, weighted average.
T_{XOH}	—	2.84 × 10^{-5} mol/g	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
T_{XNa}	—	2.2 × 10^{-5} mol/g	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)

[a] Ion exchange selectivity coefficient determined for I = 0.1 M $NaNO_3$.

The FITEQL-derived values for Log $K_{XOH\text{-}NpO2}$ and Log $K_{XO\text{-}NpO2OH}$ differed by only 0.1 or less for the two experimental data sets, while the ion exchange parameter (Log K_{XNpO2}) differed by about 0.4.

Summary of Model Results

9/10/2002 DB

As developed for this test case, the combined electrostatic DLM/ion exchange model describes complex sorption behavior over a range in chemical conditions using relatively simple postulated surface chemistry. The model uses a generic surface model determined by Wanner et al. (1994), with site concentrations scaled to the experimental conditions using M/V and CEC. The model required optimizing Np-montmorillonite sorption data to determine three parameters, Log $K_{XOH\text{-}NpO2}$, Log $K_{XO\text{-}NpO2OH}$, and Log K_{XNpO2}. Determining these three parameters requires a data set over a sufficiently wide pH range to capture the Np-montmorillonite sorption behavior as a function of pH. The CNWRA experiments were conducted under different P_{CO2} conditions and allowed consideration of the effects of CO_2 on Np-montmorillonite sorption behavior. However, all of the CNWRA experiments were performed at the same ionic strength (I = 0.1 M $NaNO_3$) and with similar M/V ratios and Np concentrations, so we could not test the sensitivity of the model to the effects of ionic strength or surface loading.

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 (Test Case 5, DLM with EDL/ion exchange, CNWRA data)

```
Np-Montmorillonite Sorption; Exp. NpM1: Np(t)=8.79e-07(M)
DLM(Composite,Wanner94);I=0.1m NaNO3;M/V=3.97g/L;Capped vials
25.00 MOLAL  0.000  0.00000E-01
0 0 1 0 1 0 0 0 1 1 2 4 3
24 H+1                    ACTIVITY   mol/L
1 330   1.000
   7.20   7.27   7.30   7.37   7.42   7.62
   7.52   7.70   7.61   7.73   7.56   7.62
   7.60   7.62   7.64   7.68   7.76   7.93
   7.80   8.75   9.13   9.56   9.98  10.54
t5cnwra1.123 8115520 8115521   55520     552
4   1   7
3.970E+00    9.70 0.000 0.000 81
    330  0.000E-01   -2.00 y                    /H+1
    552  8.790E-07   -6.06 y                    /NpO2+1
    500  1.000E-01   -1.00 y                    /Na+1
    492  1.000E-01   -1.00 y                    /NO3-1
    140  3.286E-07   -6.48 y                    /CO3-2
    005  9.708E-05   -4.01 y                    /XNa
    813  0.000E-01    0.00 y                    /ADS1PSIo
    811  1.252E-04   -3.87 y                    /ADS1TYP1

  2   6
5523300   -11.3000    64.7900                   /npo2(oh)(aq)
5523301   -23.6000   118.6100                   /npo2(oh)2-
5521400     4.9600    54.6500                   /npo2(co3)-
5521401     6.5300    28.9400                   /npo2(co3)2-3
5521402     5.5000   -13.2500                   /npo2(co3)3-5
5521403    -5.3100     0.0000                   /npo2(co3)2(oh)-4
  3   1
    330     2.0000     0.0000                   /H+1
  6   1
    813     0.0000     0.0000                   /ADS1PSIo

  2   6
8113300 >xo-            0.0000   -6.6800   0.000   0.000-1.00 0.00 0.00   0.0000
```

DB 6/mm

```
 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  0.000    0    0.000    0    0.000    0
8113301 >xoh2+            0.0000     5.3900    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    0.000    0
0  0.000    0    0.000    0    0.000    0
8115520 >xohnpo2          0.0000     2.2000    0.000    0.000 0.00 0.00 0.00    0.0000
 0.00 3    1.000 811   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    0.000    0
0  0.000    0    0.000    0    0.000    0
8115521 >xonpo2oh-        0.0000   -12.7000    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    0.000    0
0  0.000    0    0.000    0    0.000    0
  53300 >xh               0.0000     4.5700    0.000    0.000 0.00 0.00 0.00    0.0000
 0.00 3    1.000 005   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    0.000    0
0  0.000    0    0.000    0    0.000    0
  55520 >xnpo2            0.0000     1.8200    0.000    0.000 0.00 0.00 0.00    0.0000
 0.00 3    1.000 005   1.000 552  -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    0.000    0
0  0.000    0    0.000    0    0.000    0
```

9/10/2002 DBS

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):

$$\text{Goodness-of-Fit} = [\text{Log}\,(K_{d,model}/R_{d,experiment})]^2 \qquad [1]$$

Smaller values indicate a better prediction of the observed sorption behavior. The goodness-of-fit calculated using this measure for the four CNWRA data sets is typically small, in most cases ranging from 10^{-5} to 10^{-2}, with a few values at the pH extremes as high as 4 or 5. For the no-CO_2 and trace CO_2 experiments, the model provides an excellent description of sorption behavior over the entire observed pH range, agreeing with observed sorption values within about 5 percent sorbed Np or less. The model simulates the continuous increase in sorption over the entire pH range, and correctly predicts the observed inflection points in the sorption data at pH of about 8.5. It provides reasonable prediction of the reduction in Np uptake in the presence of atmospheric CO_2 ($P_{CO2} = 10^{-3.5}$ atm), but tends to underpredict sorption under alkaline conditions (pH>8). This underprediction, combined with the slight underprediction of sorption for the trace CO_2 experiment, suggests the possibility of a neptunyl-carbonate (e.g., $>XOH_2\text{-}NpO_2CO_3$) surface complex. To keep the number of adjustable parameters small, however, the model was not modified to include the sorption of a carbonate species.

For the one CNWRA experiment (NpM2-reverse) with sorption data reported below pH = 5, the model underpredicts sorption in the region where observed sorption is low (pH < 5). This underprediction does not seem to be large in an absolute sense, [e.g., 0.1 (predicted) versus 2 mL/g (observed)], but it still represents a relative underprediction by a factor of 20. This is better represented by expressing sorption in terms of Log K_d (mL/g). This suggests some further modifications are necessary to address the ion exchange part of the model. It is worth noting that these data are below the pH range of the data used to calibrate the sorption model. The model is chemically plausible with regard to Np(V) speciation. The dominant Np species is NpO_2^+ for pH up to about 8, and continues to be a significant species over the range of experimental conditions (Turner et al., 1998). The model does not consider sorption of background electrolytes, and does not invoke sorption of carbonate species such as $NpO_2(CO_3)_2^{3-}$, CO_3^{2-}, or HCO_3^-. The model accurately predicts decreasing NpO_2^+ sorption under increasing CO_2 by increasing competition of aqueous neptunyl carbonate species for available NpO_2^+. The postulated surface reactions are also consistent with EXAFS data on Np-sorption on goethite (Combes et al., 1992).

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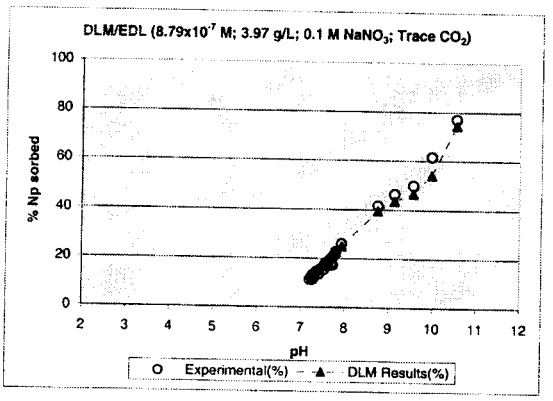
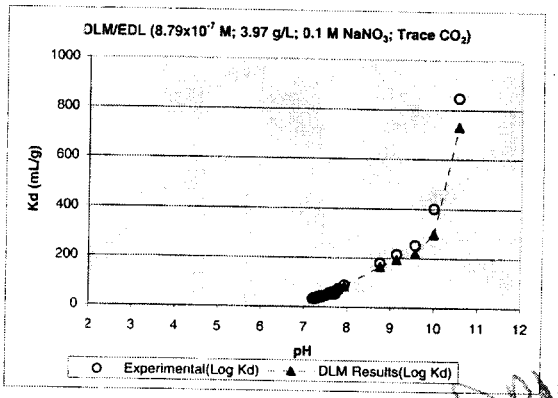
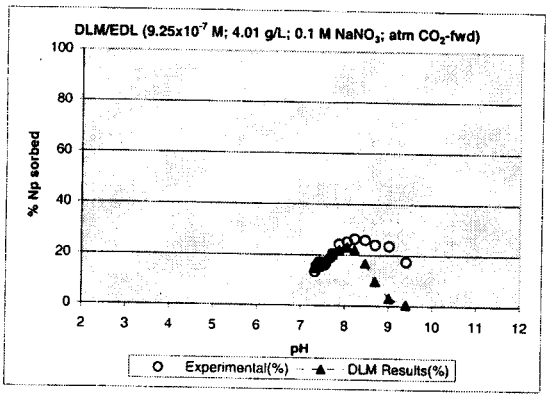
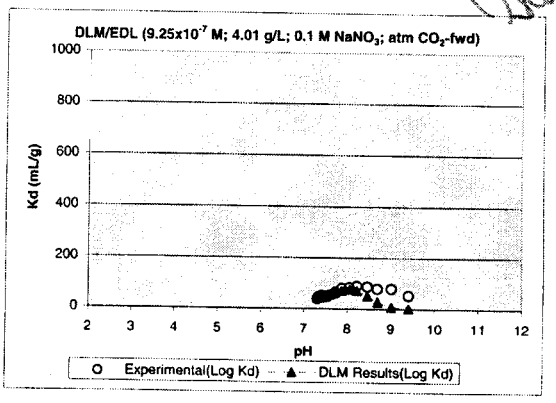
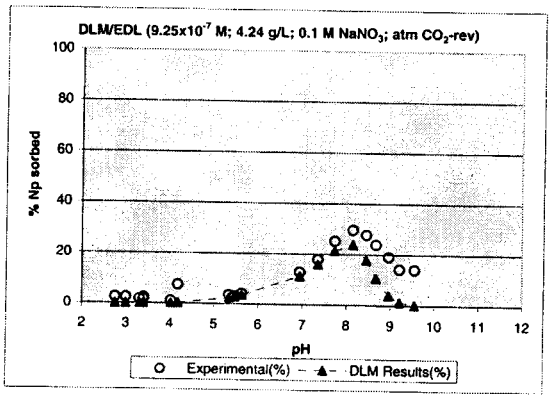
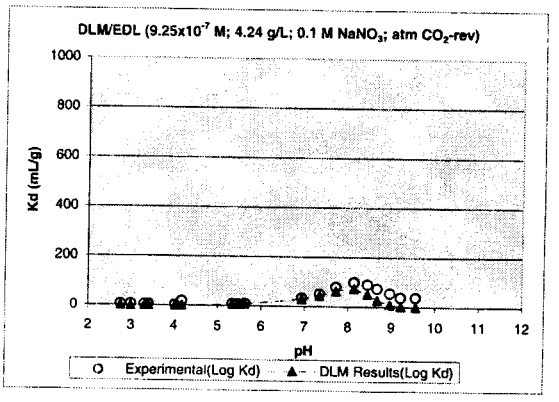

DLM/EDL (8.79x10^{-7} M; 3.97 g/L; 0.1 M $NaNO_3$; Trace CO_2)
% Np sorbed
pH
Experimental(%)
DLM Results(%)

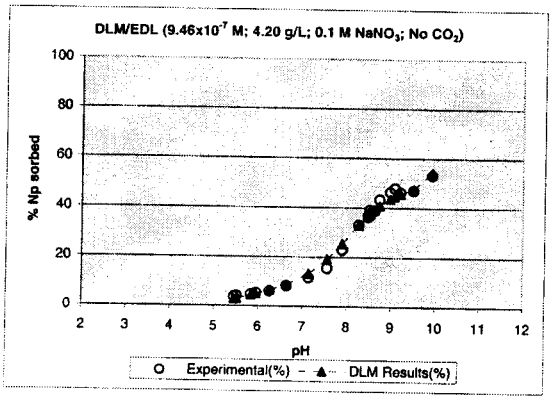

DLM/EDL (8.79x10^{-7} M; 3.97 g/L; 0.1 M $NaNO_3$; Trace CO_2)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)

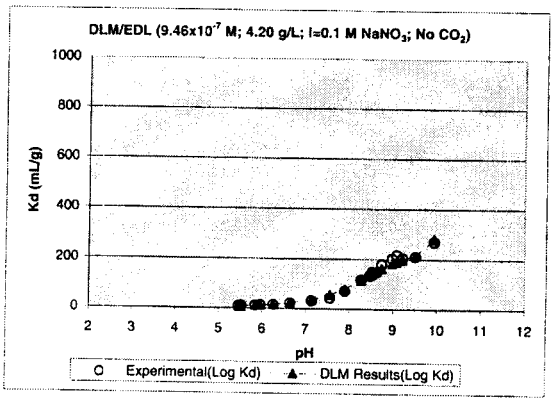

DLM/EDL (9.25x10^{-7} M; 4.01 g/L; 0.1 M $NaNO_3$; atm CO_2-fwd)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.25x10^{-7} M; 4.01 g/L; 0.1 M $NaNO_3$; atm CO_2-fwd)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)


DLM/EDL (9.25x10^{-7} M; 4.24 g/L; 0.1 M $NaNO_3$; atm CO_2-rev)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.25x10^{-7} M; 4.24 g/L; 0.1 M $NaNO_3$; atm CO_2-rev)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)


DLM/EDL (9.46x10^{-7} M; 4.20 g/L; 0.1 M $NaNO_3$; No CO_2)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.46x10^{-7} M; 4.20 g/L; I=0.1 M $NaNO_3$; No CO_2)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)

Based on the modeling results, the DLM developed here is applicable to simulate sorption behavior over a broad range in pH and P_{CO2}. It captures most of the key points of sorption behavior, and generally agrees closely with observed values. Results suggest, however, that there are limitations with regard to the effects of CO_2. More complicated surface speciation models that include the sorption of neptunyl-carbonate species may be required to closely match the observed data at alkaline pH > 8, but will require additional parameters. The DLM developed here assumed only Np(V) in solution.

9/10/2002

GOREGEON (Unpublished) Np-MONTMORILLONITE DATA: MODELING DECISIONS

Mineral-Radioelement System

Np(V) sorption on montmorillonite (Gorgeon, unpublished).

Model Selected

Combined DLM with electrostatic corrections and ion exchange. The sorption site types and concentration were described using a generic surface model developed by Wanner et al. (1994) to describe montmorillonite potentiometric titration data.

Predicting the Np-montmorillonite sorption data of Gorgeon (unpublished)

As instructed by the technical direction team, we used the parameter values derived for the CNWRA Np-montmorillonite sorption data (Table 3) to predict the sorption data of Gorgeon (unpublished). The only modification to the model was scaling site concentrations to the experimental conditions. For both data sets, the total site concentration was estimated at

$$T_{XOH} = (2.84 \times 10^{-5}\ \text{mol/g}) \times (8.70\ \text{g/L}) \times [(109\ \text{meq/100g})/108\ \text{meq/100g})] = 2.49 \times 10^{-4}\ \text{mol/L}$$

$$T_{XNa} = (2.2 \times 10^{-5}\ \text{mol/g}) \times (8.70\ \text{g/L}) \times [(109\ \text{meq/100g})/108\ \text{meq/100g})] = 1.93 \times 10^{-4}\ \text{mol/L}$$

One additional assumption was in estimating the surface area for the montmorillonite used by Gorgeon (unpublished). The value provided by the technical direction team is 740 m^2/g. Although not indicated in the information provided, we assumed that this value was determined by ethylene glycol monoethyl (EGME) vapor adsorption. As indicated by Chiou and Rutherford (1993), EGME adsorption results for montmorillonite represent adsorption to interlayer sites that are not accessible to N_2. For this reason, Chiou and Rutherford (1993) suggested that EGME surface areas exceed those determined using N_2/BET by a factor of 7.6. Using this factor and the 740 m_2/g provided by the technical direction team, we calculated a 'N_2/BET equivalent' surface area of 97.4 m^2/g for the Gorgeon (unpublished) montmorillonite, effectively equivalent to the value reported by Turner et al. (1998). Ten percent (9.7 m^2/g) of this value was used to represent the edge site surface area for the DLM simulations.

Example MINTEQA2 Input File (Test Case 5, DLM with EDL/ion exchange, Gorgeon data)

```
Np-Montmorillonite Sorption; Gorgeon; Np(t)=1.10e-06(M)
DLM(Composite,Wanner94);I=0.1 NaClO4; M/V=8.70g/L; No CO2
25.00 MOLAL  0.000  0.00000E-01
0 0 1 0 1 0 0 0 1 1 2 6 3
28 H+1                    ACTIVITY   mol/L
1 330   1.000
   2.61   2.64   3.07   3.07   3.08   3.39
   3.45   3.67   3.67   4.16   4.28   4.62
```

 9/10/2002 (DR)

```
   4.87   5.58   5.85   6.58   6.63   7.36
   7.71   8.10   9.92   9.96  10.41  10.51
  10.67  10.85  11.18  11.21
t5gorg2.123  8115520 8115521   55520     552 5523300 5523301
4   1   7
8.700E+00    9.70 0.000 0.000 81
    330  0.000E-01   -2.00 y                    /H+1
    552  1.100E-06   -5.96 y                    /NpO2+1
    500  1.000E-01   -1.00 y                    /Na+1
    181  1.000E-01   -1.00 y                    /ClO4-
    005  1.932E-04   -3.71 y                    /XNa
    813  0.000E-01    0.00 y                    /ADS1PSIo
    811  2.494E-04   -3.60 y                    /ADS1TYP1

  2   2
5523300   -11.3000    64.7900                   /npo2(oh)(aq)
5523301   -23.6000   118.6100                   /npo2(oh)2-
  3   1
    330     2.0000     0.0000                   /H+1
  6   1
    813     0.0000     0.0000                   /ADS1PSIo

  2   6
8113300 >xo-            0.0000   -6.6800   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8113301 >xoh2+          0.0000    5.3900   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8115520 >xohnpo2        0.0000    2.2000   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8115521 >xonpo2oh-      0.0000  -12.7000   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   0.000   0
0  0.000   0   0.000   0   0.000   0
  53300 >xh             0.0000    4.5700   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 005   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   0.000   0
0  0.000   0   0.000   0   0.000   0
  55520 >xnpo2          0.0000    1.8200   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 005   1.000 552  -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   0.000   0
0  0.000   0   0.000   0   0.000   0
```

Summary of Model Results

The data of Gorgeon (unpublished) cover a much broader range in pH than the CNWRA data set. Except for ionic strength, however, which was fixed at either 0.025 or 0.1 M $NaClO_4$, the two data sets of Gorgeon (unpublished) were obtained under identical conditions (CO_2-free atmosphere, M/V = 8.70 g/L, $Np_{total} = 1.10 \times 10^{-6}$ M). For this reason, we could not test the ability of the model to predict the effects of CO_2, Np concentration, or M/V on Np-montmorillonite sorption behavior.

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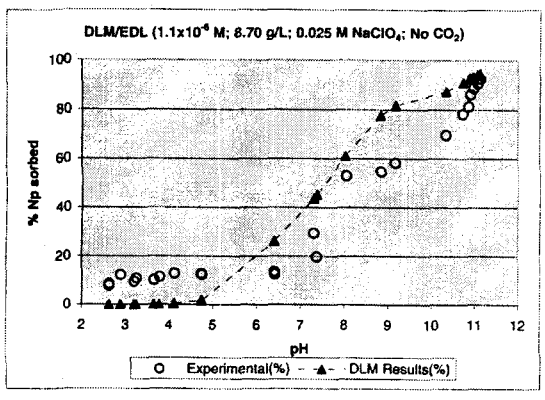

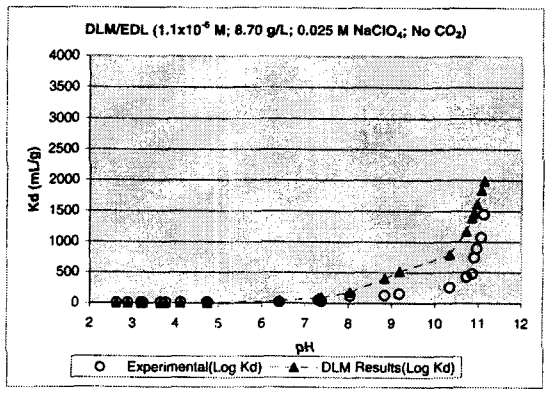

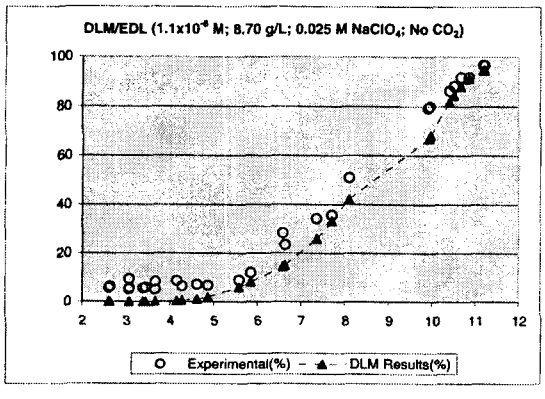

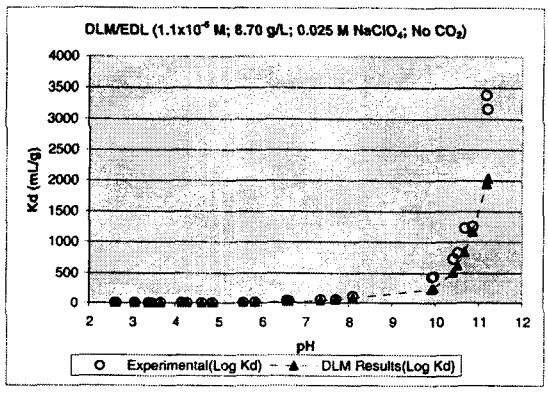

The calculated goodness-of-fit values for the Gorgeon (unpublished) data were higher than those calculated for the four CNWRA data sets, ranging from 10^{-4} to 10^{0}. The combined electrostatic DLM/ion exchange model developed to describe the CNWRA data (Turner et al., 1998) does a reasonable job of predicting the Gorgeon (unpublished) data for I = 0.1 M $NaClO_4$. It correctly predicts increased sorption over the entire pH range for the Gorgeon (unpublished) data set, most likely reflecting the higher M/V of the experimental conditions. The model predicts the concave upwards shape of the sorption curve. It slightly underpredicts sorption over the entire pH range, however, with the discrepancy being the greatest at the extremes of the pH range. Like the CNWRA data, the model predicts an inflection in Np uptake at a pH of about 8 to 10, but there is a gap in the data that prevents evaluating the validity of this prediction.

For the low ionic strength data set, the model correctly predicts the general increase in sorption with increasing pH, but it tends to underpredict Np uptake at low pH (pH < 6) and overpredict sorption over much of the rest of the pH range. For data expressed in terms of percent sorbed, the convex upward shape of the predicted sorption curve does not match the concave upward shape of the observed data. When expressed as K_d (mL/g), however, the predicted and observed curves exhibit a similar shape.

The discrepancy between experimental and predicted results appears to be largely due to an increase in predicted ion exchange by a factor of about 2.5 to 3 at the lower ionic strength. At low pH (pH<6), the data of Gorgeon (unpublished) indicate a low level of Np sorption that is not sensitive to pH, suggesting ion exchange. This interpretation is supported by a higher sorption of about 10 percent for the low ionic strength (0.025 M $NaClO_4$) solution and about five percent for the 0.1 M $NaClO_4$ solution. Despite the inclusion of an ion exchange reaction, the sorption model developed here does not capture this sorption behavior, predicting a steady decrease in sorption with decreasing pH. This is best seen by plotting the data as Log K_d. This is most likely due to the fact

that the FITEQL-derived selectivity coefficient (Table 3) for NpO_2^+ exchange (Log K_{XNpO2}) is about a factor of three less than that derived by Wanner et al. (1994) for the proton-exchanged site (Log K_{XH}). Therefore, at low pH, H^+ 'out competes' for the ion exchange sites, suppressing NpO_2^+ uptake.

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The better predictive success for data sets at similar ionic strength (I = 0.1 M $NaNO_3$ or $NaClO_4$) suggests that the ion exchange aspects of the model need to be strengthened. The selectivity coefficient K_{XNpO2} was derived for a CNWRA data set at I = 0.1 M, and is not strictly applicable at the lower ionic strength. In addition to further investigation of NpO_2^+ exchange, this would require revisiting the H^+ exchange equilibria to improve predictions at low pH. There are probably several contributors to the discrepancies observed in the model predictions. The first is the composition of the starting material. The montmorillonite used in the CNWRA experiments was from Arizona (SAz-1) and pre-treated to obtain an almost pure Na end member. The montmorillonite in the Gorgeon (unpublished) experiments was purified from Wyoming bentonite, but still contained significant amounts of Ca^{2+} and Mg^{2+}. If these divalent ions are in exchangeable sites, they may contribute to the discrepancies between predicted and observed Np uptake at low ionic strength. In addition, as indicated by the assumptions made in setting up the model, there is uncertainty in comparing the EGME and N_2/BET surface areas.

References for Test Case 5

Chiou, C.T. and D.W. Rutherford. Sorption of N_2 and EGME vapors on some soils, clays, and mineral oxides and determination of sample surface areas by use of sorption data.

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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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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.

List of worksheets for Test Case 5						
Sheet 1	General Information					
Sheet 2	Detailed instructions					
Sheet 3	Thermodynamic data					
Sheet 4	Data for Np sorption on montmorillonite, trace CO2					
Sheet 5	Data for Np sorption on montmorillonite, atmosperic CO2					
Sheet 6	Data for Np sorption on montmorillonite, no CO2					
Sheet 7	Model constants					
Sheet 8	Prediction to data of Gorgeon					

Input files
provide by NEA Technical Direction Team

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Test case 5	Np(V) Sorption on Montmorillonite

DATA SOURCE

Turner, D.R., Pabalan, R.T., and Bertetti, F.P., 1998, Neptunium(V) sorption on montmorillonite:
An experimental and surface complexation modelling study, Clays and Clay Minerals, v. 46, p. 259-269.
Original raw data are available from D. Turner.
Gorgeon, L., Contribution a la modelisation physico-chimique de le retention de radioelements a vie longue par des materiaux argileux.
This work includes Np sorption on bentonite study.

GOAL

Fit the selected data with a mass action model. Then extend the model in a predictive fashion
to other system given by Gorgeon.

OUTLINE OF EXPERIMENTAL STUDY OF TURNER ET AL

Np(V) sorption onto a laboratory preparation of Na-montmorillonite was studied at fixed initial Np(V) concentration (approximately 1e-6 M 237Np)
in solutions containing the electrolyte sodium nitrate (0.1 molal $NaNO_3$) at room temperature (20 ± 2 °C) over a pH range of about 4 to 11.

Four sets of sorption experiments were conducted with different PCO_2: trace CO_2 (worksheet 4), atmospheric CO_2 (forward and
reverse (worksheet 5)) and no CO_2 (worksheet 6). The authors report the sorption was reversible and therefore both
forward and reverse data can be used for model fitting in atmospheric conditions

A reaction time 14 days was used to reach sorptive and pH equilibrium under all the conditions studied.
The reaction time was so long mainly to relatively slow mass transfer of CO_2 between the gas and aqueous phases.

The Na-montmorillonite was obtained natural Ca-smectite (SAz-1) by conversion with NaCl solution and purification.
The measured (N_2-BET) specific surface area was 97 +/- 2 m^2/g.
X-ray powder diffraction analyses performed at different phases of preparation showed the interlayer
spacing consistent of ion exchange of Na for Ca.

OUTLINE OF EXPERIMENTAL STUDY OF GORGEON

Np(V) sorption onto a laboratory preparation of montmorillonite was studied at fixed initial Np(V) concentration (approximately 1e-6 M)
in solutions containing the electrolyte sodium perchlorate (0.025 and 0.1 molal $NaClO_4$) at room temperature over a pH range of about 2 to 12.
The montmorillonite was purified from Wyoming bentonite - after purification only 1.4 % quartz was left as an impurity.
The cation exchange capacity was measured to be 109 meq/100g (K^+ 0.42, Na^+ 90.5, Ca^{++} 13.8 and Mg^{++} 4.69 meq/100g).
The measured total surface area was 740 m^2/g (all types of pores included).

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INSTRUCTIONS TO MODELING TEAMS

1 Develop a surface complexation model to describe the neptunium sorption data (worksheets 4 to 6).
It is assumed that the neptunium adsorption data were collected after the experimental systems achieved chemical equilibrium.
The modeling team can choose any model for electrostatic correction that it wishes (diffuse double-layer, triple layer, etc).
The inclusion of a double layer term is optional, but its inclusion or exclusion should be justified.

2 The objective is to obtain a good fit to the neptunium sorption data provided with a chemically reasonable (plausible) model with as few fitting parameters as possible.
However, it is recognised that an increase in the number of fitting parameters in models can lead to a better fit of the adsorption data.
The final simulations of all participants will be compared to ascertain which approaches lead to better mathematical and chemical descriptions of the sorption data.

3 Aqueous reaction equilibrium constants at zero ionic strength (Sheet 3) should be used in the model simulations.
Each participant may also do additional simulations using different aqueous reaction equilibrium constants.
They should indicate which aqueous constants were changed and the consequences of the different choice of parameter values.
If additional simulations are undertaken, the results should be reported on additional spreadsheets.

4 Extend the model in a predictive fashion to other system given by Gorgeon (worksheet 8).
The modellers are free to fix the carbonate concentrations.

5 At all steps during model development, the choice of parameter values should be documented.
It should be indicated which parameter values are fitted, those that are assigned values from the literature (give source or reference), those that are assumed, etc.
Some justification or comments should be provided regarding choice of particular species, e.g., simplest reaction possible, spectroscopic studies; best fit from trial-and-error, etc.

DBLamm

6 Document the development of the model in a written format to submit to the TDT.

7 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).

8 Enter the calculated values for %Np adsorbed and Kd (mL/g) in Worksheets 4,5, 6 and 8.
Add sufficient columns to these tables to indicate all surface and solution species.
Add the concentrations of surface species and solution species for each experimental point to that row of the spreadsheet.
Include all surface and aqueous species comprising greater than 0.1% of the total Np concentration.

9 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+), etc. The TDT must be able to understand the identity of species in these files.

10 Provide a table of the formation constants for all surface species (Worksheet 7).

11 For each set of data, 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 alculated values with a dotted line.

12 Provide written summary comments describing the modeling results and the Modeling Team's opinion of:
a) the strengths and weaknesses of the modeling approach
b) the goodness-of-fit of the model
c) the chemical plausibility of the model
d) number of fitting parameters required
e) data requirements for the modeling approach
f) the range of applicability of the each modeling approach

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

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DR

Thermodynamic data at zero ionic strength			
Species	**Formation reaction**	**Log K**	**Source**
Np(V) data			
NpO2+		0	
NpO2OH	NpO2+ + H2O -H+ -> NpO2OH	-11.3	NEA 01
NpO2(OH)2-	NpO2+ + 2H2O - 2H+ -> NpO2(OH)2-	-23.6	NEA 01
NpO2(CO3)2OH-4	NpO2+ + 2CO3-2 + H2O - H+ -> NpO2(CO3)2OH-4	-5.31	NEA 01
NpO2CO3-	NpO2+ + CO3-2 -> NpO2(CO3)-	4.96	NEA 01
NpO2(CO3)2-3	NpO2+ + 2CO3-2 -> NpO2(CO3)2-3	6.53	NEA 01
NpO2(CO3)3-5	NpO2+ + 3CO3-2 -> NpO2(CO3)3-5	5.499	NEA 01
NpO2SO4-	NpO2+ + SO4-2 -> NpO2SO4-	0.44	NEA 01
Solids			
NpO2(OH)(s)	NpO2(OH)(s) + H+ -> NpO2+(aq) + 2H2O	5.3	NEA 01
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	1E-3.5		

Neptunium sorption data

Neptunium 8.79E-07 M

I = 0.1 M NaNO3

(capped vials)

INSERT MODEL OUTPUT IN THIS SECTION

(only include species comprising greater than 0.1% of the total Np concentration).

	Montmorillonite:		3.97 g/L			Calculated concentrations of all surface species Modeling team to label these columns			Calculated concentrations of all Np aqueous species Modeling team to label these columns					
				Calculated % Np adsorbed	Calculated Kd (mL/g)	>xoh-npo2+ (M)	>xo-npo2oh- (M)	xnpo2 (IE) (M)	npo2+ (M)	npo2oh (M)	npo2(oh)2- (M)	npo2co3- (M)	npo2(co3)2-3 (M)	npo2(co3)3-5 (M)
Data point number	**pH**	**% adsorbed**	**Kd (mL/g)**											
1	7.20	11.4	32.38	13.3	38.6	6.91E-08	2.78E-10	4.74E-08	7.62E-07	4.60E-11	4.78E-16	1.16E-11	5.17E-19	4.20E-28
2	7.27	11.3	32.31	14.1	41.5	7.68E-08	3.34E-10	4.72E-08	7.55E-07	5.36E-11	6.53E-16	1.36E-11	7.26E-19	7.03E-28
3	7.30	12.2	34.97	14.5	42.8	8.03E-08	3.62E-10	4.70E-08	7.51E-07	5.71E-11	7.46E-16	1.46E-11	8.39E-19	8.74E-28
4	7.37	14.7	43.61	15.5	46.1	8.89E-08	4.35E-10	4.67E-08	7.43E-07	6.64E-11	1.02E-15	1.72E-11	1.17E-18	1.45E-27
5	7.42	13.5	39.55	16.2	48.6	9.53E-08	4.96E-10	4.64E-08	7.37E-07	7.39E-11	1.27E-15	1.92E-11	1.48E-18	2.07E-27
7	7.52	15.3	45.13	17.7	54.1	1.09E-07	6.44E-10	4.57E-08	7.23E-07	9.13E-11	1.98E-15	2.41E-11	2.36E-18	4.20E-27
11	7.56	17.9	55.18	18.3	56.5	1.15E-07	7.16E-10	4.54E-08	7.18E-07	9.93E-11	2.36E-15	2.63E-11	2.83E-18	5.55E-27
13	7.60	16.8	50.96	19.0	59.0	1.21E-07	7.94E-10	4.51E-08	7.12E-07	1.08E-10	2.82E-15	2.87E-11	3.40E-18	7.33E-27
9	7.61	17.0	51.13	19.2	59.7	1.23E-07	8.16E-10	4.50E-08	7.11E-07	1.10E-10	2.94E-15	2.93E-11	3.56E-18	7.85E-27
6	7.62	18.7	57.79	19.3	60.3	1.24E-07	8.37E-10	4.49E-08	7.09E-07	1.13E-10	3.07E-15	2.99E-11	3.72E-18	8.42E-27
12	7.62	18.1	55.59	19.3	60.3	1.24E-07	8.37E-10	4.49E-08	7.09E-07	1.13E-10	3.07E-15	2.99E-11	3.72E-18	8.42E-27
14	7.62	18.3	55.77	19.3	60.3	1.24E-07	8.37E-10	4.49E-08	7.09E-07	1.13E-10	3.07E-15	2.99E-11	3.72E-18	8.42E-27
15	7.64	19.0	58.99	19.7	61.7	1.27E-07	8.82E-10	4.48E-08	7.06E-07	1.18E-10	3.36E-15	3.13E-11	4.08E-18	9.66E-27
16	7.68	19.7	61.35	20.4	64.4	1.34E-07	9.79E-10	4.44E-08	7.00E-07	1.28E-10	4.00E-15	3.41E-11	4.89E-18	1.27E-26
8	7.70	17.8	54.80	20.7	65.8	1.37E-07	1.03E-09	4.43E-08	6.97E-07	1.33E-10	4.37E-15	3.56E-11	5.35E-18	1.46E-26
10	7.73	17.3	52.06	21.2	67.9	1.42E-07	1.12E-09	4.40E-08	6.92E-07	1.42E-10	4.98E-15	3.79E-11	6.11E-18	1.79E-26
17	7.76	21.5	68.77	21.8	70.1	1.47E-07	1.21E-09	4.37E-08	6.87E-07	1.51E-10	5.68E-15	4.04E-11	6.99E-18	2.20E-26
19	7.80	22.7	74.45	22.5	73.2	1.53E-07	1.34E-09	4.33E-08	6.81E-07	1.64E-10	6.76E-15	4.39E-11	8.35E-18	2.89E-26
18	7.93	26.0	88.97	25.0	83.8	1.76E-07	1.88E-09	4.20E-08	6.59E-07	2.14E-10	1.19E-14	5.76E-11	1.48E-17	6.92E-26
20	8.75	41.6	179.69	39.6	165.0	2.98E-07	1.56E-08	3.39E-08	5.30E-07	1.14E-09	4.18E-13	2.88E-10	4.63E-16	1.35E-23
21	9.13	46.3	215.59	43.5	194.1	3.09E-07	4.20E-08	3.16E-08	4.93E-07	2.54E-09	2.24E-12	5.78E-10	2.00E-15	1.25E-22
22	9.56	49.8	252.58	46.6	219.5	2.55E-07	1.25E-07	2.96E-08	4.62E-07	6.40E-09	1.52E-11	1.12E-09	7.98E-15	1.03E-21
23	9.98	61.5	401.34	54.0	296.3	1.42E-07	3.08E-07	2.49E-08	3.88E-07	1.41E-08	8.83E-11	1.54E-09	1.80E-14	3.84E-21
24	10.54	77.0	847.78	74.3	729.9	2.89E-08	6.12E-07	1.27E-08	1.98E-07	2.61E-08	5.93E-10	1.10E-09	1.81E-14	5.39E-21

Note: the data point numbers are the same as those provided by the TDT, but the data have been sorted by pH-ascending

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Neptunium sorption data

Neptunium 9.25E-07 **M**

I = 0.1 **M NaNO3**

Atm. CO2

INSERT MODEL OUTPUT IN THIS SECTION

(only include species comprising greater than 0.1% of the total Np concentration).

						Calculated concentrations of all surface species Modeling team to label these columns			Calculated concentrations of all Np aqueous species Modeling team to label these columns					
Forward	**Montmorillonite:**		**4.01 g/L**											
Data point number	**pH**	**% adsorbed**	**Kd (mL/g)**	Calculated % Np adsorbed	Calculated Kd (mL/g)	>xoh-npo2+ (M)	>xo-npo2oh- (M)	xnpo2 (IE) (M)	npo2+ (M)	npo2oh (M)	npo2(oh)2- (M)	npo2co3- (M)	npo2(co3)2-3 (M)	npo2(co3)3-5 (M)
25	7.31	13.3	38.75	14.7	42.9	8.59E-08	3.91E-10	4.95E-08	7.83E-07	6.09E-11	8.14E-16	6.68E-09	1.68E-13	7.70E-20
26	7.34	15.6	46.36	15.1	44.2	8.96E-08	4.23E-10	4.93E-08	7.78E-07	6.49E-11	9.29E-16	7.63E-09	2.21E-13	1.16E-19
27	7.38	15.0	43.76	15.6	46.1	9.47E-08	4.69E-10	4.90E-08	7.72E-07	7.06E-11	1.11E-15	9.10E-09	3.16E-13	2.00E-19
28	7.41	17.1	52.05	16.0	47.5	9.87E-08	5.07E-10	4.87E-08	7.67E-07	7.51E-11	1.26E-15	1.04E-08	4.14E-13	3.00E-19
29	7.48	17.0	51.29	16.9	50.9	1.08E-07	6.07E-10	4.81E-08	7.54E-07	8.68E-11	1.72E-15	1.41E-08	7.76E-13	7.77E-19
31	7.48	15.6	46.26	16.9	50.9	1.08E-07	6.07E-10	4.81E-08	7.54E-07	8.68E-11	1.72E-15	1.41E-08	7.76E-13	7.77E-19
30	7.51	17.0	51.69	17.4	52.4	1.12E-07	6.55E-10	4.77E-08	7.48E-07	9.23E-11	1.95E-15	1.61E-08	1.02E-12	1.17E-18
32	7.54	16.1	48.03	17.8	54.0	1.17E-07	7.06E-10	4.74E-08	7.42E-07	9.81E-11	2.23E-15	1.83E-08	1.33E-12	1.75E-18
33	7.56	16.6	49.59	18.1	55.1	1.19E-07	7.43E-10	4.72E-08	7.38E-07	1.02E-10	2.43E-15	1.99E-08	1.59E-12	2.30E-18
34	7.67	19.0	58.50	19.6	61.0	1.35E-07	9.78E-10	4.56E-08	7.11E-07	1.27E-10	3.88E-15	3.19E-08	4.22E-12	1.01E-17
35	7.72	20.6	64.37	20.3	63.6	1.42E-07	1.10E-09	4.48E-08	6.98E-07	1.40E-10	4.79E-15	3.94E-08	6.55E-12	1.98E-17
36	7.87	24.3	79.69	22.1	70.8	1.61E-07	1.57E-09	4.17E-08	6.47E-07	1.83E-10	8.88E-15	7.29E-08	2.42E-11	1.46E-16
37	8.05	25.1	83.29	23.2	75.2	1.76E-07	2.29E-09	3.64E-08	5.65E-07	2.41E-10	1.77E-14	1.46E-07	1.11E-10	1.54E-15
38	8.22	26.4	88.85	22.2	71.1	1.72E-07	3.03E-09	2.97E-08	4.60E-07	2.91E-10	3.16E-14	2.59E-07	4.33E-10	1.32E-14
39	8.46	26.0	86.54	16.8	50.2	1.33E-07	3.72E-09	1.84E-08	2.84E-07	3.12E-10	5.89E-14	4.84E-07	2.44E-09	2.25E-13
40	8.69	24.1	78.47	9.6	26.6	7.66E-08	3.52E-09	9.05E-09	1.40E-07	2.60E-10	8.35E-14	6.86E-07	1.00E-08	2.69E-12
41	9.01	23.6	78.19	3.0	7.7	2.29E-08	2.34E-09	2.45E-09	3.76E-08	1.46E-10	9.83E-14	8.07E-07	5.23E-08	6.31E-11
42	9.40	17.5	52.50	0.4	1.0	2.56E-09	9.07E-10	3.34E-10	5.00E-09	4.72E-11	7.87E-14	6.47E-07	2.67E-07	2.18E-09
Reverse	**Montmorillonite:**		**4.24 g/L**											
Data point number	**pH**	**% adsorbed**	**Kd (mL/g)**											
43	2.76	2.5	6.15	0.0	0.0	2.63E-11	2.53E-16	7.65E-11	9.25E-07	2.03E-15	7.64E-25	6.28E-18	1.26E-31	4.65E-47
44	3.00	2.4	5.86	0.0	0.0	4.12E-11	7.80E-16	1.33E-10	9.25E-07	3.52E-15	2.31E-24	1.90E-17	1.15E-30	1.27E-45
45	3.31	1.7	4.16	0.0	0.1	7.22E-11	2.96E-15	2.71E-10	9.25E-07	7.19E-15	9.62E-24	7.90E-17	1.99E-29	9.14E-44
51	3.40	1.7	4.11	0.0	0.1	8.47E-11	4.26E-15	3.33E-10	9.25E-07	8.85E-15	1.46E-23	1.20E-16	4.56E-29	3.17E-43
49	3.41	2.5	5.97	0.0	0.1	8.62E-11	4.43E-15	3.40E-10	9.25E-07	9.06E-15	1.52E-23	1.25E-16	5.00E-29	3.64E-43
46	4.02	1.1	2.74	0.2	0.4	2.50E-10	4.21E-14	1.36E-09	9.23E-07	3.69E-14	2.53E-22	2.07E-15	1.37E-26	1.65E-39
52	4.18	7.5	19.12	0.2	0.6	3.31E-10	7.22E-14	1.95E-09	9.23E-07	5.32E-14	5.27E-22	4.33E-15	5.99E-26	1.51E-38
47	5.34	3.5	8.55	2.4	5.8	2.69E-09	2.31E-12	1.95E-08	9.03E-07	7.53E-13	1.08E-19	8.85E-13	2.56E-21	1.34E-31
48	5.47	3.2	7.88	2.9	7.1	3.43E-09	3.29E-12	2.35E-08	8.98E-07	1.01E-12	1.95E-19	1.60E-12	8.43E-21	8.05E-31
50	5.63	4.2	10.29	3.6	8.9	4.64E-09	5.05E-12	2.89E-08	8.92E-07	1.45E-12	4.05E-19	3.32E-12	3.65E-20	7.29E-30
53	6.94	12.8	34.71	11.3	29.9	5.09E-08	1.56E-10	5.32E-08	8.20E-07	2.72E-11	1.55E-16	1.27E-09	5.83E-15	4.86E-22
54	7.35	17.9	51.49	15.9	44.7	9.53E-08	4.55E-10	5.16E-08	7.70E-07	6.57E-11	9.62E-16	7.90E-09	2.39E-13	1.32E-19
55	7.73	25.3	79.89	21.4	64.1	1.50E-07	1.18E-09	4.66E-08	6.87E-07	1.41E-10	4.94E-15	4.06E-08	7.07E-12	2.24E-17
56	8.14	29.7	99.65	23.9	74.3	1.84E-07	2.80E-09	3.45E-08	5.06E-07	2.66E-10	2.40E-14	1.97E-07	2.28E-10	4.78E-15
57	8.45	27.8	90.65	17.9	51.3	1.42E-07	3.88E-09	1.97E-08	2.88E-07	3.09E-10	5.71E-14	4.69E-07	2.26E-09	1.99E-13
58	8.67	23.9	74.22	10.7	28.4	8.55E-08	3.75E-09	1.02E-08	1.49E-07	2.65E-10	8.13E-14	6.68E-07	8.90E-09	2.18E-12
59	8.96	19.1	55.57	3.9	9.5	3.01E-08	2.68E-09	3.24E-09	4.70E-08	1.63E-10	9.75E-14	8.01E-07	4.11E-08	3.91E-11
60	9.21	14.3	39.23	1.2	3.0	8.90E-09	1.63E-09	9.94E-10	1.43E-08	8.78E-11	9.39E-14	7.71E-07	1.28E-07	4.04E-10
61	9.55	14.1	38.75	0.2	0.4	8.23E-10	5.43E-10	1.38E-10	1.89E-09	2.50E-11	5.95E-14	4.89E-07	4.25E-07	7.70E-09

Note: the data point numbers are the same as those provided by the TDT, but the data have been sorted by pH-ascending

9/10/2002

Neptunium sorption data

Neptunium 9.46E-07 M

I = 0.1 M NaNO3

CO2-free (glove box)

Montmorillonite: 4.2 g/L

INSERT MODEL OUTPUT IN THIS SECTION

(only include species comprising greater than 0.1% of the total Np concentration).

Data point number	pH	% adsorbed	Kd (mL/g)	Calculated % Np adsorbed	Calculated Kd (mL/g)	Calculated concentrations of all surface species Modeling team to label these columns: >xoh-npo2+ (M)	>xo-npo2oh- (M)	xnpo2 (IE) (M)	Calculated concentrations of all Np aqueous species Modeling team to label these columns: npo2+ (M)	npo2oh (M)	npo2(oh)2- (M)
62	5.46	3.9	9.91	2.8	7.0	3.41E-09	3.24E-12	2.35E-08	9.19E-07	1.01E-12	1.91E-19
63	5.52	4.3	10.75	3.1	7.6	3.82E-09	3.81E-12	2.55E-08	9.17E-07	1.16E-12	2.51E-19
64	5.84	4.8	12.08	4.6	11.4	6.98E-09	8.91E-12	3.63E-08	9.03E-07	2.38E-12	1.08E-18
65	5.96	5.5	14.07	5.2	12.9	8.76E-09	1.22E-11	4.00E-08	8.97E-07	3.12E-12	1.86E-18
66	6.26	6.2	15.91	6.6	16.9	1.54E-08	2.68E-11	4.75E-08	8.83E-07	6.13E-12	7.30E-18
67	6.64	8.3	22.09	8.8	23.1	3.08E-08	7.23E-11	5.27E-08	8.62E-07	1.44E-11	4.10E-17
68	7.14	11.7	31.75	13.2	36.4	7.13E-08	2.69E-10	5.38E-08	8.21E-07	4.32E-11	3.90E-16
69	7.56	15.5	43.50	19.2	56.6	1.30E-07	8.06E-10	5.12E-08	7.64E-07	1.06E-10	2.51E-15
70	7.90	23.0	72.66	25.5	81.3	1.91E-07	1.95E-09	4.75E-08	7.05E-07	2.13E-10	1.11E-14
71	8.27	33.1	118.19	32.8	116.3	2.63E-07	5.06E-09	4.30E-08	6.35E-07	4.51E-10	5.49E-14
72	8.47	36.5	135.21	36.5	137.1	2.97E-07	8.45E-09	4.06E-08	6.00E-07	6.74E-10	1.30E-13
73	8.48	36.5	136.03	36.7	138.2	2.98E-07	8.68E-09	4.05E-08	5.98E-07	6.88E-10	1.36E-13
74	8.48	36.1	134.19	36.7	138.2	2.98E-07	8.68E-09	4.05E-08	5.98E-07	6.88E-10	1.36E-13
75	8.50	37.2	137.75	37.1	140.3	3.01E-07	9.13E-09	4.03E-08	5.95E-07	7.17E-10	1.48E-13
76	8.52	36.7	138.93	37.4	142.3	3.04E-07	9.61E-09	4.00E-08	5.91E-07	7.46E-10	1.62E-13
77	8.52	39.1	150.40	37.4	142.3	3.04E-07	9.61E-09	4.00E-08	5.91E-07	7.46E-10	1.62E-13
78	8.53	37.3	139.31	37.6	143.4	3.06E-07	9.87E-09	3.99E-08	5.90E-07	7.62E-10	1.69E-13
79	8.61	38.9	149.81	38.9	151.6	3.17E-07	1.21E-08	3.91E-08	5.77E-07	8.96E-10	2.39E-13
80	8.63	38.7	149.65	39.2	153.6	3.19E-07	1.28E-08	3.89E-08	5.74E-07	9.34E-10	2.61E-13
81	8.74	43.2	180.14	40.8	164.3	3.31E-07	1.70E-08	3.79E-08	5.59E-07	1.17E-09	4.21E-13
82	8.98	46.3	204.02	43.6	184.4	3.45E-07	3.16E-08	3.60E-08	5.31E-07	1.93E-09	1.21E-12
83	9.08	47.8	218.21	44.6	191.3	3.45E-07	4.10E-08	3.54E-08	5.22E-07	2.39E-09	1.88E-12
84	9.21	46.3	205.91	45.5	199.0	3.39E-07	5.74E-08	3.47E-08	5.12E-07	3.17E-09	3.36E-12
85	9.50	46.9	210.91	47.5	215.6	2.96E-07	1.20E-07	3.33E-08	4.91E-07	5.91E-09	1.22E-11
86	9.93	53.2	271.10	54.2	281.8	1.74E-07	3.11E-07	2.85E-08	4.20E-07	1.36E-08	7.58E-11

Model output

List all surface reactions in the sorption model and their log K values

Neptunium

Surface reaction	Log K	Describe how log K was determined (fitting data, other source, etc.)
Ion Exchange		
XNa + H+ = XH + Na+	4.57	Montmorillonite titration data of Wanner et al. (1994)
XNa + NpO2+ = XNpO2 + Na+	1.82	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously.
DLM (with EDL)		
XOH + H+ = XOH2+	5.39	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
XOH = XO- + H+	-6.68	Generic surface complexation site from montmorillonite titration data of Wanner et al. (1994)
XOH + NpO2+ = XOHNpO2+	2.20	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously.
XOH + NpO2+ + H2O = XONpO2OH- +2H+	-12.70	FITEQL, Version 2.0 fitting of CNWRA data for NpM1 (Trace CO2) and NpM3 (No CO2). Optimizing for all Np-surface reactions simultaneously.

Note: Site concentrations [T(xoh) and T(xna)] determined by Wanner et al. (1994) were normalized to experimental conditions of CNWRA and Gorgeon data using M/V and CEC ratios For example, T(xoh) = (2.84e-5 mol/g)*(4.20 g/L)*[(120 meq/100g)/108 meq/100g)] = 1.325e-4 mol/L for CNWRA NpM3 (no CO2) experiment.

9/10/2002

Neptunium sorption data for prediction

Gorgeon

Neptunium 1.10E-06 M

INSERT MODEL OUTPUT IN THIS SECTION

(only include species comprising greater than 0.1% of the total Np concentration).

CO2-free

***I* = 0.025 M NaClO4**

				Calculated % Np adsorbed	Calculated Kd (mL/g)	Calculated concentrations of all surface species. Modeling team to label these columns			Calculated concentrations of all Np aqueous species. Modeling team to label these columns		
	Montmorillonite:		**8.7 g/L**			>xoh-npo2+	>xo-npo2oh-	xnpo2 (IE)	npo2+	npo2oh	npo2(oh)2-
Data point number	**pH**	**% adsorbed**	**Kd (mL/g)**			(M)	(M)	(M)	(M)	(M)	(M)
87	2.63	7.71	9.33	0.0	0.0	4.04E-11	1.05E-15	1.38E-10	1.10E-06	2.00E-15	5.02E-25
88	2.63	8.53	10.96	0.0	0.0	4.04E-11	1.05E-15	1.38E-10	1.10E-06	2.00E-15	5.02E-25
89	2.89	12.24	14.79	0.0	0.0	6.41E-11	3.15E-15	2.51E-10	1.10E-06	3.64E-15	1.66E-24
90	3.20	9.39	12.02	0.1	0.1	1.10E-10	1.04E-14	5.13E-10	1.10E-06	7.44E-15	6.93E-24
91	3.25	10.80	14.45	0.1	0.1	1.21E-10	1.25E-14	5.76E-10	1.10E-06	8.35E-15	8.72E-24
92	3.65	10.08	13.18	0.2	0.2	2.43E-10	5.03E-14	1.44E-09	1.10E-06	2.10E-14	5.50E-23
93	3.78	11.38	14.45	0.2	0.2	3.06E-10	7.68E-14	1.95E-09	1.10E-06	2.83E-14	9.99E-23
94	4.12	12.83	17.38	0.4	0.5	5.64E-10	2.21E-13	4.23E-09	1.10E-06	6.17E-14	4.77E-22
95	4.73	12.73	17.38	1.7	2.0	1.76E-09	1.26E-12	1.66E-08	1.08E-06	2.48E-13	7.82E-21
96	4.75	12.33	16.98	1.7	2.0	1.83E-09	1.33E-12	1.74E-08	1.08E-06	2.60E-13	8.57E-21
97	6.40	13.57	18.20	26.0	40.4	4.06E-08	7.06E-11	2.45E-07	8.14E-07	8.75E-12	1.29E-17
98	6.41	12.49	16.98	26.2	40.8	4.13E-08	7.22E-11	2.47E-07	8.12E-07	8.92E-12	1.35E-17
99	7.31	29.43	48.98	43.6	88.9	1.88E-07	5.63E-10	2.91E-07	6.20E-07	5.42E-11	6.48E-16
100	7.38	19.71	29.51	45.1	94.4	2.08E-07	6.60E-10	2.87E-07	6.04E-07	6.20E-11	8.71E-16
101	8.04	52.84	123.03	61.0	179.9	4.53E-07	2.84E-09	2.15E-07	4.29E-07	2.01E-10	1.29E-14
102	8.84	54.50	131.83	77.7	399.4	7.14E-07	1.56E-08	1.25E-07	2.45E-07	7.25E-10	2.94E-13
103	9.18	58.18	154.88	81.7	513.3	7.63E-07	3.35E-08	1.02E-07	2.00E-07	1.30E-09	1.15E-12
104	10.34	69.71	263.03	87.3	789.4	4.02E-07	4.93E-07	6.52E-08	1.28E-07	1.20E-08	1.53E-10
105	10.73	78.31	426.58	91.0	1166.6	1.47E-07	8.13E-07	4.07E-08	7.98E-08	1.83E-08	5.77E-10
106	10.86	81.29	478.63	92.3	1385.3	9.38E-08	8.89E-07	3.25E-08	6.37E-08	1.97E-08	8.38E-10
107	10.90	86.11	741.31	92.7	1462.8	8.09E-08	9.09E-07	3.02E-08	5.91E-08	2.01E-08	9.35E-10
108	10.97	88.64	891.25	93.3	1609.3	6.18E-08	9.39E-07	2.64E-08	5.16E-08	2.06E-08	1.13E-09
109	11.07	90.56	1071.52	94.1	1837.7	4.13E-08	9.72E-07	2.15E-08	4.21E-08	2.11E-08	1.46E-09
110	11.13	92.52	1445.44	94.5	1983.6	3.22E-08	9.89E-07	1.90E-08	3.72E-08	2.14E-08	1.70E-09

***I* = 0.1 M NaClO4**

	Montmorillonite:		**8.7 g/L**								
Data point number	**pH**	**% adsorbed**	**Kd (mL/g)**								
111	2.61	5.84	7.4	0.0	0.0	4.50E-11	2.09E-16	1.20E-10	1.10E-06	1.71E-15	4.55E-25
112	2.64	6.55	7.9	0.0	0.0	4.77E-11	2.45E-16	1.29E-10	1.10E-06	1.83E-15	5.23E-25
113	3.07	5.30	6.6	0.0	0.0	1.08E-10	1.98E-15	3.46E-10	1.10E-06	4.92E-15	3.79E-24
114	3.07	9.59	12.6	0.0	0.0	1.08E-10	1.98E-15	3.46E-10	1.10E-06	4.92E-15	3.79E-24
115	3.08	5.90	6.5	0.0	0.0	1.10E-10	2.07E-15	3.54E-10	1.10E-06	5.04E-15	3.97E-24
116	3.39	5.71	7.2	0.1	0.1	1.92E-10	7.86E-15	7.20E-10	1.10E-06	1.03E-14	1.65E-23
117	3.45	6.14	7.4	0.1	0.1	2.14E-10	1.00E-14	8.26E-10	1.10E-06	1.18E-14	2.18E-23
118	3.67	8.49	11.0	0.2	0.2	3.15E-10	2.38E-14	1.37E-09	1.10E-06	1.96E-14	6.00E-23
119	3.67	5.21	6.6	0.2	0.2	3.15E-10	2.38E-14	1.37E-09	1.10E-06	1.96E-14	6.00E-23
120	4.16	8.84	11.2	0.4	0.5	7.38E-10	1.38E-13	4.12E-09	1.10E-06	6.03E-14	5.71E-22
121	4.28	6.57	8.1	0.6	0.7	9.09E-10	2.06E-13	5.38E-09	1.09E-06	7.94E-14	9.91E-22
122	4.62	7.31	9.3	1.2	1.4	1.65E-09	6.08E-13	1.12E-08	1.09E-06	1.73E-13	4.71E-21
123	4.87	6.91	8.7	1.9	2.3	2.57E-09	1.29E-12	1.86E-08	1.08E-06	3.05E-13	1.48E-20
124	5.58	9.17	12.0	6.2	7.5	9.21E-09	9.37E-12	5.85E-08	1.03E-06	1.50E-12	3.72E-19
125	5.85	12.20	15.8	8.4	10.5	1.50E-08	1.91E-11	7.69E-08	1.01E-06	2.72E-12	1.26E-18
126	6.58	28.25	44.7	14.7	19.8	5.54E-08	1.28E-10	1.06E-07	9.38E-07	1.36E-11	3.38E-17
127	6.63	23.40	35.5	15.2	20.6	6.03E-08	1.46E-10	1.07E-07	9.33E-07	1.52E-11	4.23E-17
128	7.36	34.23	58.9	25.9	40.1	1.82E-07	9.57E-10	1.02E-07	8.15E-07	7.12E-11	1.07E-15
129	7.71	35.69	61.7	33.3	57.4	2.71E-07	2.32E-09	9.27E-08	7.34E-07	1.43E-10	4.81E-15
130	8.1	50.92	117.5	42.1	83.7	3.77E-07	6.13E-09	8.09E-08	6.36E-07	3.05E-10	2.52E-14
131	9.92	79.43	436.5	67.1	234.0	2.07E-07	4.86E-07	4.48E-08	3.51E-07	1.11E-08	6.06E-11
132	9.96	79.93	446.7	68.1	245.9	1.89E-07	5.18E-07	4.32E-08	3.39E-07	1.18E-08	7.03E-11
133	10.41	86.24	741.3	81.8	517.9	4.81E-08	8.29E-07	2.32E-08	1.82E-07	1.78E-08	3.00E-10
134	10.51	88.07	831.8	84.5	625.9	3.31E-08	8.77E-07	1.94E-08	1.52E-07	1.87E-08	3.96E-10
135	10.67	91.59	1230.3	88.1	847.4	1.75E-08	9.37E-07	1.42E-08	1.11E-07	1.98E-08	6.06E-10
136	10.85	91.64	1258.9	91.1	1174.2	8.26E-09	9.84E-07	9.76E-09	7.65E-08	2.06E-08	9.56E-10
137	11.18	96.59	3388.4	94.4	1947.4	1.94E-09	1.03E-06	4.76E-09	3.73E-08	2.15E-08	2.13E-09
138	11.21	96.43	3162.3	94.6	2033.3	1.70E-09	1.04E-06	4.45E-09	3.48E-08	2.15E-08	2.29E-09

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| DLM with EDL | | gas phase | | |

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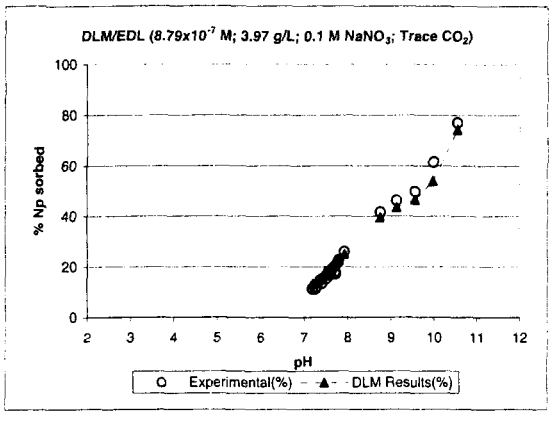
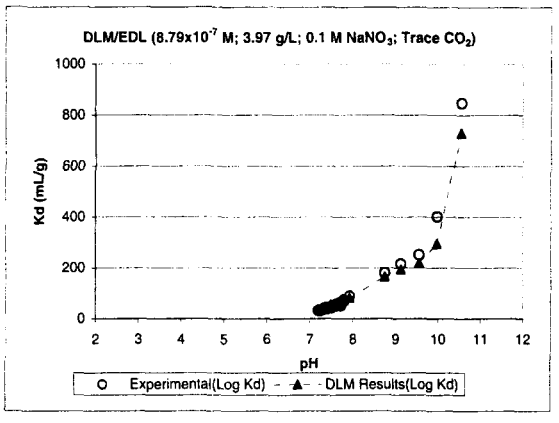
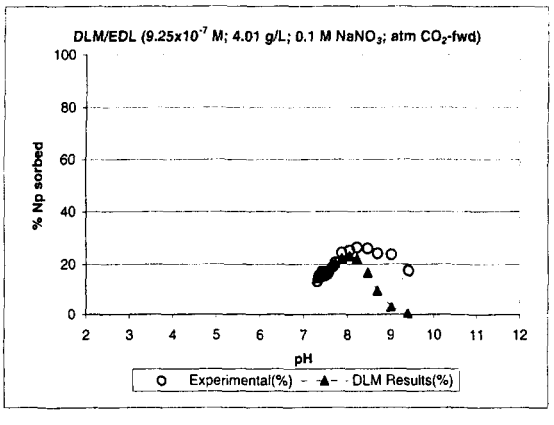
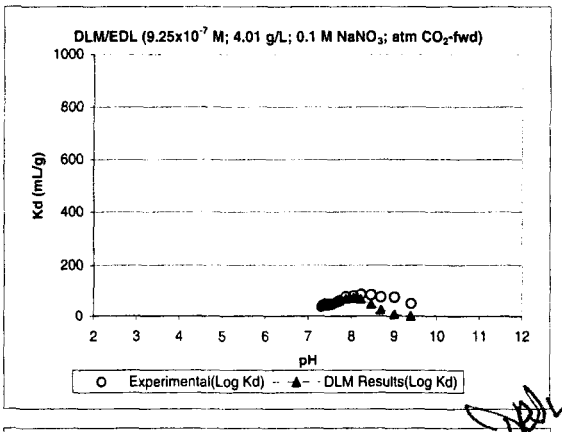
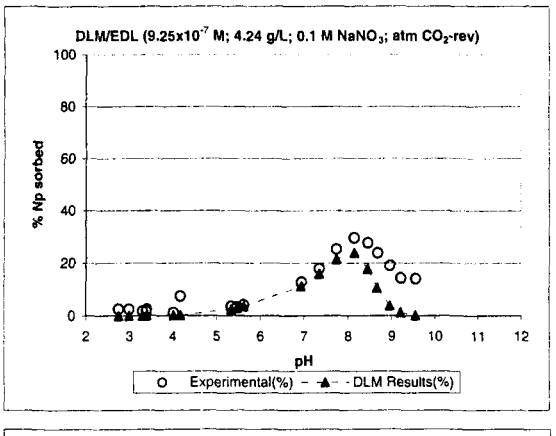
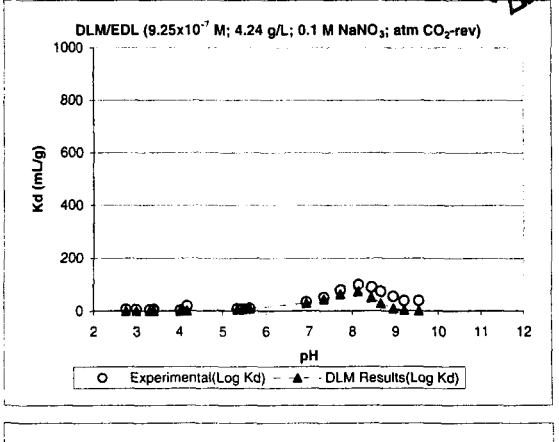

DLM/EDL (8.79x10^{-7} M; 3.97 g/L; 0.1 M $NaNO_3$; Trace CO_2)
% Np sorbed
pH
Experimental(%)
DLM Results(%)

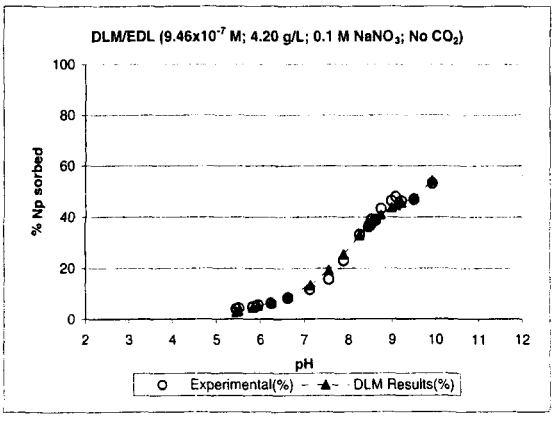

DLM/EDL (8.79x10^{-7} M; 3.97 g/L; 0.1 M $NaNO_3$; Trace CO_2)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)

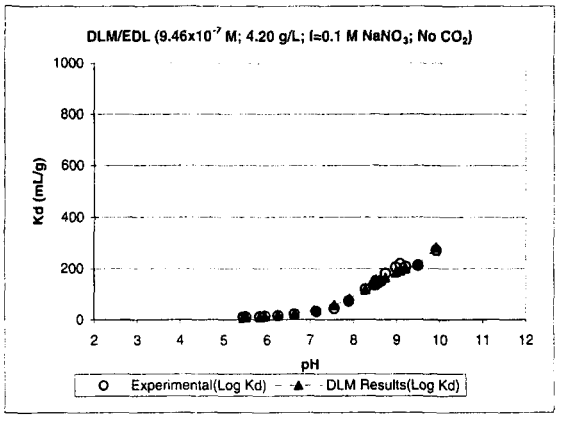

DLM/EDL (9.25x10^{-7} M; 4.01 g/L; 0.1 M $NaNO_3$; atm CO_2-fwd)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.25x10^{-7} M; 4.01 g/L; 0.1 M $NaNO_3$; atm CO_2-fwd)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)


DLM/EDL (9.25x10^{-7} M; 4.24 g/L; 0.1 M $NaNO_3$; atm CO_2-rev)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.25x10^{-7} M; 4.24 g/L; 0.1 M $NaNO_3$; atm CO_2-rev)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)


DLM/EDL (9.46x10^{-7} M; 4.20 g/L; 0.1 M $NaNO_3$; No CO_2)
% Np sorbed
pH
Experimental(%)
DLM Results(%)


DLM/EDL (9.46x10^{-7} M; 4.20 g/L; I=0.1 M $NaNO_3$; No CO_2)
Kd (mL/g)
pH
Experimental(Log Kd)
DLM Results(Log Kd)

| SLB with BBL Gorgeon Np-Mont data | | gas phase | | |

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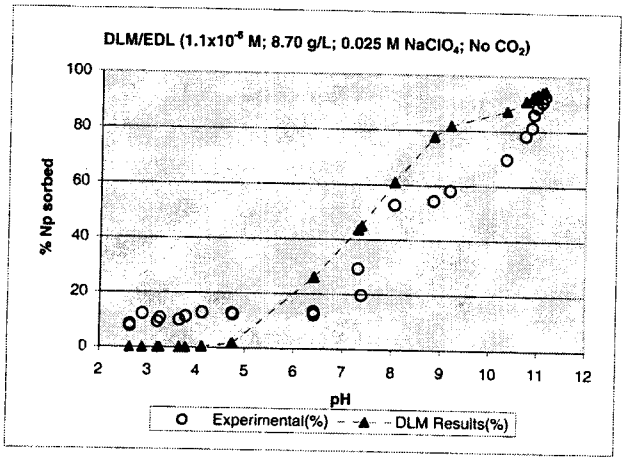
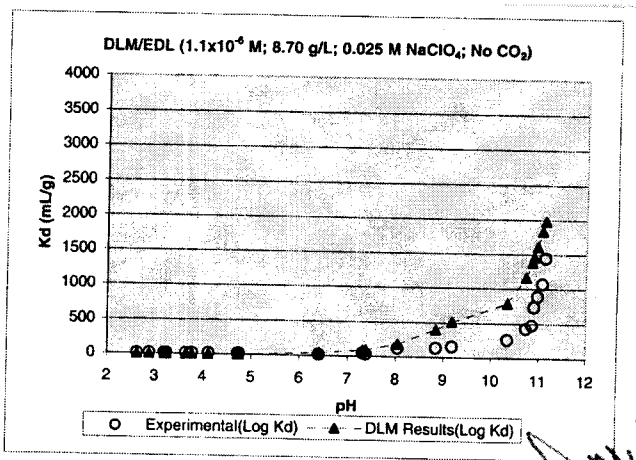
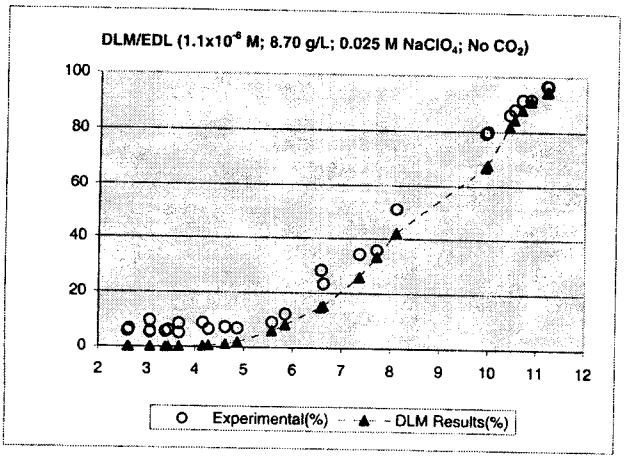
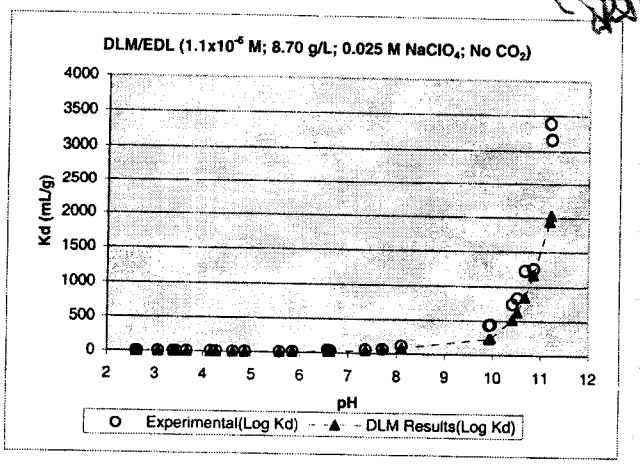
DRJ









DRJ 9/10/2002

Diffuse Layer Model using LogK(xohnpo2+), LogK(xonpo2oh-), and LogK(xnpo2) as fitting parameters

Mineral	Reference	Electrolyte	I.S.	LogK(xohnpo2+)	sig K(xohnpo2+)	LogK(xonpo2oh-)	sig K(xonpo2oh-)	LogK(xnpo2)	sig K(xnpo2)	SOS/DF
Montmorillonite	Trace CO2 (NpM1)	NaNO3	0.1000	2.24	0.0480	-12.65	0.1136	1.43	3.09E-01	0.6329
	No CO2 (NpM3)	NaNO3	0.1000	2.18	0.0250	-12.75	0.1310	1.85	3.06E-02	0.7768

Mineral	um 1/sigK(xohnpo2	w.f.	wf*Log K(xohnpo2+	LogK(xohnpo2+)	um 1/sigK(xonpo2oh	w.f.	wf*LogK(xonpo2oh-	LogK(xonpo2oh-)	sum 1/sigK(xnpo2)	w.f.	wf*LogK(xnpo2)	LogK(xnpo2)
Montmorillonite	60.85	0.342653509	0.77	**2.20**	16.44	0.535568275	-6.77	**-12.70**	35.91	0.090052972	0.128595644	**1.82**
		0.657346491	1.43			0.464431725	-5.92			0.909947028	1.687041789	

LogK(xohnpo2+) sum wf*diff^2	LogK(xohnpo2+) Sx^2	LogK(xohnpo2+) conf lim (95%)	LogK(xonpo2oh-) sum wf*diff	LogK(xonpo2oh-) Sx^2	LogK(xonpo2oh-) conf lim (95%)	K(xnpo2) sum wf*diff	K(xnpo2) Sx^2	K(xnpo2) conf lim (95%)
0.000515404	0.000784068	**0.25**	0.001155204	0.002487349	**0.45**	0.01353161	0.014870767	**1.10**
0.000268664			0.001332145			0.001339157		

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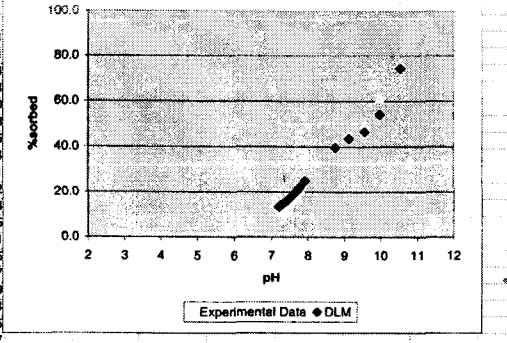
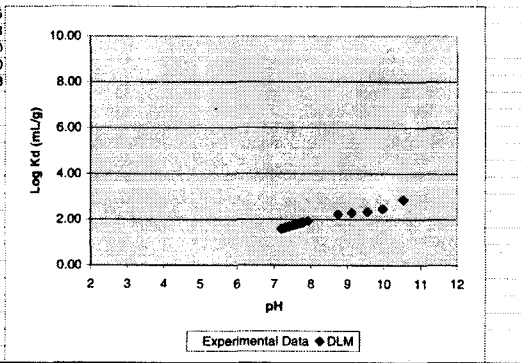
	pH	xoh-npo2	xo-npo2oh-	xoh2npo2co3	xnpo2	%sorbed	Kd	Log Kd	Experimental Data pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
1	7.20	6.91E-08	2.78E-10	0.00E+00	4.74E-08	13.3	38.6	1.59	7.20	9.98E-08	11.4	32.4	1.51
2	7.27	7.68E-08	3.34E-10	0.00E+00	4.72E-08	14.1	41.5	1.62	7.27	9.92E-08	11.3	32.3	1.51
3	7.30	8.03E-08	3.62E-10	0.00E+00	4.70E-08	14.5	42.8	1.63	7.30	1.07E-07	12.2	35.0	1.54
4	7.37	8.89E-08	4.35E-10	0.00E+00	4.67E-08	15.5	46.1	1.66	7.37	1.29E-07	14.7	43.6	1.64
5	7.42	9.53E-08	4.96E-10	0.00E+00	4.64E-08	16.2	48.6	1.69	7.42	1.19E-07	13.5	39.6	1.60
6	7.62	1.24E-07	8.37E-10	0.00E+00	4.49E-08	19.3	60.3	1.78	7.62	1.64E-07	18.7	57.8	1.76
7	7.52	1.09E-07	6.44E-10	0.00E+00	4.57E-08	17.7	54.1	1.73	7.52	1.34E-07	15.3	45.1	1.65
8	7.70	1.37E-07	1.03E-09	0.00E+00	4.43E-08	20.7	65.8	1.82	7.70	1.56E-07	17.8	54.8	1.74
9	7.61	1.23E-07	8.16E-10	0.00E+00	4.50E-08	19.2	59.7	1.78	7.61	1.49E-07	17.0	51.1	1.71
10	7.73	1.42E-07	1.12E-09	0.00E+00	4.40E-08	21.2	67.9	1.83	7.73	1.52E-07	17.3	52.1	1.72
11	7.56	1.15E-07	7.16E-10	0.00E+00	4.54E-08	18.3	56.5	1.75	7.56	1.58E-07	17.9	55.2	1.74
12	7.62	1.24E-07	8.37E-10	0.00E+00	4.49E-08	19.3	60.3	1.78	7.62	1.59E-07	18.1	55.6	1.75
13	7.60	1.21E-07	7.94E-10	0.00E+00	4.51E-08	19.0	59.0	1.77	7.60	1.48E-07	16.8	51.0	1.71
14	7.62	1.24E-07	8.37E-10	0.00E+00	4.49E-08	19.3	60.3	1.78	7.62	1.61E-07	18.3	55.8	1.75
15	7.64	1.27E-07	8.82E-10	0.00E+00	4.48E-08	19.7	61.7	1.79	7.64	1.67E-07	19.0	59.0	1.77
16	7.68	1.34E-07	9.79E-10	0.00E+00	4.44E-08	20.4	64.4	1.81	7.68	1.73E-07	19.7	61.4	1.79
17	7.76	1.47E-07	1.21E-09	0.00E+00	4.37E-08	21.8	70.1	1.85	7.76	1.89E-07	21.5	68.8	1.84
18	7.93	1.76E-07	1.88E-09	0.00E+00	4.20E-08	25.0	83.8	1.92	7.93	2.28E-07	26.0	89.0	1.95
19	7.80	1.53E-07	1.34E-09	0.00E+00	4.33E-08	22.5	73.2	1.86	7.80	2.00E-07	22.7	74.5	1.87
20	8.75	2.98E-07	1.56E-08	0.00E+00	3.39E-08	39.6	165.0	2.22	8.75	3.66E-07	41.6	179.7	2.25
21	9.13	3.09E-07	4.20E-08	0.00E+00	3.16E-08	43.5	194.1	2.29	9.13	4.07E-07	46.3	215.6	2.33
22	9.56	2.55E-07	1.25E-07	0.00E+00	2.96E-08	46.6	219.5	2.34	9.56	4.38E-07	49.8	252.6	2.40
23	9.98	1.42E-07	3.08E-07	0.00E+00	2.49E-08	54.0	296.3	2.47	9.98	5.41E-07	61.5	401.3	2.60
24	10.54	2.89E-08	6.12E-07	0.00E+00	1.27E-08	74.3	729.9	2.86	10.54	6.77E-07	77.0	847.8	2.93

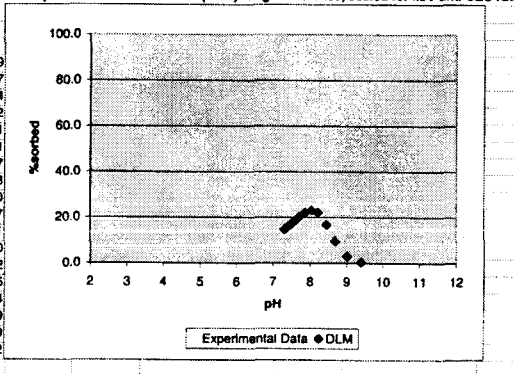


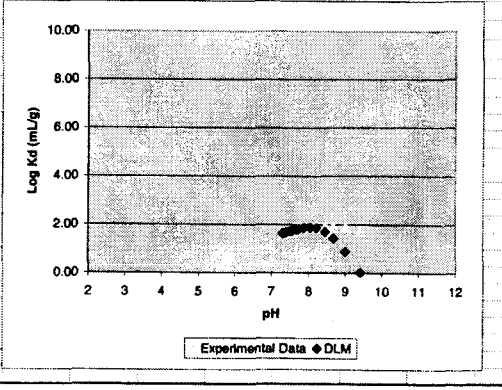


CNWRA
Np-montmorillonite
Trace CO_2 (capped vials)

Np(total)(M) 9.25E-07 Log K based on weighted averages of simultaneously fitting LogK(xohnpo2), LogK(xonpo2oh-), and LogK(xnpo2) for experiments NpM1 (Trace CO2) and NpM3 (no CO2). Site concentrations and site equilibria from Wanner et al (1994) for generic sites, scaled for M/V and CEC ratios
M/V(g/L) 4.01 LogK(xohnpo2)=2.20 LogK(xonpo2oh-)=-1:LogK(xnpo2)=1.82

	pH	xoh-npo2	xo-npo2oh-	xoh2npo2co3	xnpo2	%sorbed	Kd(mL/g)	LogKd	Experimental Data pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
25	7.31	8.59E-08	3.91E-10	0.00E+00	4.95E-08	14.7	42.9	1.63	7.31	1.23E-07	13.3	38.75	1.59
26	7.34	8.96E-08	4.23E-10	0.00E+00	4.93E-08	15.1	44.2	1.65	7.34	1.44E-07	15.6	46.36	1.67
27	7.38	9.47E-08	4.69E-10	0.00E+00	4.90E-08	15.6	46.1	1.66	7.38	1.38E-07	15.0	43.76	1.64
28	7.41	9.87E-08	5.07E-10	0.00E+00	4.87E-08	16.0	47.5	1.68	7.41	1.59E-07	17.1	52.05	1.72
29	7.48	1.08E-07	6.07E-10	0.00E+00	4.81E-08	16.9	50.9	1.71	7.48	1.58E-07	17.0	51.29	1.71
30	7.51	1.12E-07	6.55E-10	0.00E+00	4.77E-08	17.4	52.4	1.72	7.51	1.57E-07	17.0	51.69	1.71
31	7.48	1.08E-07	6.07E-10	0.00E+00	4.81E-08	16.9	50.9	1.71	7.48	1.44E-07	15.6	46.26	1.67
32	7.54	1.17E-07	7.06E-10	0.00E+00	4.74E-08	17.8	54.0	1.73	7.54	1.49E-07	16.1	48.03	1.68
33	7.56	1.19E-07	7.43E-10	0.00E+00	4.72E-08	18.1	55.1	1.74	7.56	1.54E-07	16.6	49.59	1.70
34	7.67	1.35E-07	9.78E-10	0.00E+00	4.56E-08	19.6	61.0	1.78	7.67	1.76E-07	19.0	58.50	1.77
35	7.72	1.42E-07	1.10E-09	0.00E+00	4.48E-08	20.3	63.6	1.80	7.72	1.91E-07	20.6	64.37	1.81
36	7.87	1.61E-07	1.57E-09	0.00E+00	4.17E-08	22.1	70.8	1.85	7.87	2.25E-07	24.3	79.69	1.90
37	8.05	1.76E-07	2.29E-09	0.00E+00	3.64E-08	23.2	75.2	1.88	8.05	2.33E-07	25.1	83.29	1.92
38	8.22	1.72E-07	3.03E-09	0.00E+00	2.97E-08	22.2	71.1	1.85	8.22	2.44E-07	26.4	88.85	1.95
39	8.46	1.33E-07	3.72E-09	0.00E+00	1.84E-08	16.8	50.2	1.70	8.46	2.40E-07	26.0	86.54	1.94
40	8.69	7.66E-08	3.52E-09	0.00E+00	9.05E-09	9.6	26.6	1.42	8.69	2.23E-07	24.1	78.47	1.89
41	9.01	2.29E-08	2.34E-09	0.00E+00	2.45E-09	3.0	7.7	0.89	9.01	2.19E-07	23.6	78.19	1.89
42	9.40	2.56E-09	9.07E-10	0.00E+00	3.34E-10	0.4	1.0	0.01	9.40	1.62E-07	17.5	52.50	1.72





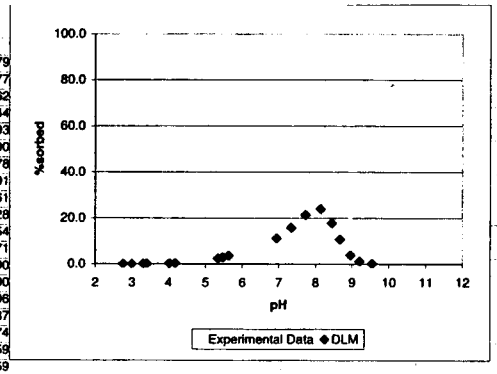
CNWRA
Np-montmorillonite
Atmospheric $10^{-3.5}$ atm PCO_2
Forward

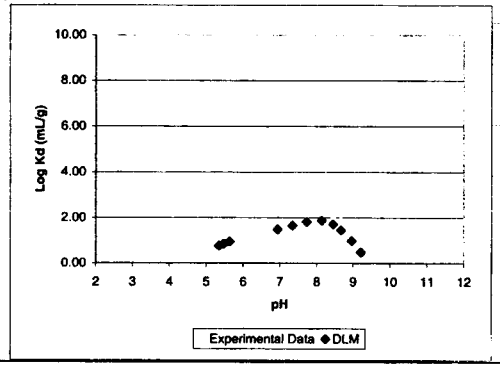
M/V(g/L) 4.24 LogK(xohnpo2)=2.20 LogK(xonpo2oh-)=-1: LogK(xnpo2)=1.82

pH	xoh-npo2	xo-npo2oh-	xoh2npo2co3	xnpo2	%sorbed	Kd	Log Kd
43	2.76	2.63E-11	2.53E-16	0.00E+00	7.65E-11	0.0	0.0
44	3.00	4.12E-11	7.80E-16	0.00E+00	1.33E-10	0.0	0.0
45	3.31	7.22E-11	2.96E-15	0.00E+00	2.71E-10	0.0	0.1
46	4.02	2.50E-10	4.21E-14	0.00E+00	1.36E-09	0.2	0.4
47	5.34	2.69E-09	2.31E-12	0.00E+00	1.95E-08	2.4	5.8
48	5.47	3.43E-09	3.29E-12	0.00E+00	2.35E-08	2.9	7.1
49	3.41	8.62E-11	4.43E-15	0.00E+00	3.40E-10	0.0	0.1
50	5.63	4.64E-09	5.05E-12	0.00E+00	2.89E-08	3.6	8.9
51	3.40	8.47E-11	4.26E-15	0.00E+00	3.33E-10	0.0	0.1
52	4.18	3.31E-10	7.22E-14	0.00E+00	1.95E-09	0.2	0.8
53	6.94	5.09E-08	1.56E-10	0.00E+00	5.32E-08	11.3	29.9
54	7.35	9.53E-08	4.55E-10	0.00E+00	5.16E-08	15.9	44.7
55	7.73	1.50E-07	1.18E-09	0.00E+00	4.66E-08	21.4	64.1
56	8.14	1.84E-07	2.80E-09	0.00E+00	3.45E-08	23.9	74.3
57	8.45	1.42E-07	3.88E-09	0.00E+00	1.97E-08	17.9	51.3
58	8.67	8.55E-08	3.75E-09	0.00E+00	1.02E-08	10.7	28.4
59	8.96	3.01E-08	2.68E-09	0.00E+00	3.24E-09	3.9	9.5
60	9.21	8.90E-09	1.63E-09	0.00E+00	9.94E-10	1.2	3.0
61	9.55	8.23E-10	5.43E-10	0.00E+00	1.38E-10	0.2	0.4

Experimental Data

pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
2.76	2.35E-08	2.5	6.15	0.79
3.00	2.24E-08	2.4	5.86	0.77
3.31	1.60E-08	1.7	4.16	0.62
4.02	1.06E-08	1.1	2.74	0.44
5.34	3.24E-08	3.5	8.55	0.93
5.47	2.99E-08	3.2	7.88	0.90
3.41	2.28E-08	2.5	5.97	0.78
5.63	3.87E-08	4.2	10.29	1.01
3.40	1.58E-08	1.7	4.11	0.61
4.18	6.94E-08	7.5	19.12	1.28
6.94	1.19E-07	12.8	34.71	1.54
7.35	1.66E-07	17.9	51.49	1.71
7.73	2.34E-07	25.3	79.89	1.90
8.14	2.75E-07	29.7	99.65	2.00
8.45	2.57E-07	27.8	90.65	1.96
8.67	2.21E-07	23.9	74.22	1.87
8.96	1.76E-07	19.1	55.57	1.74
9.21	1.32E-07	14.3	39.23	1.59
9.55	1.31E-07	14.1	38.75	1.59





CNWRA Data
Np-Montmorillonite
Atmospheric $P_{CO_2} = 10^{-3.5}$
Reverse

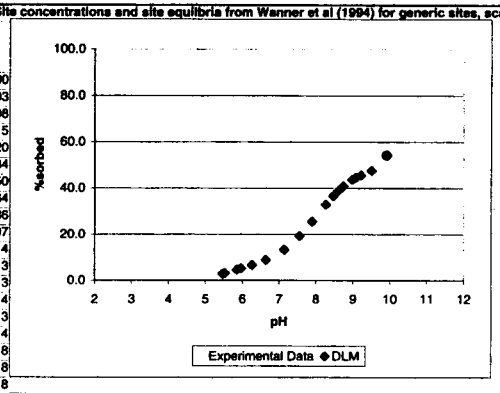
Np(total)(M) 9.46E-07 Log K based on weighted averages of simultaneously fitting LogK(xohnpo2), LogK(xonpo2oh-), and LogK(xnpo2) for experiments NpM1 (Trace CO2) and NpM3 (no CO2). Site concentrations and site equilibria from Wanner et al (1994) for generic sites, scaled for M/V and CEC ratios

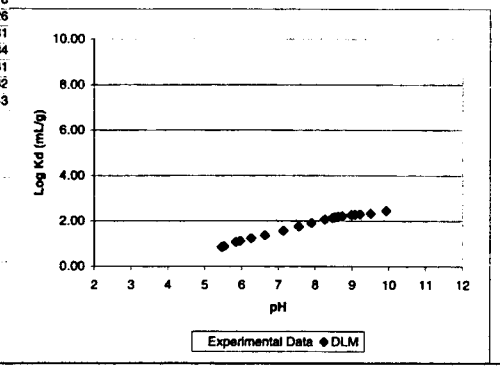
M/V(g/L) 4.20 LogK(xohnpo2)=2.20 LogK(xonpo2oh-)=-1: LogK(xnpo2)=1.82

pH	xoh-npo2	xo-npo2oh-	xnpo2	%sorbed	Kd	Log Kd
62	5.46	3.41E-09	3.24E-12	2.35E-08	2.8	7.0
63	5.52	3.82E-09	3.81E-12	2.55E-08	3.1	7.6
64	5.84	6.98E-09	8.91E-12	3.63E-08	4.6	11.4
65	5.96	8.76E-09	1.22E-11	4.00E-08	5.2	12.9
66	6.26	1.54E-08	2.68E-11	4.75E-08	6.6	16.9
67	6.64	3.08E-08	7.23E-11	5.27E-08	8.8	23.1
68	7.14	7.13E-08	2.69E-10	5.38E-08	13.2	36.4
69	7.56	1.30E-07	8.06E-10	5.12E-08	19.2	56.6
70	7.90	1.91E-07	1.95E-09	4.75E-08	25.5	81.3
71	8.27	2.63E-07	5.06E-09	4.30E-08	32.8	116.3
72	8.50	3.01E-07	9.13E-09	4.03E-08	37.1	140.3
73	8.48	2.98E-07	8.68E-09	4.05E-08	36.7	138.2
74	8.48	2.98E-07	8.68E-09	4.05E-08	36.7	138.2
75	8.52	3.04E-07	9.61E-09	4.00E-08	37.4	142.3
76	8.47	2.97E-07	8.45E-09	4.06E-08	36.5	137.1
77	8.53	3.06E-07	9.87E-09	3.99E-08	37.6	143.4
78	8.63	3.19E-07	1.28E-08	3.89E-08	39.2	153.6
79	8.61	3.17E-07	1.21E-08	3.91E-08	38.9	151.6
80	8.52	3.04E-07	9.61E-09	4.00E-08	37.4	142.3
81	8.74	3.31E-07	1.70E-08	3.79E-08	40.8	164.3
82	8.98	3.45E-07	3.16E-08	3.60E-08	43.6	184.4
83	9.08	3.45E-07	4.10E-08	3.54E-08	44.6	191.3
84	9.21	3.39E-07	5.74E-08	3.47E-08	45.5	199.0
85	9.50	2.96E-07	1.20E-07	3.33E-08	47.5	215.6
86	9.93	1.74E-07	3.11E-07	2.85E-08	54.2	281.8

Experimental Data

pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
5.46	3.70E-08	3.9	9.91	1.00
5.52	4.04E-08	4.3	10.75	1.03
5.84	4.59E-08	4.8	12.08	1.08
5.96	5.21E-08	5.5	14.07	1.15
6.26	5.88E-08	6.2	15.91	1.20
6.64	7.89E-08	8.3	22.09	1.34
7.14	1.10E-07	11.7	31.75	1.50
7.56	1.47E-07	15.5	43.50	1.64
7.90	2.18E-07	23.0	72.66	1.86
8.27	3.13E-07	33.1	118.19	2.07
8.50	3.52E-07	37.2	137.75	2.14
8.48	3.46E-07	36.5	136.03	2.13
8.48	3.42E-07	36.1	134.19	2.13
8.52	3.47E-07	36.7	138.93	2.14
8.47	3.46E-07	36.5	135.21	2.13
8.53	3.53E-07	37.3	139.31	2.14
8.63	3.66E-07	38.7	149.65	2.18
8.61	3.68E-07	38.9	149.81	2.18
8.52	3.70E-07	39.1	150.40	2.18
8.74	4.09E-07	43.2	180.14	2.26
8.98	4.38E-07	46.3	204.02	2.31
9.08	4.52E-07	47.8	218.21	2.34
9.21	4.38E-07	46.3	205.91	2.31
9.50	4.44E-07	46.9	210.91	2.32
9.93	5.03E-07	53.2	271.10	2.43

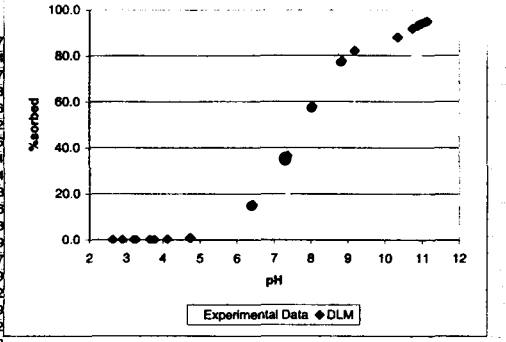


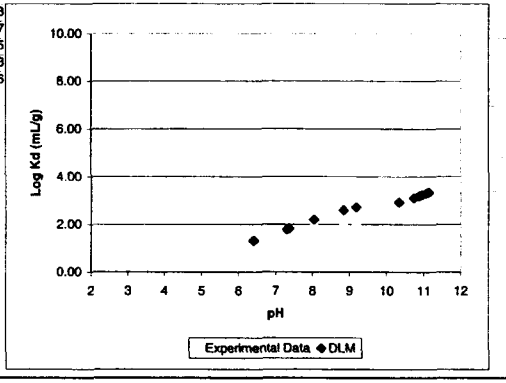


CNWRA
Np-montmorillonite
No CO_2

pH	xo-npo2	xo-npo2oh-	xnpo2	%sorbed	Kd(mL/g)	Log Kd	pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
							Experimental Data				
87	2.63	4.43E-11	1.18E-15	5.62E-11	0.0	0.0	-1.98	2.63	8.48E-08	7.7	9.3	0.97
88	2.63	4.42E-11	1.18E-15	5.62E-11	0.0	0.0	-1.98	2.63	9.38E-08	8.5	11.0	1.04
89	2.89	7.03E-11	3.53E-15	1.02E-10	0.0	0.0	-1.74	2.89	1.35E-07	12.2	14.8	1.17
90	3.20	1.21E-10	1.17E-14	2.09E-10	0.0	0.0	-1.46	3.20	1.03E-07	9.4	12.0	1.08
91	3.25	1.32E-10	1.41E-14	2.35E-10	0.0	0.0	-1.42	3.25	1.19E-07	10.8	14.5	1.16
92	3.65	2.67E-10	5.64E-14	5.89E-10	0.1	0.1	-1.05	3.65	1.11E-07	10.1	13.2	1.12
93	3.78	3.36E-10	8.63E-14	7.93E-10	0.1	0.1	-0.93	3.78	1.25E-07	11.4	14.5	1.16
94	4.12	6.20E-10	2.49E-13	1.73E-09	0.2	0.2	-0.61	4.12	1.41E-07	12.8	17.4	1.24
95	4.73	1.95E-09	1.43E-12	6.83E-09	0.8	0.9	-0.03	4.73	1.40E-07	12.7	17.4	1.24
96	4.75	2.03E-09	1.51E-12	7.14E-09	0.8	1.0	-0.01	4.75	1.36E-07	12.3	17.0	1.23
97	6.40	5.11E-08	9.09E-11	1.15E-07	15.1	20.4	1.31	6.40	1.49E-07	13.6	18.2	1.26
98	6.41	5.20E-08	9.31E-11	1.16E-07	15.2	20.7	1.32	6.41	1.37E-07	12.5	17.0	1.23
99	7.31	2.40E-07	7.35E-10	1.38E-07	34.4	60.3	1.78	7.31	3.24E-07	29.4	49.0	1.69
100	7.38	2.64E-07	8.58E-10	1.36E-07	36.4	65.9	1.82	7.38	2.17E-07	19.7	29.5	1.47
101	8.04	5.37E-07	3.45E-09	9.50E-08	57.8	157.4	2.20	8.04	5.81E-07	52.8	123.0	2.09
102	8.84	7.85E-07	1.76E-08	5.10E-08	77.6	397.4	2.60	8.84	6.00E-07	54.5	131.8	2.12
103	9.18	8.24E-07	3.70E-08	4.09E-08	82.0	522.4	2.72	9.18	6.40E-07	58.2	154.9	2.19
104	10.34	4.18E-07	5.25E-07	2.52E-08	87.9	838.5	2.92	10.34	7.67E-07	69.7	263.0	2.42
105	10.73	1.49E-07	8.44E-07	1.54E-08	91.7	1272.2	3.10	10.73	8.61E-07	78.3	426.6	2.63
106	10.86	9.44E-08	9.16E-07	1.22E-08	93.0	1520.3	3.18	10.86	8.94E-07	81.3	478.6	2.68
107	10.90	8.12E-08	9.34E-07	1.13E-08	93.3	1607.6	3.21	10.90	9.47E-07	86.1	741.3	2.87
108	10.97	6.19E-08	9.61E-07	9.80E-09	93.9	1774.4	3.25	10.97	9.75E-07	88.6	891.3	2.95
109	11.07	4.12E-08	9.92E-07	7.97E-09	94.7	2034.6	3.31	11.07	9.96E-07	90.6	1071.5	3.03
110	11.13	3.20E-08	1.01E-06	7.01E-09	95.0	2184.9	3.34	11.13	1.02E-06	92.5	1445.4	3.16

Gorgeon Data
Np-montmorillonite
No CO_2

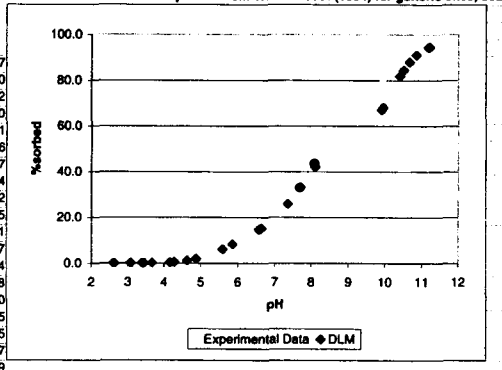


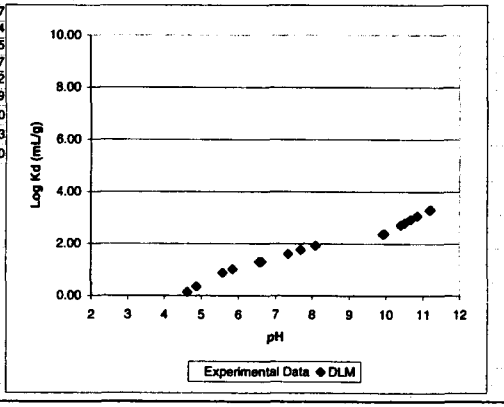


Np(total)(M) 1.10E-06 Log K based on weighted averages of simultaneously fitting LogK(xohnpo2), LogK(xonpo2oh-), and LogK(xnpo2) for experiments NpM1 (Trace CO2) and NpM3 (no CO2). Site concentrations and site equilibria from Wanner et al (1994) for generic sites, scaled for M/V and CEC ratios
M/V(g/L) 8.70 LogK(xohnpo2)=2.20 LogK(xonpo2oh-)=-1; LogK(xnpo2)=1.82

pH	xo-npo2	xo-npo2oh-	xnpo2	%sorbed	Kd(mL/g)	Log Kd	pH	Np Sorbed	%sorb	Kd(mL/g)	Log Kd
							Experimental Data				
111	2.61	4.50E-11	2.09E-16	1.20E-10	0.0	0.0	-1.76	2.61	6.42E-08	5.8	7.4	0.87
112	2.64	4.77E-11	2.45E-16	1.29E-10	0.0	0.0	-1.73	2.64	7.20E-08	6.5	7.9	0.90
113	3.07	1.08E-10	1.98E-15	3.46E-10	0.0	0.0	-1.32	3.07	5.83E-08	5.3	6.6	0.82
114	3.07	1.08E-10	1.98E-15	3.46E-10	0.0	0.0	-1.32	3.07	1.05E-07	9.6	12.6	1.10
115	3.08	1.10E-10	2.07E-15	3.54E-10	0.0	0.0	-1.31	3.08	6.49E-08	5.9	6.5	0.81
116	3.39	1.92E-10	7.86E-15	7.20E-10	0.1	0.1	-1.02	3.39	6.28E-08	5.7	7.2	0.86
117	3.45	2.14E-10	1.00E-14	8.26E-10	0.1	0.1	-0.96	3.45	6.75E-08	6.1	7.4	0.87
118	3.67	3.15E-10	2.38E-14	1.37E-09	0.2	0.2	-0.75	3.67	9.34E-08	8.5	11.0	1.04
119	3.67	3.15E-10	2.38E-14	1.37E-09	0.2	0.2	-0.75	3.67	5.73E-08	5.2	6.6	0.82
120	4.16	7.38E-10	1.38E-13	4.12E-09	0.4	0.5	-0.29	4.16	9.72E-08	8.8	11.2	1.05
121	4.28	9.09E-10	2.06E-13	5.38E-09	0.6	0.7	-0.18	4.28	7.22E-08	6.6	8.1	0.91
122	4.62	1.65E-09	6.08E-13	1.12E-08	1.2	1.4	0.13	4.62	8.04E-08	7.3	9.3	0.97
123	4.87	2.57E-09	1.29E-12	1.86E-08	1.9	2.3	0.35	4.87	7.60E-08	6.9	8.7	0.94
124	5.58	9.21E-09	9.37E-12	5.85E-08	6.2	7.5	0.88	5.58	1.01E-07	9.2	12.0	1.08
125	5.85	1.50E-08	1.91E-11	7.69E-08	8.4	10.5	1.02	5.85	1.34E-07	12.2	15.8	1.20
126	6.58	5.54E-08	1.28E-10	1.06E-07	14.7	19.8	1.30	6.58	3.11E-07	28.2	44.7	1.65
127	6.63	6.03E-08	1.46E-10	1.07E-07	15.2	20.6	1.31	6.63	2.57E-07	23.4	35.5	1.55
128	7.36	1.82E-07	9.57E-10	1.02E-07	25.9	40.1	1.60	7.36	3.77E-07	34.2	58.9	1.77
129	7.71	2.71E-07	2.32E-09	9.27E-08	33.3	57.4	1.76	7.71	3.93E-07	35.7	61.7	1.79
130	8.10	3.77E-07	6.13E-09	8.09E-08	42.1	83.7	1.92	8.1	5.60E-07	50.9	117.5	2.07
131	9.92	2.07E-07	4.86E-07	4.48E-08	67.1	234.0	2.37	9.92	8.74E-07	79.4	436.5	2.64
132	9.96	1.89E-07	5.18E-07	4.32E-08	68.1	245.9	2.39	9.96	8.79E-07	79.9	446.7	2.65
133	10.41	4.81E-08	8.29E-07	2.32E-08	81.8	517.9	2.71	10.41	9.49E-07	86.2	741.3	2.87
134	10.51	3.31E-08	8.77E-07	1.94E-08	84.5	625.9	2.80	10.51	9.69E-07	88.1	831.8	2.92
135	10.67	1.75E-08	9.37E-07	1.42E-08	88.1	847.4	2.93	10.67	1.01E-06	91.8	1230.3	3.09
136	10.85	8.26E-09	9.84E-07	9.76E-09	91.1	1174.2	3.07	10.85	1.008E-06	91.6	1258.9	3.10
137	11.18	1.94E-09	1.03E-06	4.76E-09	94.4	1947.4	3.29	11.18	1.063E-06	96.6	3388.4	3.53
138	11.21	1.70E-09	1.04E-06	4.45E-09	94.6	2033.3	3.31	11.21	1.061E-06	96.4	3162.3	3.50

Gorgeon Data
Np-montmorillonite
No CO_2





4/30/2003

Equation parameters and summary of fit results for model curves at discrete PCO_2. Derived using complete MINTEQA2 generated data setswith polynomial fitting by Microsoft Excel 97. Sorption modeling includes electrostatic DLM with model parameters defined in Turner et al. (2002). Excel files are stored in electronic form on disc in back pocket of this SN

Turner, D.R., F.P. Bertetti, and R.T. Pabalan. 2002. The role of radionuclide sorption in high-level waste performance assessment: Approaches for the abstraction of detailed models. *Soil Science Society of America Proceedings Volume: Soil Geochemical Processes of Radionuclides*. pp. 211–252.

Expressed in terms of $\log_{10}$ ($K_{a'}$, in $mL \cdot m^{-2}$) = $a + bx + cx^2 + dx^3 + ex^4 + fx^5] = \log_{10} (K_d/S_a)$

Am(III)

PCO_2 (atm)	Coefficients: [log ($K_{a'}$, in $mL \cdot m^{-2}$) = $a + bx + cx^2 + dx^3 + ex^4 + fx^5$]						pH range
	a	b	c	d	e	f	
$10^{-0.5}$	307.5900	-200.7300	48.8690	-5.3439	0.2446	-0.0031	5.0 to 9.5
$10^{-1.0}$	-1270.7000	961.1200	-288.7700	43.0520	-3.1737	0.0923	5.0 to 9.5
$10^{-1.5}$	-1045.5000	775.0800	-228.0800	33.2760	-2.3964	0.0679	5.0 to 9.5
$10^{-2.0}$	-529.7000	382.5800	-109.8300	15.6420	-1.0950	0.0299	5.0 to 9.5
$10^{-2.5}$	9.9912	-19.1220	8.4351	-1.5725	0.1437	-0.0053	5.0 to 9.5
$10^{-3.0}$	207.9700	-163.9100	50.2670	-7.5391	0.5634	-0.0169	5.0 to 9.5
$10^{-3.5}$	275.2200	-211.8300	63.6820	-9.3781	0.6861	-0.0200	5.0 to 9.5
$10^{-4.0}$	277.3800	-210.4600	62.2980	-9.0147	0.6465	-0.0185	5.0 to 9.5
$10^{-4.5}$	130.7300	-98.6220	28.5100	-3.9583	0.2715	-0.0074	5.0 to 9.5
$10^{-5.0}$	33.7410	-25.6580	6.7852	-0.7580	0.0381	-0.0007	5.0 to 9.5

Np(V)

PCO_2 (atm)	Coefficients: [log ($K_{a'}$, in $mL \cdot m^{-2}$) = $a + bx + cx^2 + dx^3 + ex^4 + fx^5$]						pH range
	a	b	c	d	e	f	
$10^{-0.5}$	1319.8000	-915.1600	247.7200	-32.7320	2.1136	-0.0535	5.0 to 9.5
$10^{-1.0}$	-1855.4000	1426.2000	-433.6500	65.0770	-4.8121	0.1400	5.0 to 9.5
$10^{-1.5}$	-2608.4000	1941.3000	-570.8700	82.8050	-5.9182	0.1666	5.0 to 9.5
$10^{-2.0}$	-929.3700	667.7500	-188.8300	26.1710	-1.7708	0.0466	5.0 to 9.5
$10^{-2.5}$	604.1500	-471.1900	145.2600	-22.1950	1.6837	-0.0507	5.0 to 9.5
$10^{-3.0}$	764.2400	-579.3200	173.4000	-25.6820	1.8848	-0.0549	5.0 to 9.5
$10^{-3.5}$	359.6500	-271.5300	80.6210	-11.8280	0.8598	-0.0248	5.0 to 9.5
$10^{-4.0}$	201.9000	-151.4900	44.4240	-6.4202	0.4594	-0.0130	5.0 to 9.5
$10^{-4.5}$	144.5800	-107.4200	30.9910	-4.3907	0.3074	-0.0085	5.0 to 9.5
$10^{-5.0}$	95.8120	-70.4200	19.8710	-2.7359	0.1855	-0.0050	5.0 to 9.5

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DRS

Pu(V)

PCO_2 (atm)	Coefficients: [log ($K_{a'}$, in mL·m^{-2}) = a + bx + cx^2 + dx^3 + ex^4 + fx^5]						pH range
	a	b	c	d	e	f	
$10^{-0.5}$	1246.3000	-903.7300	257.5100	-36.0670	2.4887	-0.0679	5.0 to 9.5
$10^{-1.0}$	-587.0200	460.0700	-143.1000	22.0030	-1.6648	0.0494	5.0 to 9.5
$10^{-1.5}$	-1184.5000	883.8700	-261.0300	38.0760	-2.7366	0.0774	5.0 to 9.5
$10^{-2.0}$	-50.0260	30.6840	-7.1459	0.7192	-0.0192	-0.0008	5.0 to 9.5
$10^{-2.5}$	393.2200	-296.8800	88.4680	-13.0530	0.9590	-0.0281	5.0 to 9.5
$10^{-3.0}$	-95.1200	-67.0850	-18.8600	2.6056	-0.1720	0.0042	5.0 to 9.5
$10^{-3.5}$	-230.0100	165.0600	-46.9880	6.5997	-0.4531	0.0121	5.0 to 9.5
$10^{-4.0}$	-120.5700	82.0230	-22.1140	2.9266	-0.1861	0.0045	5.0 to 9.5
$10^{-4.5}$	7.9051	-13.3230	5.8040	-1.1017	0.1101	-0.0035	5.0 to 9.5
$10^{-5.0}$	74.8550	-61.9290	19.6830	-3.0471	0.2337	-0.0071	5.0 to 9.5

Th(IV)

PCO_2 (atm)	Coefficients: [log ($K_{a'}$, in mL·m^{-2}) = a + bx + cx^2 + dx^3 + ex^4 + fx^5]						pH range
	a	b	c	d	e	f	
$10^{-0.5}$	-312.1500	243.9900	-73.0380	10.6870	-0.7657	0.0215	5.0 to 9.0
$10^{-1.0}$	-178.6000	137.7300	-39.6220	5.5028	-0.3696	0.0096	5.0 to 9.0
$10^{-1.5}$	-22.1540	17.7840	-3.2759	0.0671	0.0312	-0.0021	5.0 to 9.0
$10^{-2.0}$	22.1900	-14.8300	6.1263	-1.2564	0.1217	-0.0045	5.0 to 9.0
$10^{-2.5}$	0.0099	3.4401	0.1396	-0.2809	0.0427	-0.0019	5.0 to 9.0
$10^{-3.0}$	-30.3670	27.3220	-7.3225	0.8777	-0.0467	0.0008	5.0 to 9.0
$10^{-3.5}$	-50.3620	42.9980	-12.2000	1.6305	-0.1043	0.0026	5.0 to 9.0
$10^{-4.0}$	-59.3560	49.9850	-14.3540	1.9601	-0.1294	0.0033	5.0 to 9.0
$10^{-4.5}$	-62.8560	52.7030	-15.1910	2.0878	-0.1390	0.0036	5.0 to 9.0
$10^{-5.0}$	-63.8010	53.4380	-15.4180	2.1224	-0.1417	0.0037	5.0 to 9.0

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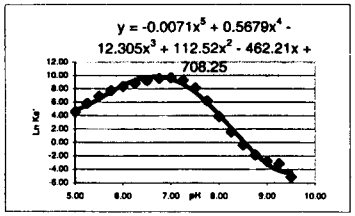
U(VI)

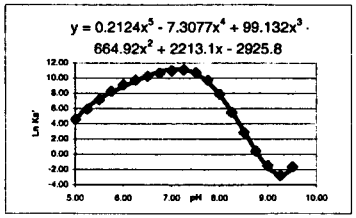
PCO_2 (atm)	Coefficients: [log (K_a, in mL·m^{-2}) = a + bx + cx^2 + dx^3 + ex^4 + fx^5]						pH range
	a	b	c	d	e	f	
$10^{-0.5}$	2004.0000	-1485.7000	433.5700	-62.1520	4.3726	-0.1210	5.0 to 9.5
$10^{-1.0}$	478.5100	-327.8200	86.4890	-10.8250	0.6317	-0.0135	5.0 to 9.5
$10^{-1.5}$	-504.8000	393.5300	-121.9500	18.8080	-1.4387	0.0434	5.0 to 9.5
$10^{-2.0}$	-558.4700	413.8500	-121.7400	17.8140	-1.2930	0.0370	5.0 to 9.5
$10^{-2.5}$	-445.0900	316.4300	-89.1890	12.5080	-0.8695	0.0238	5.0 to 9.5
$10^{-3.0}$	-456.3600	317.9800	-87.7270	12.0280	-0.8164	0.0218	5.0 to 9.5
$10^{-3.5}$	-258.6200	168.9700	-43.4750	5.5496	-0.3485	0.0084	5.0 to 9.5
$10^{-4.0}$	210.8900	-174.7600	55.8300	-8.6083	0.6480	-0.0192	5.0 to 9.5
$10^{-4.5}$	609.0000	-459.9900	136.3700	-19.8150	1.4167	-0.0400	5.0 to 9.5
$10^{-5.0}$	475.3400	-350.5600	101.2000	-14.2730	0.9882	-0.0270	5.0 to 9.5

Graphic results expressed as Ln Ka'

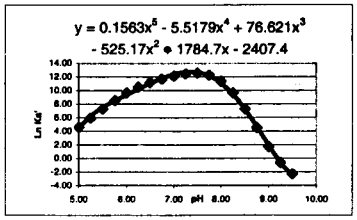
Am(III)
Log p(CO2)
-0.5



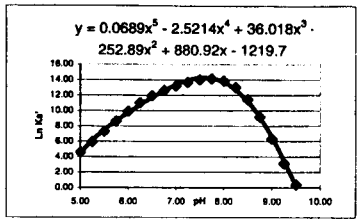
Am(III)
Log p(CO2)
-1.0



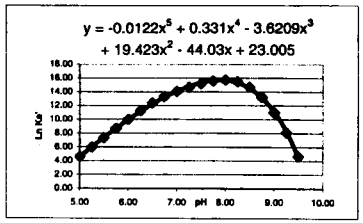
Am(III)
Log p(CO2)
-1.5



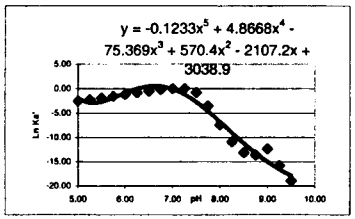
Am(III)
Log p(CO2)
-2.0



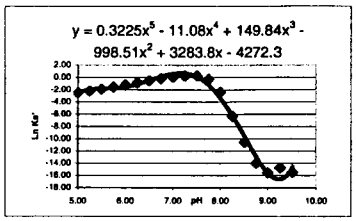
Am(III)
Log p(CO2)
-2.5



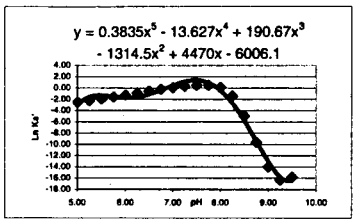
Np(V)
Log p(CO2)
-0.5



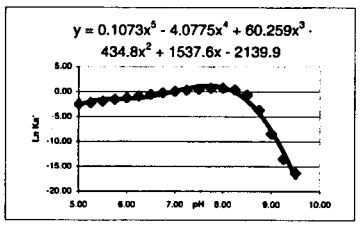
Np(V)
Log p(CO2)
-1.0



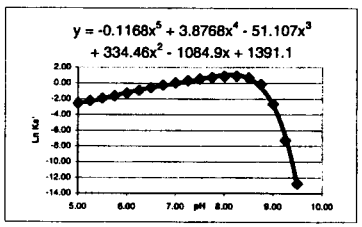
Np(V)
Log p(CO2)
-1.5



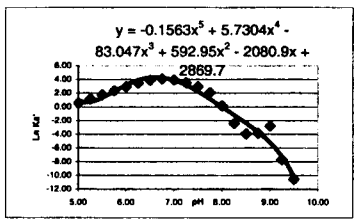
Np(V)
Log p(CO2)
-2.0



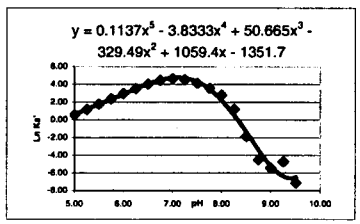
Np(V)
Log p(CO2)
-2.5



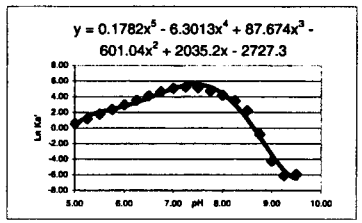
Pu(V)
Log p(CO2)
-0.5



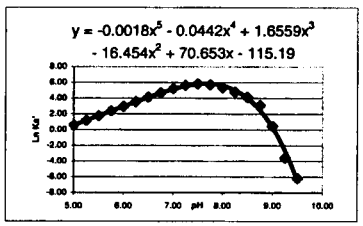
Pu(V)
Log p(CO2)
-1.0



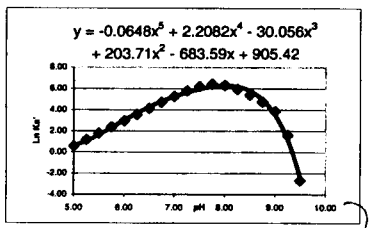
Pu(V)
Log p(CO2)
-1.5



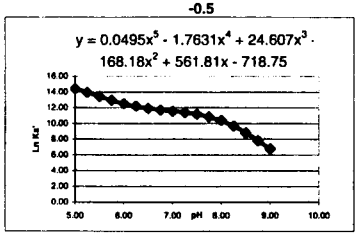
Pu(V)
Log p(CO2)
-2.0



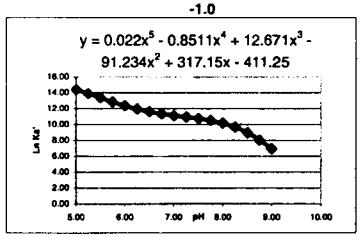
Pu(V)
Log p(CO2)
-2.5



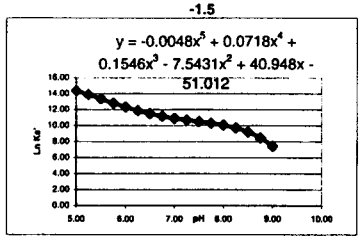
Th(IV)
Log p(CO2)
-0.5



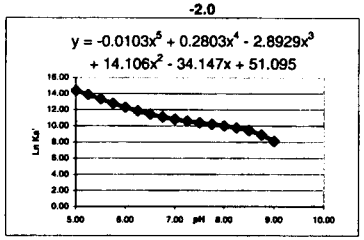
Th(IV)
Log p(CO2)
-1.0



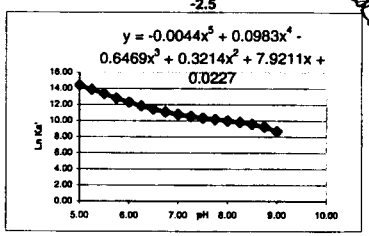
Th(IV)
Log p(CO2)
-1.5



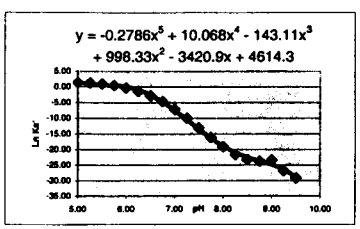
Th(IV)
Log p(CO2)
-2.0



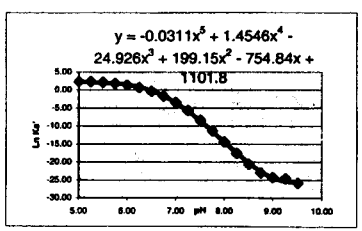
Th(IV)
Log p(CO2)
-2.5



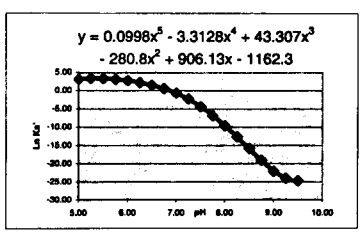
U(VI)
Log p(CO2)
-0.5



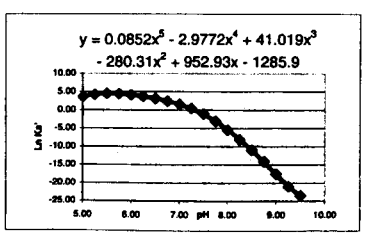
U(VI)
Log p(CO2)
-1.0



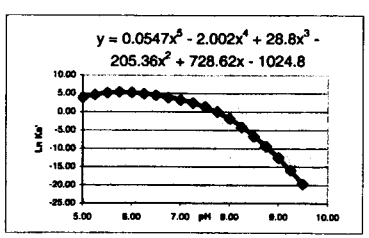
U(VI)
Log p(CO2)
-1.5



U(VI)
Log p(CO2)
-2.0



U(VI)
Log p(CO2)
-2.5



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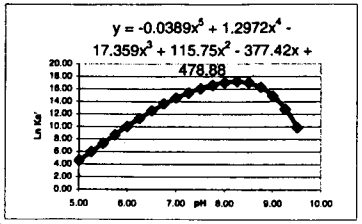
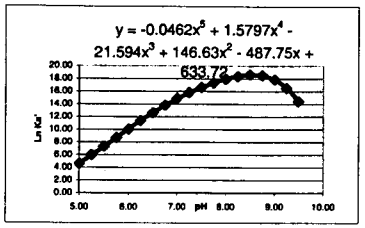
Graphical Results as Ln K_A'

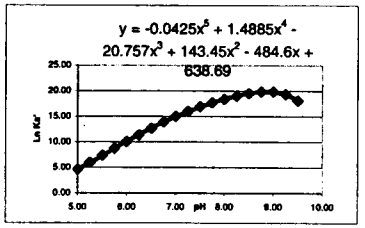
Am(III)
Log p(CO2)
-3.0



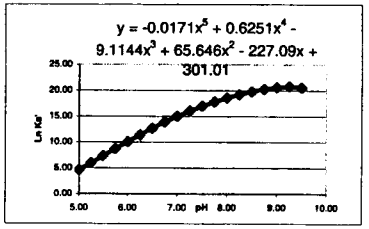
Am(III)
Log p(CO2)
-3.5



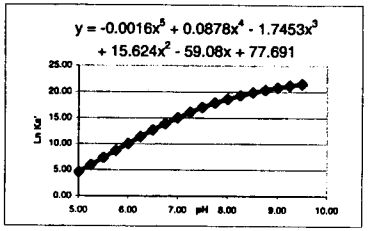
Am(III)
Log p(CO2)
-4.0



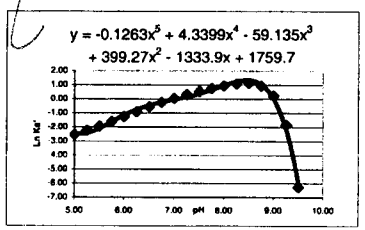
Am(III)
Log p(CO2)
-4.5



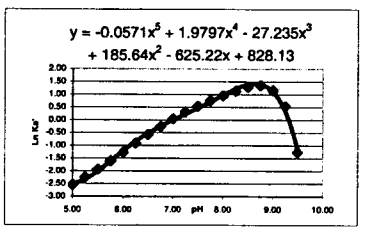
Am(III)
Log p(CO2)
-5.0



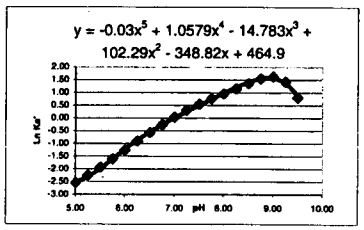
Np(V)
Log p(CO2)
-3.0



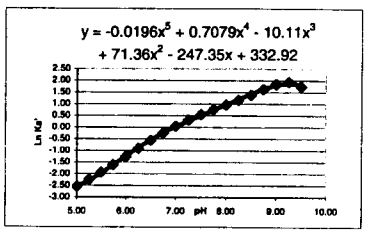
Np(V)
Log p(CO2)
-3.5



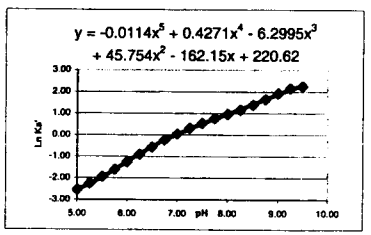
Np(V)
Log p(CO2)
-4.0



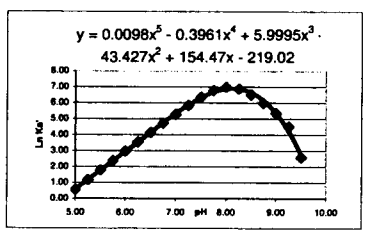
Np(V)
Log p(CO2)
-4.5



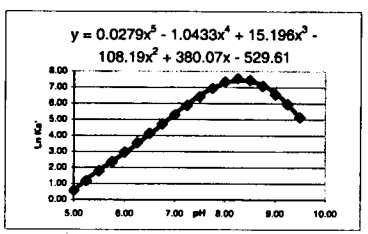
Np(V)
Log p(CO2)
-5.0



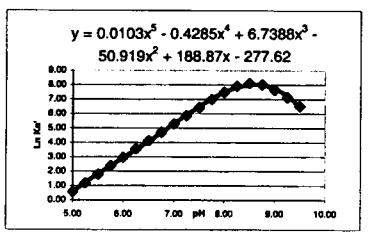
Pu(V)
Log p(CO2)
-3.0



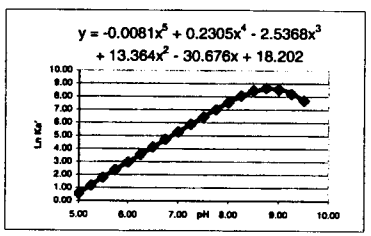
Pu(V)
Log p(CO2)
-3.5



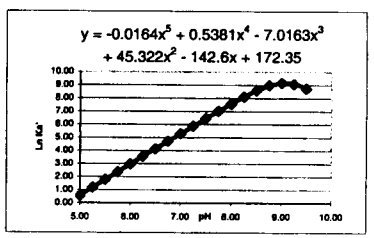
Pu(V)
Log p(CO2)
-4.0



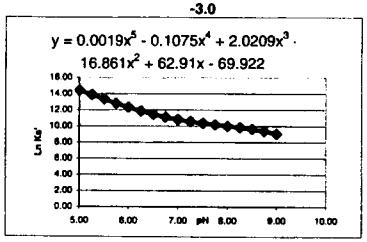
Pu(V)
Log p(CO2)
-4.5



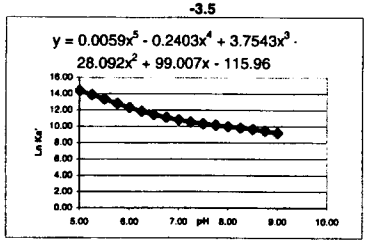
Pu(V)
Log p(CO2)
-5.0



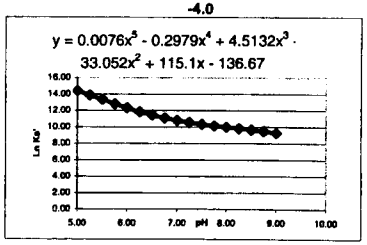
Th(IV)
Log p(CO2)
-3.0



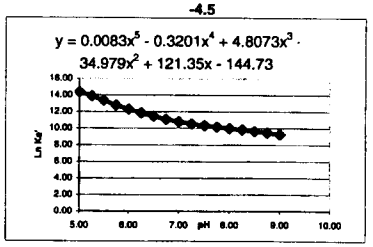
Th(IV)
Log p(CO2)
-3.5



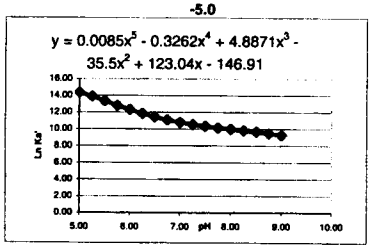
Th(IV)
Log p(CO2)
-4.0



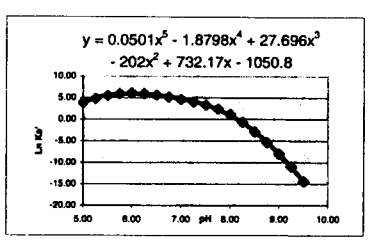
Th(IV)
Log p(CO2)
-4.5



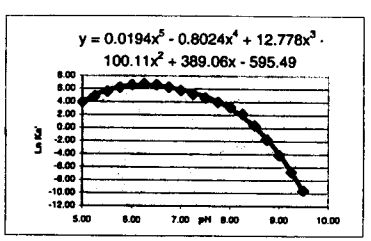
Th(IV)
Log p(CO2)
-5.0



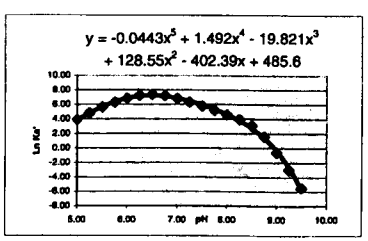
U(VI)
Log p(CO2)
-3.0



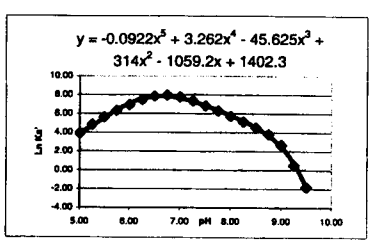
U(VI)
Log p(CO2)
-3.5



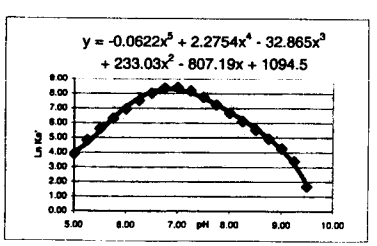
U(VI)
Log p(CO2)
-4.0



U(VI)
Log p(CO2)
-4.5

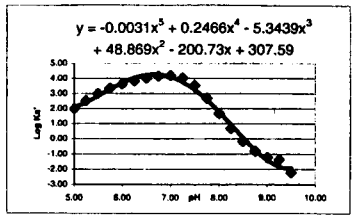


U(VI)
Log p(CO2)
-5.0

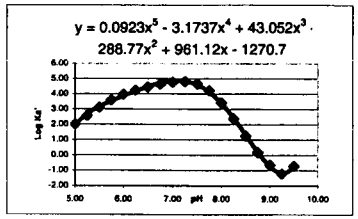


Graphical Results as Log Ka'

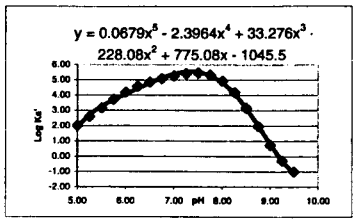
Am(III)
Log p(CO2)
-0.5



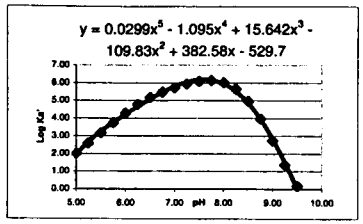
Am(III)
Log p(CO2)
-1.0



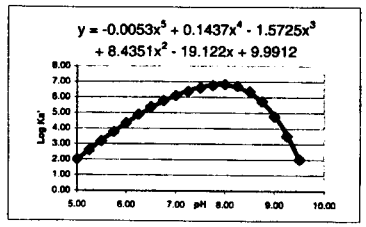
Am(III)
Log p(CO2)
-1.5



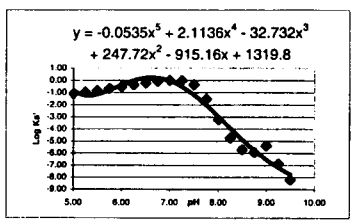
Am(III)
Log p(CO2)
-2.0



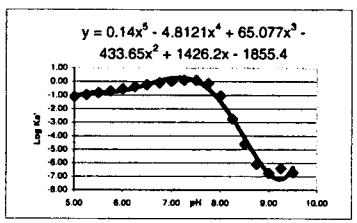
Am(III)
Log p(CO2)
-2.5



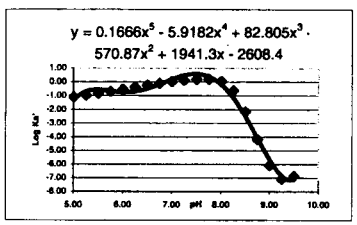
Np(V)
Log p(CO2)
-0.5



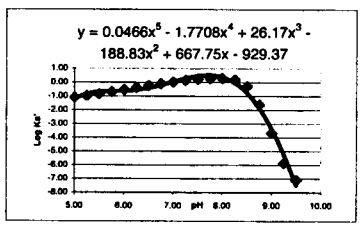
Np(V)
Log p(CO2)
-1.0



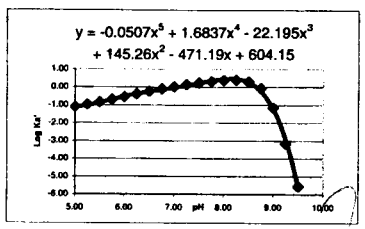
Np(V)
Log p(CO2)
-1.5



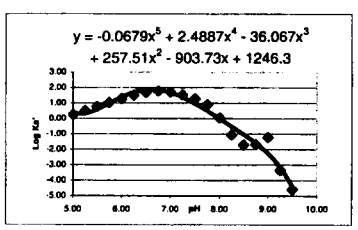
Np(V)
Log p(CO2)
-2.0



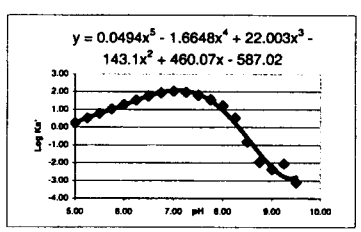
Np(V)
Log p(CO2)
-2.5



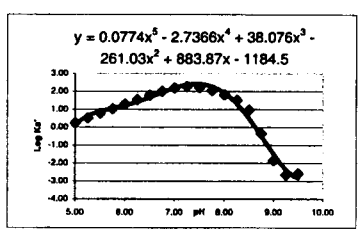
Pu(V)
Log p(CO2)
-0.5



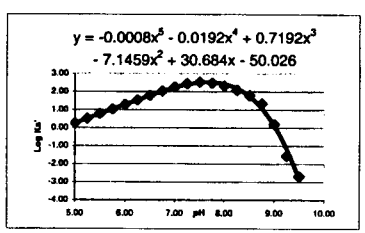
Pu(V)
Log p(CO2)
-1.0



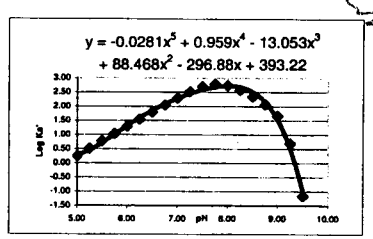
Pu(V)
Log p(CO2)
-1.5



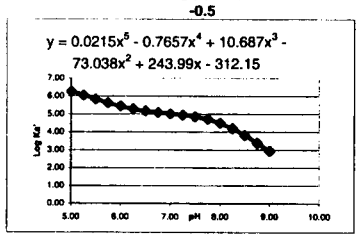
Pu(V)
Log p(CO2)
-2.0



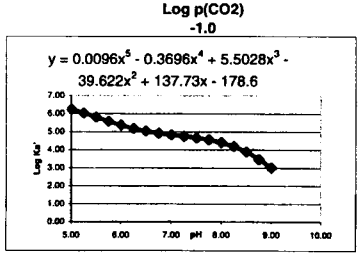
Pu(V)
Log p(CO2)
-2.5



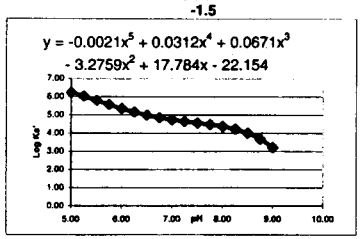
Th(IV)
Log p(CO2)
-0.5



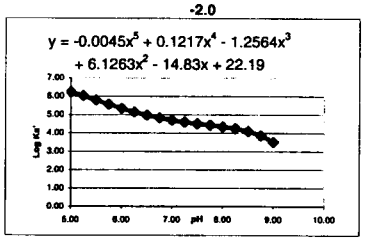
Th(IV)
Log p(CO2)
-1.0



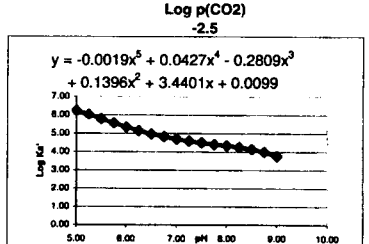
Th(IV)
Log p(CO2)
-1.5



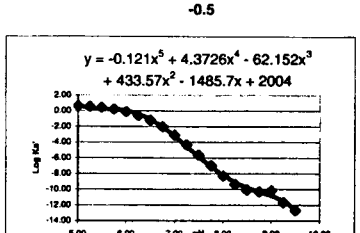
Th(IV)
Log p(CO2)
-2.0



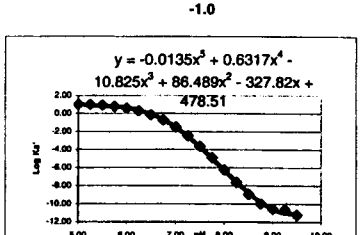
Th(IV)
Log p(CO2)
-2.5



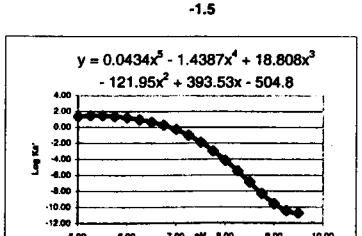
U(VI)
Log p(CO2)
-0.5



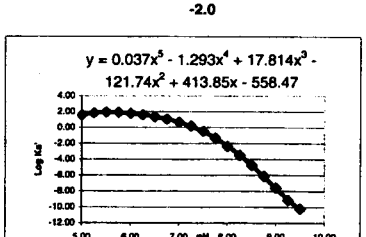
U(VI)
Log p(CO2)
-1.0



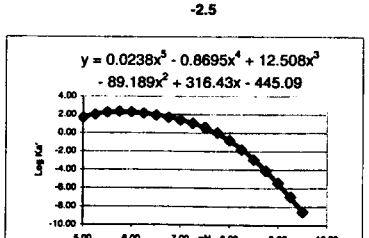
U(VI)
Log p(CO2)
-1.5



U(VI)
Log p(CO2)
-2.0

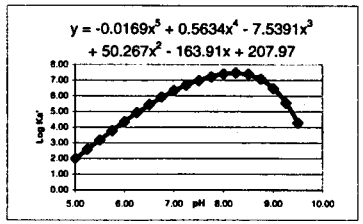


U(VI)
Log p(CO2)
-2.5

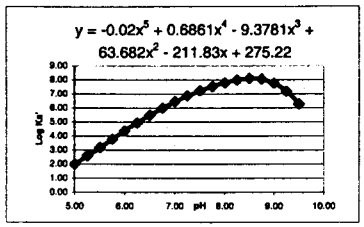


Graphical Results as LogKA'

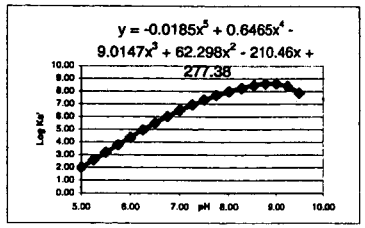
Am(III)
Log p(CO2)
-3.0



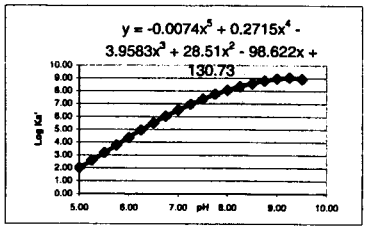
Am(III)
Log p(CO2)
-3.5



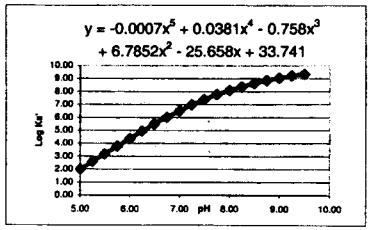
Am(III)
Log p(CO2)
-4.0



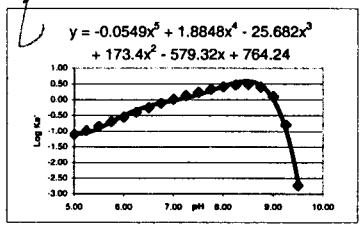
Am(III)
Log p(CO2)
-4.5



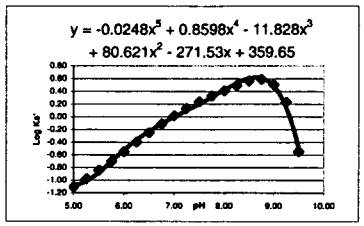
Am(III)
Log p(CO2)
-5.0



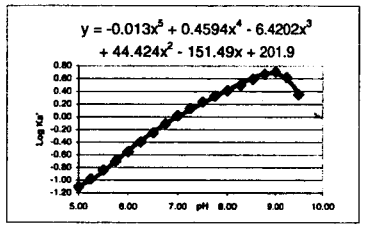
Np(V)
Log p(CO2)
-3.0



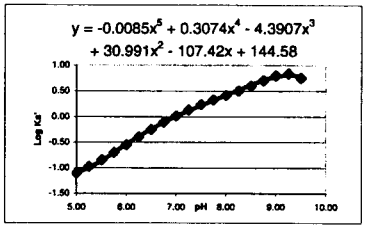
Np(V)
Log p(CO2)
-3.5



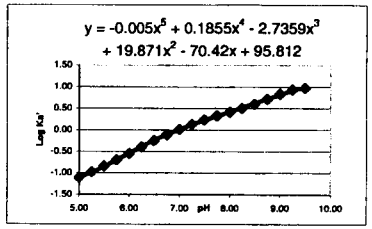
Np(V)
Log p(CO2)
-4.0



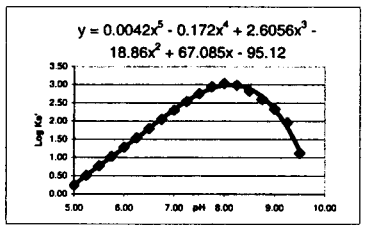
Np(V)
Log p(CO2)
-4.5



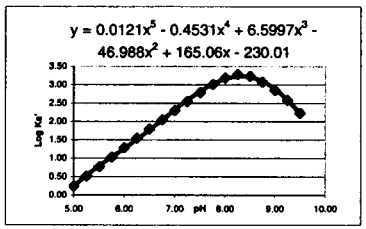
Np(V)
Log p(CO2)
-5.0



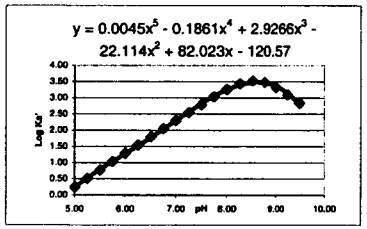
Pu(V)
Log p(CO2)
-3.0



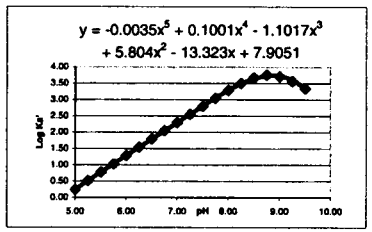
Pu(V)
Log p(CO2)
-3.5



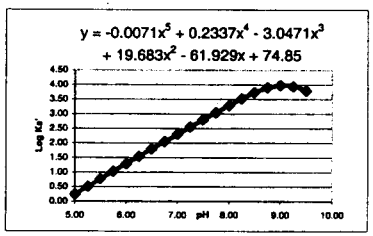
Pu(V)
Log p(CO2)
-4.0



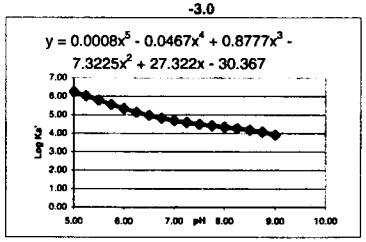
Pu(V)
Log p(CO2)
-4.5



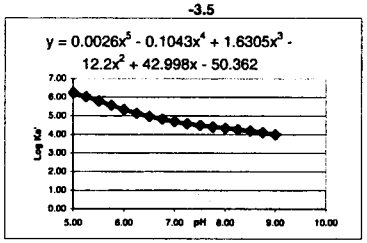
Pu(V)
Log p(CO2)
-5.0



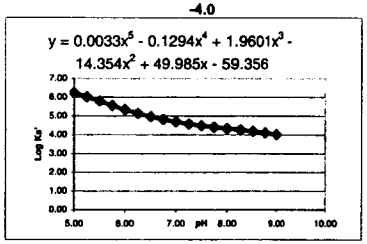
Th(IV)
Log p(CO2)
-3.0



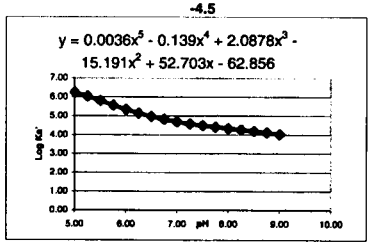
Th(IV)
Log p(CO2)
-3.5



Th(IV)
Log p(CO2)
-4.0



Th(IV)
Log p(CO2)
-4.5



Th(IV)
Log p(CO2)
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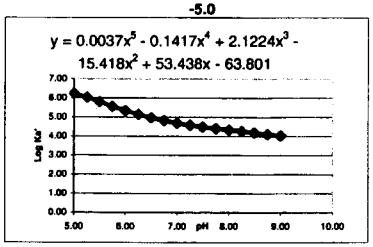
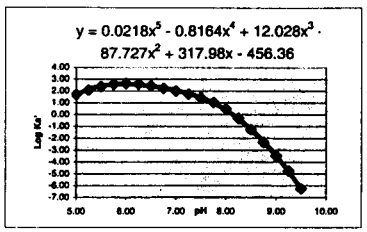
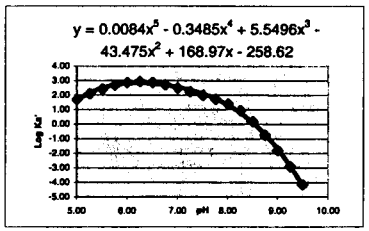


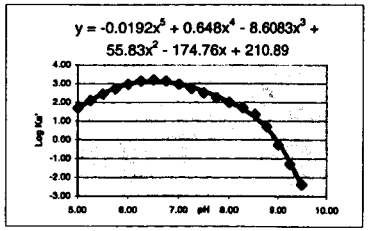
U(VI)
Log p(CO2)
-3.0



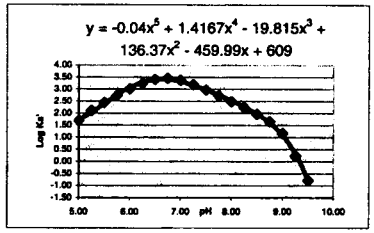
U(VI)
Log p(CO2)
-3.5



U(VI)
Log p(CO2)
-4.0



U(VI)
Log p(CO2)
-4.5



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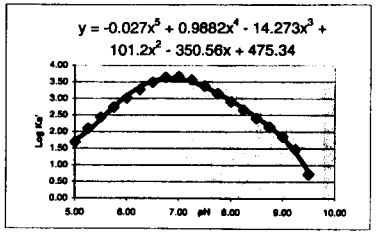
Log p(CO2)
-5.0



SCOPE OF THE VALIDATION

The geochemical equilibrium speciation code PHREEQC, Version 2.6 (April 2002 release; Parkhurst and Appelo, 1999) is an acquired code, originally developed by the U.S. Geological Survey.

THERMODYNAMIC DATA USED IN TESTING

The PHREEQC database minteq.dat (based on the MINTEQA2 database (Allison et al., 1991)) has been modified to match the thermodynamic data in MINTEQA2, Version 4.02. This modification includes additional thermodynamic data (ΔH_r° 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 Thermodynamic Database Project (Grenthe et al., 1992; Silva et al., 1995, Rard et al., 1999, and Lemire et al., 2001). The source for other radioelement data is the EQ3/6 database (Release Gembochs.v2-eq8-data0.alt.r2, 02Aug95).

TEST CASES

The test cases to be used in the validation testing have been identified previously (Turner, 2003). The following sections are intended to report the results of the testing. For simple systems of a few components the same thermodynamic data (e.g., log K at 298K) were used to ensure consistency between calculational results. For more complicated systems with a large number of components, the problems were run using the overall databases.

Installation Check—Results

The installation of PHREEQC, Version 2.6 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 18 different example problems provided with PHREEQC, Version 2.6. The results are documented in the configuration management package for PHREEQC, Version 2.6 stored in the CNWRA QA Records Room.

Validation Check—Results

PHREEQC, Version 2.6 results are tested against hand calculations reported in geochemical text books and against computer simulations using the U.S. Environmental Protection Agency (EPA) geochemical speciation code MINTEQA2, Version 4.02 (Allison et al., 1991; EPA, 1999a,b). The PHREEQC family of geochemical codes have been developed by the USGS separately from MINTEQA2, Version 4.02 and similar results from the two codes provides confidence that PHREEQC, Version 2.6 is correctly implementing the thermodynamics for solving geochemical problems.

Aqueous Speciation

With the update to both PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 to include data from the Nuclear Energy Agency thermodynamic databases (Grenthe, et al., 1992; Silva, et al., 1995; Rard, et al., 1999; Lemire, et al., 2001), we used the values from the databases for uranium speciation, rather than specifying thermodynamic data in the input files. Also, the entire problem was formulated to control all redox reactions, including uranium speciation, only by atmospheric oxygen.

Although there are order of magnitude differences between calculated concentrations of several species (e.g., $UO_2(CO_3)_3^{5-}$ and UO_2CO_3), most calculated values agree well on a log molality - log molality scale. Calculated mineral saturations also show reasonable agreement, and MINTEQA2 results are consistent with PHREEQC predictions of saturation and undersaturation.

5/6/03
DRD

A likely cause of the differences in the results from the two computer codes is differences in how activity coefficients, (γ) are calculated for aqueous species and in how the redox equilibrium of the system was controlled. Comparing results from the two codes indicates that there are differences in calculated values for γ . Typically, MINTEQA2, Version 4.02 calculates a higher activity coefficient than PHREEQC, Version 2.6, due in part to slightly different equations for activity coefficients. In PHREEQC, Version 2.6, the **b** term in the Davies equation is -0.3*(I.S.), compared with -0.24*(I.S.) in MINTEQA2, Version 4.02 (Parkhurst and Appelo, 1999; Allison, et al., 1991). The differences in calculated γ become significant at the elevated ionic strength of seawater (0.6 to 0.7 molal). 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. For example, for $UO_2(CO_3)_3^{4-}$, the dominant uranium species in the simulation, γ = 9.0 × 10^{-3} for MINTEQA2, Version 4.02 compared to γ = 6.0 × 10^{-4} calculated using PHREEQC, Version 2.6. This effect is also compounded by slight differences in calculated ionic strengths for the two solutions (0.6653 for MINTEQA2, Version 4.02, versus 0.6794 for PHREEQC, Version 2.6).

Redox equilibrium also contributes to the differences in PHREEQC and MINTEQA2 results. The Larger differences in calculated molality are for highly-charged aqueous complexes for redox sensitive elements. Both codes calculate oxidizing conditions for the system (pe > 0), but the MINTEQA2 system is considerably more oxidizing [pe = 12.4 (MINTEQA2) vs 8.5 (PHREEQC)]. This is also reflected in the greater differences in concentrations for redox sensitive species such as uranium and iron, as opposed to the excellent agreement between non-redox sensitive species such as Na^+ and Cl^-.

DRDunn 05/06/03

ID	Name	Molality	Log Molalit	Activity	Log Activity	Gamma	Log Gamma	Name	Molality	Log Molalit	Activity	Log Activity	Gamma	Log Gamma
330	H+1	8.08E-09	-8.092	6.03E-09	-8.22	0.74553	-0.128	OH-	2.68E-06	-5.572	1.63E-06	-5.788	0.60814	-0.216
3300020	oh-	2.20E-06	-5.658	1.64E-06	-5.78564	0.74553	-0.128	H+	7.98E-09	-8.098	6.03E-09	-8.22	0.75509	-0.122
8931404	(uo2)11(co3)6(oh)12-2	1.00E-76	-76.000	3.09E-77	-76.51013	0.30893	-0.510	(UO2)11(CO3)6(OH)12-2	0.00E+00	-86.436	0.00E+00	-87.242	0.15631	-0.806
8933304	(uo2)2oh+++	5.01E-27	-26.301	3.56E-28	-27.44841	0.07115	-1.148	(UO2)2(OH)+3	1.83E-28	-27.737	4.54E-30	-29.343	0.02477	-1.606
8933305	(uo2)2(oh)2++	2.26E-22	-21.647	6.97E-23	-22.15706	0.30893	-0.510	(UO2)2(OH)2+2	5.08E-24	-23.294	8.88E-25	-24.051	0.17498	-0.757
8931405	(uo2)2co3(oh)3-	8.17E-15	-14.088	6.09E-15	-14.21531	0.74553	-0.128	(UO2)2CO3(OH)3-	1.10E-16	-15.96	6.89E-17	-16.162	0.62806	-0.202
8931403	(uo2)3(co3)6-6	9.42E-22	-21.026	2.41E-26	-25.61732	0.00003	-4.523	(UO2)3(CO3)6-6	3.05E-22	-21.515	1.69E-29	-28.772	0.00000	-7.257
8933306	(uo2)3(oh)4++	1.04E-28	-27.984	3.20E-29	-28.49423	0.30893	-0.510	(UO2)3(OH)4+2	2.64E-31	-30.579	4.62E-32	-31.336	0.17498	-0.757
8933307	(uo2)3(oh)5+	1.57E-24	-23.805	1.17E-24	-23.93287	0.74553	-0.128	(UO2)3(OH)5+	2.68E-27	-26.573	1.68E-27	-26.774	0.62806	-0.202
8933308	(uo2)3(oh)7-	1.47E-23	-22.833	1.10E-23	-22.96016	0.74553	-0.128	(UO2)3(OH)7-	2.51E-26	-25.6	1.58E-26	-25.801	0.62806	-0.202
8931406	(uo2)3co2(oh5)+	8.58E-30	-29.066	6.40E-30	-29.19384	0.74553	-0.128	(UO2)3CO2(OH)5+	1.30E-32	-31.886	8.17E-33	-32.088	0.62806	-0.202
8933309	(uo2)4(oh)7+	6.13E-31	-30.213	4.57E-31	-30.34005	0.74553	-0.128	(UO2)4(OH)7+	1.18E-34	-33.927	7.44E-35	-34.129	0.62806	-0.202
1504902	ca(nh3)2+2	5.41E-17	-16.267	1.67E-17	-16.77736	0.30893	-0.510	Ca(NH3)2+2	3.27E-17	-16.485	1.02E-17	-16.991	0.31261	-0.505
1501401	caco3(aq)	3.09E-05	-4.510	3.60E-05	-4.44349	1.16555	0.067	CaCO3	3.29E-05	-4.483	3.85E-05	-4.415	1.16950	0.068
1501400	cahco3+	4.54E-05	-4.343	3.38E-05	-4.47096	0.74553	-0.128	CaHCO3+	5.56E-05	-4.255	3.75E-05	-4.426	0.67453	-0.171
1504901	canh3+2	1.23E-09	-8.912	3.79E-10	-9.42188	0.30893	-0.510	CaNH3+2	9.57E-10	-9.019	2.99E-10	-9.525	0.31261	-0.505
1504921	cano3+	4.13E-08	-7.385	3.07E-08	-7.51216	0.74553	-0.128	CaNO3+	3.30E-08	-7.481	2.47E-08	-7.608	0.74817	-0.126
1503300	caoh+	1.19E-07	-6.924	8.87E-08	-7.05204	0.74553	-0.128	CaOH+	1.31E-07	-6.884	9.04E-08	-7.044	0.69183	-0.16
1507320	caso4(aq)	1.80E-03	-2.745	2.10E-03	-2.67824	1.16555	0.067	CaSO4	1.25E-03	-2.903	1.46E-03	-2.835	1.16950	0.068
2803302	fe(oh)2(aq)	5.45E-24	-23.264	6.35E-24	-23.19734	1.16555	0.067	Fe(OH)2	5.07E-24	-23.295	5.93E-24	-23.227	1.16950	0.068
2813301	fe(oh)2+	1.55E-08	-7.810	1.16E-08	-7.93707	0.74553	-0.128	Fe(OH)2+	1.63E-08	-7.789	1.10E-08	-7.96	0.67453	-0.171
2803301	fe(oh)3-	4.41E-24	-23.355	3.29E-24	-23.48299	0.74553	-0.128	Fe(OH)3	1.65E-08	-7.782	1.93E-08	-7.714	1.16950	0.068
2813302	fe(oh)3(aq)	1.75E-08	-7.758	2.03E-08	-7.69171	1.16555	0.067	Fe(OH)3-	4.63E-24	-23.334	3.07E-24	-23.513	0.66374	-0.178
2813303	fe(oh)4-	4.16E-09	-8.381	3.10E-09	-8.50836	0.74553	-0.128	Fe(OH)4-	4.36E-09	-8.36	2.95E-09	-8.531	0.67453	-0.171
2817321	fe(so4)2-	6.28E-20	-19.202	4.68E-20	-19.32949	0.74553	-0.128	Fe(SO4)2-	2.78E-20	-19.555	2.08E-20	-19.682	0.74817	-0.126
2813304	fe2(oh)2+4	1.20E-24	-23.922	1.09E-26	-25.96285	0.00911	-2.040	Fe2(OH)2+4	1.03E-24	-23.988	9.80E-27	-26.009	0.00953	-2.021
2813305	fe3(oh)4+5	2.81E-30	-29.551	1.82E-33	-32.73993	0.00065	-3.187	Fe3(OH)4+5	2.24E-30	-29.651	1.55E-33	-32.808	0.00070	-3.158
2811800	fecl+2	7.07E-19	-18.151	2.18E-19	-18.66078	0.30893	-0.510	FeCl+2	8.63E-19	-18.064	1.67E-19	-18.778	0.19320	-0.714
2811801	fecl2+	5.52E-19	-18.258	4.11E-19	-18.38578	0.74553	-0.128	FeCl2+	3.82E-19	-18.418	2.53E-19	-18.597	0.66374	-0.178
2811802	fecl3(aq)	1.49E-20	-19.827	1.73E-20	-19.76078	1.16555	0.067	FeCl3	7.36E-21	-20.133	8.60E-21	-20.065	1.16950	0.068
2801400	fehco3+	1.52E-21	-20.819	1.13E-21	-20.94667	0.74553	-0.128	FeHCO3+	1.25E-21	-20.903	9.36E-22	-21.029	0.74817	-0.126
2814921	feno3+2	1.99E-24	-23.701	6.14E-25	-24.21155	0.30893	-0.510	FeNO3+2	1.47E-24	-23.833	4.59E-25	-24.338	0.31261	-0.505
2803300	feoh+	6.54E-21	-20.184	4.88E-21	-20.3117	0.74553	-0.128	FeOH+	6.87E-21	-20.163	4.55E-21	-20.342	0.66374	-0.178
2813300	feoh+2	5.87E-14	-13.231	1.81E-14	-13.74143	0.30893	-0.510	FeOH+2	8.90E-14	-13.051	1.72E-14	-13.764	0.19320	-0.714
2807320	feso4(aq)	5.32E-20	-19.274	6.20E-20	-19.20791	1.16555	0.067	FeSO4	3.39E-20	-19.47	3.96E-20	-19.403	1.16950	0.068
2817320	feso4+	8.71E-19	-18.060	6.49E-19	-18.18764	0.74553	-0.128	FeSO4+	6.36E-19	-18.197	4.22E-19	-18.375	0.66374	-0.178
3301401	h2co3(aq)	1.40E-05	-4.855	1.63E-05	-4.78861	1.16555	0.067	H2CO3	1.23E-05	-4.909	1.44E-05	-4.841	1.16950	0.068
3307701	h2sio4-2	1.12E-09	-8.950	3.47E-10	-9.45973	0.30893	-0.510	H2SiO4-2	6.86E-11	-10.164	1.43E-11	-10.846	0.20797	-0.682
3307700	h3sio4-	1.37E-06	-5.864	1.02E-06	-5.99139	0.74553	-0.128	H3SiO4-	2.01E-06	-5.697	1.26E-06	-5.899	0.62806	-0.202
3301400	hco3-	1.61E-03	-2.792	1.20E-03	-2.91996	0.74553	-0.128	HCO3-	1.58E-03	-2.802	1.07E-03	-2.972	0.67453	-0.171
3307320	hso4-	2.65E-09	-8.577	1.97E-09	-8.70491	0.74553	-0.128	HSO4-	2.09E-09	-8.679	1.35E-09	-8.869	0.64714	-0.189
4107320	kso4-	2.45E-04	-3.611	1.83E-04	-3.7384	0.74553	-0.128	KSO4-	1.52E-04	-3.819	1.02E-04	-3.99	0.67453	-0.171
4601400	mgco3(aq)	1.11E-04	-3.954	1.30E-04	-3.88758	1.16555	0.067	MgCO3	1.11E-04	-3.955	1.30E-04	-3.887	1.16950	0.068
4601401	mghco3+	2.73E-04	-3.564	2.03E-04	-3.69205	0.74553	-0.128	MgHCO3+	3.25E-04	-3.488	2.04E-04	-3.69	0.62806	-0.202
4603300	mgoh+	5.21E-06	-5.283	3.88E-06	-5.41076	0.74553	-0.128	MgOH+	1.52E-05	-4.818	1.07E-05	-4.971	0.70469	-0.152
4607320	mgso4(aq)	7.66E-03	-2.116	8.92E-03	-2.04948	1.16555	0.067	MgSO4	5.90E-03	-2.229	6.89E-03	-2.162	1.16950	0.068
4704920	mn(no3)2(aq)	2.82E-20	-19.550	3.28E-20	-19.4836	1.16555	0.067	Mn(NO3)2	1.45E-20	-19.838	1.70E-20	-19.77	1.16950	0.068
4703301	mn(oh)3-	5.88E-20	-19.230	4.39E-20	-19.35799	0.74553	-0.128	Mn(OH)3-	5.51E-20	-19.259	3.65E-20	-19.437	0.66374	-0.178
4703302	mn(oh)4-2	7.51E-25	-24.124	2.32E-25	-24.63464	0.30893	-0.510	Mn(OH)4-2	1.00E-24	-24	1.93E-25	-24.714	0.19320	-0.714
4701800	mncl+	4.58E-10	-9.340	3.41E-10	-9.46706	0.74553	-0.128	MnCl+	3.45E-10	-9.462	2.29E-10	-9.641	0.66374	-0.178
4701801	mncl2(aq)	1.74E-10	-9.759	2.03E-10	-9.69206	1.16555	0.067	MnCl2	9.39E-11	-10.027	1.10E-10	-9.959	1.16950	0.068
4701802	mncl3-	3.17E-11	-10.499	2.36E-11	-10.62706	0.74553	-0.128	MnCl3-	1.55E-11	-10.81	1.03E-11	-10.988	0.66374	-0.178
4701400	mnhco3+	2.07E-11	-10.685	1.54E-11	-10.81267	0.74553	-0.128	MnHCO3+	1.71E-11	-10.766	1.14E-11	-10.944	0.66374	-0.178
4704921	mnno3+	4.89E-15	-14.310	3.65E-15	-14.43783	0.74553	-0.128	MnNO3+	3.20E-15	-14.494	2.40E-15	-14.621	0.74817	-0.126
4700020	mno4-	6.73E-10	-9.172	5.01E-10	-9.29978	0.74553	-0.128	MnO4-	7.72E-10	-9.112	4.53E-10	-9.344	0.58614	-0.232
4700021	mno4-2	1.55E-12	-11.809	4.79E-13	-12.31935	0.30893	-0.510	MnO4-2	2.20E-12	-11.657	4.26E-13	-12.371	0.19320	-0.714
4703300	mnoh+	3.55E-12	-11.450	2.64E-12	-11.57771	0.74553	-0.128	MnOH+	3.32E-12	-11.479	2.20E-12	-11.657	0.66374	-0.178
4707320	mnso4(aq)	3.31E-10	-9.480	3.86E-10	-9.41392	1.16555	0.067	MnSO4	1.88E-10	-9.726	2.20E-10	-9.658	1.16950	0.068
5001400	naco3-	8.29E-05	-4.081	6.18E-05	-4.20901	0.74553	-0.128	NaCO3-	7.73E-05	-4.112	5.22E-05	-4.282	0.67453	-0.171
5001401	nahco3(aq)	2.06E-04	-3.687	2.40E-04	-3.62001	1.16555	0.067	NaHCO3	1.73E-04	-3.761	2.03E-04	-3.693	1.16950	0.068
5007320	naso4-	8.64E-03	-2.064	6.44E-03	-2.19126	0.74553	-0.128	NaSO4-	6.22E-03	-2.206	4.20E-03	-2.377	0.67453	-0.171
3304900	nh3(aq)	9.50E-08	-7.022	1.11E-07	-6.9557	1.16555	0.067	NH3	7.34E-08	-7.134	8.58E-08	-7.066	1.16950	0.068
4907320	nh4so4-	5.68E-08	-7.246	4.23E-08	-7.37333	0.74553	-0.128	NH4SO4-	3.39E-08	-7.47	2.25E-08	-7.649	0.66374	-0.178
8911400	u(co3)4-4	9.02E-49	-48.045	8.21E-51	-50.08558	0.00911	-2.040	U(CO3)4-4	0.00E+00	-48.03	0.00E+00	-51.256	0.00060	-3.225

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8911401	u(co3)5-6	1.80E-52	-51.744	4.62E-57	-56.33519	0.00003	-4.523	U(CO3)5-6	0.00E+00	-50.3	0.00E+00	-57.558	0.00000	-7.257
8914921	u(no3)2++	6.78E-74	-73.169	2.10E-74	-73.67868	0.30893	-0.510	U(NO3)2+2	0.00E+00	-74.09	0.00E+00	-74.847	0.17498	-0.757
8913303	u(oh)4(aq)	1.42E-37	-36.848	1.65E-37	-36.78172	1.16555	0.067	U(OH)4	1.81E-38	-37.743	1.81E-38	-37.743	1.00000	0
8913304	u(oh)5-	3.61E-41	-40.443	2.69E-41	-40.57036	0.74553	-0.128	U(OH)5-	0.00E+00	-41.33	0.00E+00	-41.531	0.62806	-0.202
8917321	u(so4)2(aq)	2.59E-60	-59.587	3.01E-60	-59.52085	1.16555	0.067	U(SO4)2	0.00E+00	-60.812	0.00E+00	-60.812	1.00000	0
8913305	u6(oh)15+9	1.000-100	#VALUE!	4.67E-111	-110.33043	0	#NUM!	U6(OH)15+9	0.00E+00	-279.789	0.00E+00	-290.02	0.00000	-10.231
8911800	ucl+++	2.55E-63	-62.594	1.81E-64	-63.74214	0.07115	-1.148	UCl+3	0.00E+00	-63.192	0.00E+00	-64.798	0.02477	-1.606
8914920	uno3+++	1.22E-68	-67.915	8.65E-70	-69.06291	0.07115	-1.148	UNO3+3	0.00E+00	-68.522	0.00E+00	-70.128	0.02477	-1.606
8931401	uo2(co3)2-2	8.15E-10	-9.089	2.52E-10	-9.59911	0.30893	-0.510	UO2(CO3)2-2	1.43E-10	-9.844	2.24E-11	-10.651	0.15631	-0.806
8931402	uo2(co3)3-4	1.18E-08	-7.928	1.07E-10	-9.96872	0.00911	-2.040	UO2(CO3)3-4	1.42E-08	-7.847	8.46E-12	-11.073	0.00060	-3.225
8921400	uo2(co3)3-5	1.07E-21	-20.970	6.94E-25	-24.15872	0.00065	-3.187	UO2(CO3)3-5	7.21E-32	-31.142	6.58E-37	-36.182	0.00001	-5.04
8933301	uo2(oh)2(aq)	3.77E-11	-10.424	4.39E-11	-10.35717	1.16555	0.067	UO2(OH)2	4.96E-12	-11.304	4.96E-12	-11.304	1.00000	0
8933302	uo2(oh)3-	1.21E-11	-10.918	9.00E-12	-11.04582	0.74553	-0.128	UO2(OH)3-	1.62E-12	-11.791	1.02E-12	-11.993	0.62806	-0.202
8933303	uo2(oh)4-2	7.51E-17	-16.124	2.32E-17	-16.63446	0.30893	-0.510	UO2(OH)4-2	1.68E-17	-16.775	2.62E-18	-17.581	0.15631	-0.806
8937321	uo2(so4)2-2	1.69E-17	-16.773	5.20E-18	-17.28359	0.30893	-0.510	UO2(SO4)2-2	1.76E-18	-17.754	2.75E-19	-18.56	0.15631	-0.806
8931800	uo2cl+	2.77E-17	-16.557	2.07E-17	-16.68489	0.74553	-0.128	UO2Cl+	2.99E-18	-17.525	1.88E-18	-17.726	0.62806	-0.202
8931801	uo2cl2(aq)	4.01E-19	-18.396	4.68E-19	-18.32989	1.16555	0.067	UO2Cl2	3.43E-20	-19.465	3.43E-20	-19.465	1.00000	0
8931400	uo2co3(aq)	1.24E-12	-11.906	1.45E-12	-11.8395	1.16555	0.067	UO2CO3	1.45E-13	-12.839	1.45E-13	-12.839	1.00000	0
8934920	uo2no3+	3.18E-22	-21.498	2.37E-22	-21.62565	0.74553	-0.128	UO2NO3+	3.35E-23	-22.475	2.11E-23	-22.676	0.62806	-0.202
8933300	uo2oh+	4.56E-14	-13.341	3.40E-14	-13.46853	0.74553	-0.128	UO2OH+	6.11E-15	-14.214	3.84E-15	-14.416	0.62806	-0.202
8937320	uo2so4(aq)	1.35E-16	-15.868	1.58E-16	-15.80174	1.16555	0.067	UO2SO4	1.22E-17	-16.914	1.22E-17	-16.914	1.00000	0
8913300	uoh+++	5.40E-57	-56.268	3.84E-58	-57.41579	0.07115	-1.148	UOH+3	0.00E+00	-56.772	0.00E+00	-58.377	0.02477	-1.606
8917320	uso4++	3.40E-61	-60.469	1.05E-61	-60.97899	0.30893	-0.510	USO4+2	0.00E+00	-61.348	0.00E+00	-62.105	0.17498	-0.757

Concentration of Component Species		Molality	Log Molalit	Activity	Log Activity	Gamma	Log Gamma	Name	Molality	Log Molalit	Activity	Log Activity	Gamma	Log Gamma
150	Ca+2	8.79E-03	-2.056	2.71E-03	-2.56639	0.30893	-0.510	Ca+2	9.32E-03	-2.031	2.76E-03	-2.558	0.29648	-0.528
180	Cl-1	5.66E-01	-0.247	4.22E-01	-0.375	0.74553	-0.128	Cl-	5.66E-01	-0.247	3.40E-01	-0.469	0.59979	-0.222
140	CO3-2	3.02E-05	-4.519	9.34E-06	-5.02961	0.30893	-0.510	CO3-2	3.99E-05	-4.4	8.28E-06	-5.082	0.20797	-0.682
280	Fe+2	2.42E-19	-18.616	7.48E-20	-19.12606	0.30893	-0.510	Fe+2	3.05E-19	-18.516	6.98E-20	-19.156	0.22909	-0.64
281	Fe+3	2.41E-19	-18.618	1.71E-20	-19.76578	0.07115	-1.148	Fe+3	2.05E-19	-18.689	1.63E-20	-19.789	0.07943	-1.1
770	H4SiO4	4.48E-05	-4.349	5.22E-05	-4.28239	1.16555	0.067	H4SiO4	4.41E-05	-4.355	5.16E-05	-4.287	1.16950	0.068
410	K+1	1.03E-02	-1.986	7.70E-03	-2.11328	0.74553	-0.128	K+	1.04E-02	-1.982	6.26E-03	-2.203	0.59979	-0.222
460	Mg+2	4.71E-02	-1.327	1.45E-02	-1.83763	0.30893	-0.510	Mg+2	4.87E-02	-1.312	1.64E-02	-1.785	0.33651	-0.473
470	Mn+2	2.08E-09	-8.682	6.43E-10	-9.19206	0.30893	-0.510	Mn+2	2.34E-09	-8.632	5.35E-10	-9.272	0.22909	-0.64
471	Mn+3	9.96E-22	-21.002	7.08E-23	-22.14979	0.07115	-1.148	Mn+3	7.54E-22	-21.123	5.99E-23	-22.222	0.07943	-1.1
500	Na+1	4.77E-01	-0.322	3.55E-01	-0.4494	0.74553	-0.128	Na+	4.79E-01	-0.32	3.39E-01	-0.47	0.70632	-0.151
490	NH4+1	1.57E-06	-5.804	1.17E-06	-5.93148	0.74553	-0.128	NH4+	1.62E-06	-5.792	9.08E-07	-6.042	0.56234	-0.25
492	NO3-1	4.81E-06	-5.318	3.58E-06	-5.44577	0.74553	-0.128	NO3-	4.81E-06	-5.317	2.82E-06	-5.549	0.58614	-0.232
732	SO4-2	1.09E-02	-1.962	3.37E-03	-2.47185	0.30893	-0.510	SO4-2	1.57E-02	-1.803	2.31E-03	-2.636	0.14655	-0.834
890	U+3	2.08E-86	-85.682	1.48E-87	-86.82941	0.07115	-1.148	U+3	0.00E+00	-86.192	0.00E+00	-87.798	0.02477	-1.606
891	U+4	8.98E-64	-63.047	8.18E-66	-65.08714	0.00911	-2.040	U+4	0.00E+00	-63.349	0.00E+00	-66.049	0.00200	-2.699
892	UO2+1	5.44E-28	-27.265	4.05E-28	-27.39216	0.74553	-0.128	UO2+	7.16E-29	-28.145	4.50E-29	-28.346	0.62806	-0.202
893	UO2+2	1.07E-16	-15.970	3.31E-17	-16.47989	0.30893	-0.510	UO2+2	2.39E-17	-16.621	3.74E-18	-17.427	0.15631	-0.806

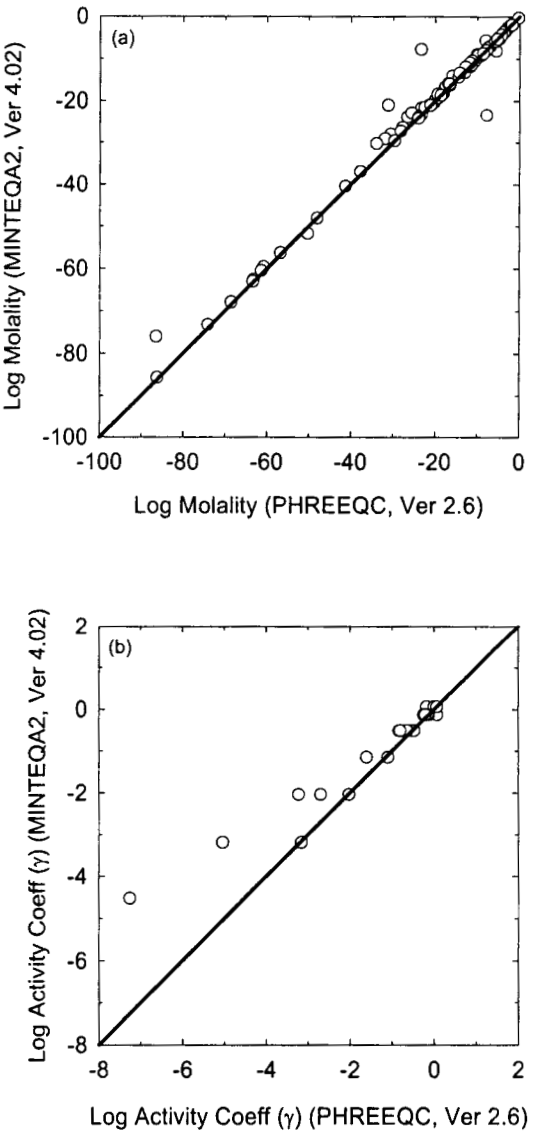
COMPONENT CONCENTRATION

140	CO3-2	2.41E-03	C(4)	2.41E-03
150	Ca+2	1.07E-02	Ca	1.07E-02
180	Cl-1	5.66E-01	Cl	5.66E-01
280	Fe+2	3.03E-19	Fe(2)	3.47E-19
281	Fe+3	3.71E-08	Fe(3)	3.71E-08
410	K+1	1.06E-02	K	1.06E-02
460	Mg+2	5.51E-02	Mg	5.51E-02
470	Mn+2	3.77E-09	Mn(2)	3.00E-09
471	Mn+3	9.96E-22	Mn(3)	7.54E-22
490	NH4+1	1.72E-06	N(-3)	1.72E-06
492	NO3-1	4.85E-06	N(5)	4.85E-06
500	Na+1	4.86E-01	Na	4.85E-01
732	SO4-2	2.93E-02	S(6)	2.93E-02
770	H4SiO4	4.62E-05	Si	4.62E-05
890	U+3	2.08E-86	U(3)	0.00E+00
891	U+4	1.42E-37	U(4)	1.81E-38
892	UO2+1	5.44E-28	U(5)	7.17E-29
893	UO2+2	1.27E-08	U(6)	1.44E-08

MINTEQA2, Version 4.02

PHREEQC, Version 2.6

5/16/03



Comparison of Aqueous Speciation of Seawater from PHREEQC, Version 2.6 and MINTEQA2, Version 4.02. (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.

Mineral Solubility

5/6/03 (DLP)

Richardson and McSween (1989, Worked Problems 3-7 and 3-8) calculate barite solubility in pure water and in a 0.2 m NaCl solution. In adapting these worked problems to solution by PHREEQC, Version 2.6, some aqueous species such as $NaSO_4^-$ were suppressed to match the simple aqueous system modeled by Richardson and McSween (1989). The results for barite solubility reported in Richardson and McSween (1989) differ slightly from the results calculated by PHREEQC, Version 2.6. The results differ by less than two percent, and are likely due to slight differences in the activity coefficient formulation, and a more complete handling of the geochemical system in PHREEQC, Version 2.6. For example, the extended Debye-Hückel is the default used in PHREEQC, Version 2.6 (Parkhurst and Appelo, 1999), versus the Debye-Hückel formulation used in Richardson and McSween (1989). PHREEQC, Version 2.6 also includes the dissociation products of water (H^+ and OH^-) in the geochemical system, resulting in small changes in calculated ionic strength. Reevaluating the Richardson and McSween (1989) calculations using the activity coefficients calculated by PHREEQC, Version 2.6 shows excellent agreement between the two sets of results. Both the PHREEQC, Version 2.6 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).

Comparison of Barite Solubility Results for Richardson and McSween (1989) and PHREEQC, Version 2.6

	m_{Ba2+} (molal)	m_{SO42-} (molal)	γ_{Ba2+} (D-H)	γ_{SO42-} (D-H)
Problem 3-7 (pure H_2O)				
PHREEQC, Version 2.6	1.055×10^{-5}	1.055×10^{-5}	0.9697	0.9697
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}	0.9697	0.9697
Blount (1977)	1.06×10^{-5}	1.06×10^{-5}	N/R	N/R
Problem 3-8 (0.2 m NaCl)				
PHREEQC, Version 2.6	3.663×10^{-5}	3.663×10^{-5}	0.29812	0.26173
Richardson and McSween (1989)	3.611×10^{-5}	3.611×10^{-5}	0.2987	0.2671
Richardson & McSween calculations with MINTEQA2 activity coefficients	3.663×10^{-5}	3.663×10^{-5}	0.29726	0.26082
Blount (1977)	3.7×10^{-5}	3.7×10^{-5}	N/R	N/R
N/R not reported				

Problem 3-7 (Richardson and McSween, 1989)

$BaSO_4 = Ba^{2+} + SO_4^{2-}$

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$K = a_{Ba^{2+}} a_{SO_4^{2-}}$

$10^{-9.98} = (\gamma_{Ba^{2+}} m_{Ba^{2+}})(\gamma_{SO_4^{2-}} m_{SO_4^{2-}})$

Assuming $m_{Ba^{2+}} = m_{SO_4^{2-}}$ and $\gamma_{Ba^{2+}} = \gamma_{SO_4^{2-}}$

$10^{-9.98} = (\gamma_{Ba^{2+}} m_{Ba^{2+}})^2$

$m_{Ba^{2+}} = \sqrt{10^{-9.98}} / \gamma_{Ba^{2+}}$

$m_{Ba^{2+}} = 10^{-4.99} / 0.9697$ from PHREEQC, Version 2.6

Problem 3-8

Same as above, but $\gamma_{Ba^{2+}} = 0.29812$, $\gamma_{SO_4^{2-}} = 0.26173$ } from PHREEQC, Version 2.6

Note - Database modified to exclude $NaSO_4^-$ and match Richardson + McSween Example 3.8

$10^{-9.98} = \gamma_{Ba^{2+}} \gamma_{SO_4^{2-}} m^2_{Ba^{2+}} =$

$m_{Ba^{2+}} = \sqrt{10^{-9.98} / \gamma_{Ba} \gamma_{SO_4^{2-}}} = 3.663 \times 10^{-5}$

Aqueous and Gas Phase Carbonate Chemistry

05/06/03 (DB)

Stumm and Morgan (1996), Example 7.8, equilibrating calcite ($CaCO_3$) in sea water at 25 °C, and open to atmosphere (fixed P_{CO2} = 3.55 × 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).

As indicated in the problem formulation, initial Ca^{2+}, HCO_3^-, and B were omitted. The model results agree very well for pH, and H_2CO_3(aq), and agree within less than a factor of two for Ca^{2+}, 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. As noted previously, there are also likely to be differences due to the thermodynamic data for aqueous speciation, and different activity coefficient models. 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.

Alternatively, Langmuir (1997) presents results for calcite solubility in fresh water at 25 °C, and under variable fixed P_{CO2}. These results are easier to interpret due to the simpler geochemical system.

Again, there are slight differences 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_{CO2} values covering two orders of magnitude, the agreement is within one percent. The overall excellent agreement indicates that PHREEQC, Version 2.6 is correctly implementing carbonate equilibria in aqueous speciation calculations.

Stumm and Morgan (1996): Calcite in equilibrium with seawater and atmospheric PCO2																		
Log PCO2	pH	pe	Ca	m_CO3-2	m_MgCO3	m_NaCO3	m_CaCO3	m_SrCO3	m_HCO3-	m_MgHCO	m_NaHCO	m_CaHCO	m_H2CO3	Total m_Ca+2	Total m_HCO3-	Total m_CO3-2	Total m_H2CO3
-3.45	8.30673	-2.80868	1.30E-03	4.72E-05	1.32E-04	9.20E-05	4.78E-06	8.54E-08	1.54E-03	3.14E-04	1.70E-04	6.57E-06	9.91E-06	1.30E-03	2.03E-03	2.76E-04	9.91E-06

PHREEQC-Calcite_H2O(Stumm)

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					
PHREEQC, Version 2.6	8.31	1.301×10^{-3}	2.03×10^{-3}	2.76×10^{-4}	9.91×10^{-6}
Stumm and Morgan (1996)	8.34	1.51×10^{-3}	2.77×10^{-3}	3.80×10^{-4}	1.05×10^{-5}

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Langmuir(1997): Calcite in equilibrium with pure water and variable PCO2

Log PCO2	pH	pe	m_Ca+2	m_CaCO3	m_CaOH+	m_CaHCO	m_HCO3-	m_Ca+2	ppm Ca+2	m_HCO3-	ppm HCO3-
-3.5	8.28615	-1.97367	4.78E-04	5.56E-06	1.64E-08	4.86E-06	9.40E-04	4.89E-04	19.6	9.45E-04	57.7
-2.5	7.6305	-1.31897	1.05E-03	5.56E-06	7.56E-09	2.24E-05	2.12E-03	1.08E-03	43.3	2.14E-03	130.5
-1.5	6.97686	-0.67155	2.36E-03	5.56E-06	3.49E-09	1.04E-04	4.82E-03	2.47E-03	99.1	4.93E-03	300.6

PHREEQC-Calcite_H2O(Langmuir)

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			
PHREEQC, Version 2.6	8.29	19.6	57.7
Langmuir (1997); Table 6.3	8.29	20	58
$P_{CO_2} = 10^{-2.5}$ bar = $10^{-2.51}$ atm			
PHREEQC, Version 2.6	7.63	43.3	130.5
Langmuir (1997); Table 6.3	7.62	44	131
$P_{CO_2} = 10^{-1.5}$ bar = $10^{-1.51}$ atm			
PHREEQC, Version 2.6	6.98	99.1	300.6
Langmuir (1997); Table 6.3	6.97	100	298

Sorption—Surface Complexation Modeling

Zn^{2+} sorption on ferrihydrite (HFO) using the diffuse-layer surface complexation model and parameters described in Dzombak and Morel (1990). Sorption at 25 °C (298 K) is investigated for two Zn^{2+} concentrations (10^{-4} and 10^{-7} molal).

The results from PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 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 2.6, pH is fixed based on titration with concentrated 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.

05/06/03

Comparison of PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 Results for Zn Sorption on Ferrihydrite (Percent Sorbed). DLM Constants from Dzombak and Morel (1990).

	$Zn_T = 1 \times 10^{-4}$ molal		$Zn_T = 1 \times 10^{-7}$ molal	
pH	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	2.3
5.75	3.0	3.0	6.2	6.1
6.00	4.5	4.5	15.3	15.1
6.25	6.2	6.2	33.0	32.6
6.50	9.2	9.1	57.3	56.9
6.75	15.1	14.9	78.7	78.4
7.00	24.8	24.6	91.1	91.0
7.25	37.4	37.2	96.6	96.6
7.50	50.4	50.2	98.8	98.8
7.75	62.4	62.3	99.6	99.6
8.00	72.3	72.5	99.8	99.8

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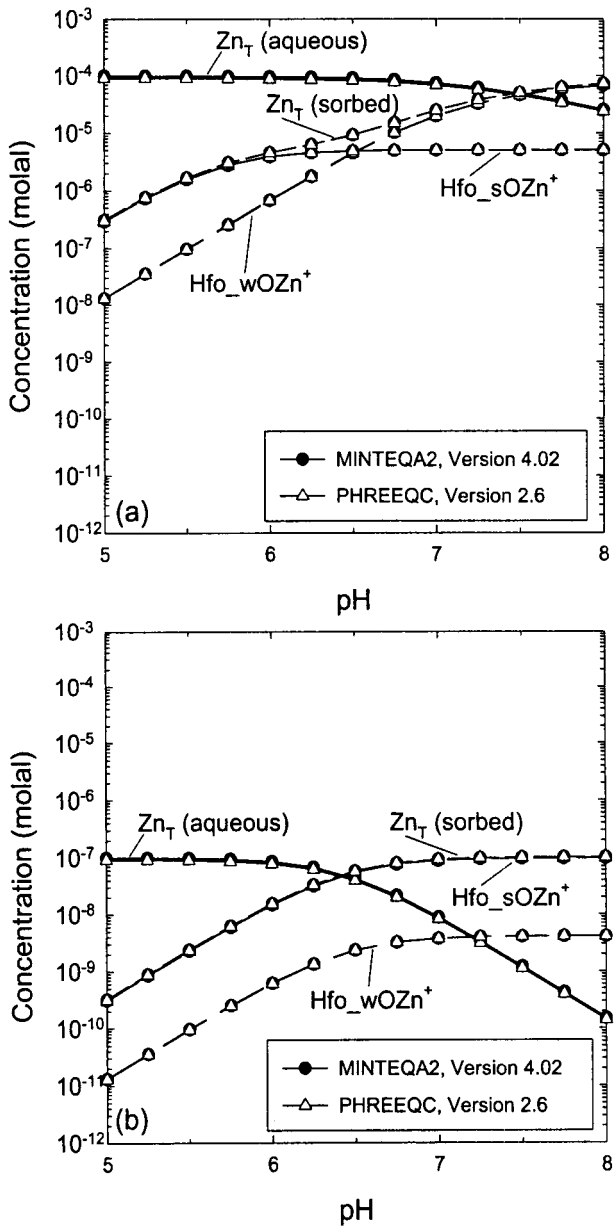
ZnT=1e-7	pH	mZn+2(tot)	Hfo_sOZn+	Hfo_wOZn-	Total sorbe	%sorbed
20020321	5.00	9.97E-08	3.11E-10	1.30E-11	3.24E-10	0.32%
20020321	5.25	9.91E-08	8.51E-10	3.57E-11	8.87E-10	0.89%
20020321	5.50	9.76E-08	2.29E-09	9.60E-11	2.39E-09	2.39%
20020321	5.75	9.37E-08	5.99E-09	2.51E-10	6.24E-09	6.24%
20020321	6.00	8.46E-08	1.47E-08	6.17E-10	1.53E-08	15.31%
20020321	6.25	6.70E-08	3.16E-08	1.33E-09	3.30E-08	32.95%
20020321	6.50	4.26E-08	5.50E-08	2.33E-09	5.73E-08	57.30%
20020321	6.75	2.13E-08	7.55E-08	3.21E-09	7.87E-08	78.67%
20020321	7.00	8.85E-09	8.74E-08	3.72E-09	9.11E-08	91.09%
20020321	7.25	3.34E-09	9.27E-08	3.96E-09	9.66E-08	96.63%
20020321	7.50	1.21E-09	9.47E-08	4.04E-09	9.88E-08	98.77%
20020321	7.75	4.27E-10	9.55E-08	4.08E-09	9.96E-08	99.56%
20020321	8.00	1.50E-10	9.58E-08	4.09E-09	9.98E-08	99.84%
ZnT=1e-4						
20020321	5.00	9.97E-05	2.93E-07	1.30E-08	3.06E-07	0.31%
20020321	5.25	9.92E-05	7.27E-07	3.56E-08	7.63E-07	0.76%
20020321	5.50	9.83E-05	1.57E-06	9.61E-08	1.67E-06	1.67%
20020321	5.75	9.70E-05	2.75E-06	2.56E-07	3.01E-06	3.01%
20020321	6.00	9.55E-05	3.82E-06	6.75E-07	4.49E-06	4.49%
20020321	6.25	9.37E-05	4.47E-06	1.76E-06	6.23E-06	6.23%
20020321	6.50	9.06E-05	4.78E-06	4.43E-06	9.21E-06	9.21%
20020321	6.75	8.47E-05	4.90E-06	1.02E-05	1.51E-05	15.07%
20020321	7.00	7.47E-05	4.95E-06	1.99E-05	2.48E-05	24.84%
20020321	7.25	6.20E-05	4.97E-06	3.24E-05	3.74E-05	37.37%
20020321	7.50	4.86E-05	4.98E-06	4.54E-05	5.04E-05	50.41%
20020321	7.75	3.61E-05	4.99E-06	5.74E-05	6.23E-05	62.35%
20020321	8.00	2.53E-05	4.99E-06	6.73E-05	7.23E-05	72.27%

MINTEQA2 (ex8), Zn-HFO

ZnT=1e-7	pH	m_Zn+2	m_Hfo_wO	m_Hfo_sO	Total sorbe	%sorbed
1	5.00	9.08E-08	1.28E-11	3.05E-10	3.18E-10	0.32%
1	5.25	9.03E-08	3.50E-11	8.36E-10	8.71E-10	0.87%
1	5.50	8.89E-08	9.43E-11	2.25E-09	2.34E-09	2.34%
1	5.75	8.54E-08	2.47E-10	5.89E-09	6.13E-09	6.13%
1	6.00	7.73E-08	6.08E-10	1.45E-08	1.51E-08	15.08%
1	6.25	6.14E-08	1.32E-09	3.12E-08	3.26E-08	32.56%
1	6.50	3.92E-08	2.31E-09	5.45E-08	5.68E-08	56.85%
1	6.75	1.96E-08	3.20E-09	7.52E-08	7.84E-08	78.37%
1	7.00	8.20E-09	3.72E-09	8.72E-08	9.10E-08	90.95%
1	7.25	3.10E-09	3.95E-09	9.26E-08	9.66E-08	96.57%
1	7.50	1.12E-09	4.04E-09	9.47E-08	9.88E-08	98.75%
1	7.75	3.96E-10	4.08E-09	9.55E-08	9.96E-08	99.55%
1	8.00	1.39E-10	4.09E-09	9.58E-08	9.98E-08	99.84%
ZnT=1e-4						
2	5.00	9.08E-05	1.28E-08	2.88E-07	3.00E-07	0.30%
2	5.25	9.04E-05	3.50E-08	7.16E-07	7.51E-07	0.75%
2	5.50	8.95E-05	9.44E-08	1.55E-06	1.65E-06	1.65%
2	5.75	8.83E-05	2.51E-07	2.73E-06	2.98E-06	2.98%
2	6.00	8.70E-05	6.63E-07	3.80E-06	4.46E-06	4.46%
2	6.25	8.53E-05	1.73E-06	4.46E-06	6.19E-06	6.19%
2	6.50	8.26E-05	4.36E-06	4.78E-06	9.13E-06	9.13%
2	6.75	7.73E-05	1.00E-05	4.90E-06	1.49E-05	14.93%
2	7.00	6.83E-05	1.97E-05	4.95E-06	2.46E-05	24.64%
2	7.25	5.67E-05	3.22E-05	4.97E-06	3.72E-05	37.15%
2	7.50	4.46E-05	4.53E-05	4.98E-06	5.02E-05	50.24%
2	7.75	3.34E-05	5.73E-05	4.99E-06	6.23E-05	62.31%
2	8.00	2.38E-05	6.75E-05	4.99E-06	7.25E-05	72.51%

PHREEQC (ex8), Zn-HFO



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Comparison of Zn-ferrihydrite Sorption Results for PHREEQC, Version 2.6 (triangles) and MINTEQA2, Version 4.02 (circles).

Redox Equilibria

Stumm and Morgan (1996), Example 8.2.

Example 8.2(a). An acid solution with $\{Fe^{3+}\} = 10^{-5}$ M; $\{Fe^{2+}\} = 10^{-3}$ M

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$$pe = \log K + \log \frac{\{Fe^{3+}\}}{\{Fe^{2+}\}} \quad (1)$$

Example 8.2(b). Natural water with pH = 7.5 in equilibrium with atmosphere (P_{O2} = 0.22 atm)

$$pe = \frac{1}{2}\log K + \frac{1}{4}\log P_{O2} - pH \quad (2)$$

Example 8.2(c). Natural water with pH = 8 in equilibrium with γ –MnO_2

$$pe = \frac{1}{2}\log K - 2pH - \frac{1}{2}\log \{Mn^{2+}\} \quad (3)$$

Equilibrium constants (log K) were modified in the PHREEQC, Version 2.6 input files to match the values provided in Stumm and Morgan (1996). Formation of ferric- and ferrous-hydroxy species was suppressed in the PHREEQC, Version 2.6 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 PHREEQC, Version 2.6 simulation. Comparison of model results 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 PHREEQC, Version 2.6 uses the Davies equation to correct for ionic strength effects. Incorporating activity coefficients calculated with the Davies equation improves the agreement significantly.

Example 8.4 (Stumm and Morgan, 1996) Speciation of HS^- and SO_4^{2-} as a function of pe, with pH = 10, and $\{HS^-\} + \{SO_4^{2-}\} = 10^{-4}$ M. Aqueous speciation log K values for the reaction in Equation (4) were modified in the PHREEQC, Version 2.6 input file to match the values (log K = 34.02) provided in Stumm and Morgan (1996). Based on the redox equilibrium reaction

$$SO_4^{2-} + 9H^+ + 8e^- = HS^- + 4H_2O \quad (4)$$

pe can be expressed in terms of pH and component activity (assuming γ_{H2O} = 1)

$$pe = \frac{1}{8}\left(\log K + \log\{SO_4^{2-}\} - \log\{HS^-\} - 9pH\right) \quad (5)$$

PHREEQC, Version 2.6 correctly predicts the crossover point (pe = -7.0) where the concentrations of HS^- and SO_4^{2-} 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 PHREEQC, Version 2.6 using the Davies equation results in a close match to the HS^- and SO_4^{2-} concentrations predicted by PHREEQC, Version 2.6.

Example 8.2 (Stumm and Morgan, 1996)

8.2a

$\{Fe^{3+}\} = 10^{-5}$ M $\quad Fe^{3+} + e^- = Fe^{2+} \quad \log k = 13.0$

$\{Fe^{2+}\} = 10^{-3}$ M

$$pe = \log k + \log \frac{\{Fe^{3+}\}}{\{Fe^{2+}\}}$$

from PHREEQC, version 2.6

$\gamma_{Fe^{3+}} = 0.6564$

$\gamma_{Fe^{2+}} = 0.8187$

$$pe = 13.0 + \log \frac{(10^{-5}m)(0.6564)}{(10^{-3}m)(0.8187)} = \boxed{10.904}$$

8.2b $\quad pH = 7.5, \; pO_2 = 0.21$ atm $\quad \frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$

$$pe = \frac{1}{2}\log k + \frac{1}{4}\log P_{O_2} - pH$$

$\log k = 41.55$

$\log P_{O_2} = \log(0.21 \text{ atm}) = -0.678$

$pH = 7.5$

$$pe = 20.78 + \frac{1}{4}(-0.678) - 7.5 = \boxed{13.111}$$

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8.2c $\{Mn^{2+}\} = 10^{-5}$ M , pH = 8.0

γ-$MnO_2(s) + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$ $\quad$ log k = 40.84

$$pe = \frac{1}{2}\log k - 2pH - \frac{1}{2}\log\{Mn^{2+}\}$$

From PHREEQC, Version 2.6

$\gamma_{Mn^{2+}} = 0.97925$

$$pe = \frac{1}{2}(40.84) - 2(8.0) - \frac{1}{2}\log(10^{-5}m)(0.97925)$$

$$\boxed{pe = 6.925}$$

Calculated Electron Activity (pe) for Example 8.2 in Stumm and Morgan (1996).

Geochemical System	pe calculated		
	PHREEQC, Version 2.6	Hand Calculation (γ = 1.0)	Hand Calculation (γ from PHREEQC, Davies equation)
$\{Fe^{2+}\} = 10^{-3}$ M $\{Fe^{3+}\} = 10^{-5}$ M	10.904	11.01	10.904
pH = 7.5 P_{O2} = 0.21 atm	13.111	13.111	13.111
$\{Mn^{2+}\} = 10^{-5}$ M Equilibrium with γ –MnO_2	6.925	6.92	6.925

pH	10		PHREEQC	PHREEQC	HandCalc	HandCalc	HandCalc	HandCalc			
S(total)	1.00E-04	pE			γ=1	γ=1	γ=PHREEC	γ=PHREEQCderived	γ=PHREEC	γ=PHREEQCderived	
			Conc(HS-)	Conc(SO4-2)	Conc(HS-)	Conc(SO4-2)	Conc(HS-)	Conc(SO4-2)	HS-	SO4-2	
		-9.00	1.00E-04	9.89E-21	1.00E-04	9.55E-21	1.00E-04	9.89E-21	0.988553	0.954716	51
		-8.75	1.00E-04	9.89E-19	1.00E-04	9.55E-19	1.00E-04	9.89E-19	0.988553	0.954716	
		-8.50	1.00E-04	9.89E-17	1.00E-04	9.55E-17	1.00E-04	9.89E-17	0.988553	0.954716	
		-8.25	1.00E-04	9.89E-15	1.00E-04	9.55E-15	1.00E-04	9.89E-15	0.988553	0.954716	
		-8.00	1.00E-04	9.89E-13	1.00E-04	9.55E-13	1.00E-04	9.89E-13	0.988553	0.954716	
		-7.75	1.00E-04	9.89E-11	1.00E-04	9.55E-11	1.00E-04	9.89E-11	0.988553	0.954716	
		-7.50	1.00E-04	9.89E-09	1.00E-04	9.55E-09	1.00E-04	9.89E-09	0.988424	0.954583	
		-7.25	9.90E-05	9.79E-07	9.91E-05	9.46E-07	9.90E-05	9.79E-07	0.988263	0.954201	
		-7.00	5.00E-05	5.00E-05	5.12E-05	4.88E-05	5.00E-05	5.00E-05	0.984887	0.940748	
		-6.75	9.82E-07	9.90E-05	1.04E-06	9.90E-05	9.82E-07	9.90E-05	0.982048	0.930006	
		-6.50	9.91E-09	1.00E-04	1.05E-08	1.00E-04	9.91E-09	1.00E-04	0.981883	0.929701	
		-6.25	9.91E-11	1.00E-04	1.05E-10	1.00E-04	9.92E-11	1.00E-04	0.981106	0.929822	
		-6.00	9.91E-13	1.00E-04	1.05E-12	1.00E-04	9.92E-13	1.00E-04	0.981106	0.929822	
		-5.75	9.91E-15	1.00E-04	1.05E-14	1.00E-04	9.92E-15	1.00E-04	0.981106	0.929822	
		-5.50	9.91E-17	1.00E-04	1.05E-16	1.00E-04	9.92E-17	1.00E-04	0.981106	0.929822	
		-5.25	9.91E-19	1.00E-04	1.05E-18	1.00E-04	9.92E-19	1.00E-04	0.981106	0.929822	
		-5.00	9.91E-21	1.00E-04	1.05E-20	1.00E-04	9.92E-21	1.00E-04	0.981106	0.929822	
		-4.75	9.91E-23	1.00E-04	1.05E-22	1.00E-04	9.92E-23	1.00E-04	0.981106	0.929822	
		-4.50	9.91E-25	1.00E-04	1.05E-24	1.00E-04	9.92E-25	1.00E-04	0.981106	0.929822	
		-4.25	9.91E-27	1.00E-04	1.05E-26	1.00E-04	9.92E-27	1.00E-04	0.981106	0.929822	
		-4.00	9.91E-29	1.00E-04	1.05E-28	1.00E-04	9.92E-29	1.00E-04	0.981106	0.929822	

Calculated HS^-–SO_4^{2-} Speciation as a Function of Electron Activity (pe) for Example 8.4 in Stumm and Morgan (1996).

	PHREEQC, Version 2.6		Hand Calculation (γ = 1.0)		Hand Calculation (γ from Davies equation)	
pe	mHS^-(molal)	mSO_4^{2-}(molal)	mHS^-(molal)	mSO_4^{2-}(molal)	mHS^-(molal)	mSO_4^{2-}(molal)
-9.00	1.00×10^{-4}	9.89×10^{-21}	1.00×10^{-4}	9.55×10^{-21}	1.00×10^{-4}	9.89×10^{-21}
-8.75	1.00×10^{-4}	9.89×10^{-19}	1.00×10^{-4}	9.55×10^{-19}	1.00×10^{-4}	9.89×10^{-19}
-8.50	1.00×10^{-4}	9.89×10^{-17}	1.00×10^{-4}	9.55×10^{-17}	1.00×10^{-4}	9.89×10^{-17}
-8.25	1.00×10^{-4}	9.89×10^{-15}	1.00×10^{-4}	9.55×10^{-15}	1.00×10^{-4}	9.89×10^{-15}
-8.00	1.00×10^{-4}	9.89×10^{-13}	1.00×10^{-4}	9.55×10^{-13}	1.00×10^{-4}	9.89×10^{-13}
-7.75	1.00×10^{-4}	9.89×10^{-11}	1.00×10^{-4}	9.55×10^{-11}	1.00×10^{-4}	9.89×10^{-11}
-7.50	1.00×10^{-4}	9.89×10^{-9}	1.00×10^{-4}	9.55×10^{-9}	1.00×10^{-4}	9.89×10^{-9}
-7.25	9.90×10^{-5}	9.79×10^{-7}	9.91×10^{-5}	9.46×10^{-7}	9.90×10^{-5}	9.79×10^{-7}
-7.00	5.00×10^{-5}	5.00×10^{-5}	5.12×10^{-5}	4.88×10^{-5}	5.00×10^{-5}	5.00×10^{-5}
-6.75	9.82×10^{-7}	9.90×10^{-5}	1.04×10^{-6}	9.90×10^{-5}	9.82×10^{-7}	9.90×10^{-5}
-6.50	9.91×10^{-9}	1.00×10^{-4}	1.05×10^{-8}	1.00×10^{-4}	9.91×10^{-9}	1.00×10^{-4}
-6.25	9.91×10^{-11}	1.00×10^{-4}	1.05×10^{-10}	1.00×10^{-4}	9.92×10^{-11}	1.00×10^{-4}
-6.00	9.91×10^{-13}	1.00×10^{-4}	1.05×10^{-12}	1.00×10^{-4}	9.92×10^{-13}	1.00×10^{-4}
-5.75	9.91×10^{-15}	1.00×10^{-4}	1.05×10^{-14}	1.00×10^{-4}	9.92×10^{-15}	1.00×10^{-4}
-5.50	9.91×10^{-17}	1.00×10^{-4}	1.05×10^{-16}	1.00×10^{-4}	9.92×10^{-17}	1.00×10^{-4}
-5.25	9.91×10^{-19}	1.00×10^{-4}	1.05×10^{-18}	1.00×10^{-4}	9.92×10^{-19}	1.00×10^{-4}
-5.00	9.91×10^{-21}	1.00×10^{-4}	1.05×10^{-20}	1.00×10^{-4}	9.92×10^{-21}	1.00×10^{-4}
-4.75	9.91×10^{-23}	1.00×10^{-4}	1.05×10^{-22}	1.00×10^{-4}	9.92×10^{-23}	1.00×10^{-4}
-4.50	9.91×10^{-25}	1.00×10^{-4}	1.05×10^{-24}	1.00×10^{-4}	9.92×10^{-25}	1.00×10^{-4}
-4.25	9.91×10^{-27}	1.00×10^{-4}	1.05×10^{-26}	1.00×10^{-4}	9.92×10^{-27}	1.00×10^{-4}
-4.00	9.91×10^{-29}	1.00×10^{-4}	1.05×10^{-28}	1.00×10^{-4}	9.92×10^{-29}	1.00×10^{-4}

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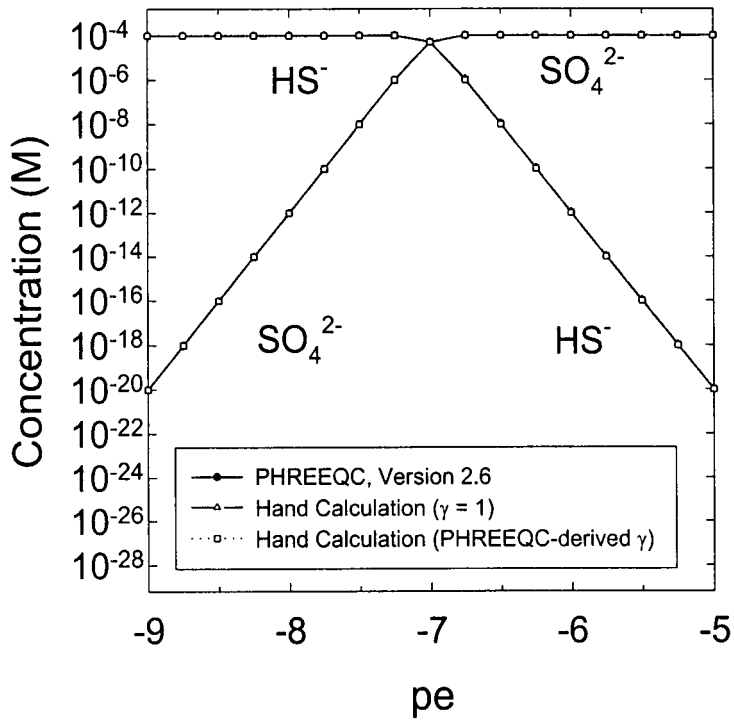

Calculated $HS^- - SO_4^{2-}$ Speciation as a Function of Electron Activity (pe) for Example 8.4 in Stumm and Morgan (1996).

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Temperature Effects

Parkhurst and Appelo (1999) provide an example of the use of PHREEQC, Version 2.6 to calculate the solubility of gypsum and anhydrite in pure water, over a range in temperature from 25 °C (298 K) to 75 °C (373 K). Only the pH and temperature are used to define a pure water solution. Gypsum and anhydrite are allowed to react to equilibrium, and the initial phase assemblage has 1 mol of each mineral. Each mineral will react either to equilibrium or until it is exhausted in the assemblage. For both PHREEQC, Version 2.6 and MINTEQA2, Version 4.02, the degree of saturation with respect to a given mineral is indicated by the saturation index (SI), such that

$$SI = \log \frac{IAP}{K} \qquad (6)$$

where IAP is the ion activity product, and K is the equilibrium constant. When a solution is undersaturated with respect to a given mineral, SI < 0. Under supersaturated conditions, SI > 0, and SI = 0 at equilibrium.

As a default, both PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 use the Van't Hoff relationship and enthalpies of reaction ($\Delta H_r°$) to correct equilibrium constants for the effects of temperature. If data are available, both PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 will employ a polynomial expression to correct equilibrium constants for the effects of temperature:

$$\text{Log } K_T = A_1 + A_2T + \frac{A_3}{T} + A_4\text{Log}(T) + A_5T^2 + \frac{A_6}{T2} + A_7\sqrt{T} \qquad (7)$$

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

If the same thermodynamic data and polynomial expressions are used, both codes should produce similar results. PHREEQC, Version 2.6 provides a polynomial expression in the phreeqc.dat database for both anhydrite and gypsum. In conducting this validation exercise, the same thermodynamic constants and polynomial expressions were used for anhydrite and gypsum.

Comparing the results shows a slight discrepancy between the SI values calculated by PHREEQC, Version 2.6 and MINTEQA2, Version 4.02. This discrepancy is likely due to differences in how the two codes calculate the activity of water. 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 mole of each). This gives a larger correction to unit activity (a_{H2O} = 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 is much smaller. Runs under this condition show a much closer agreement with the SI values calculated by PHREEQC, Version 2.6.

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Output
MINTEQA2,
Version 4.02

Temp	1 mol solid Ionic Str	1 mol solid pH	1 mol solid SI (Anhy)	1 mol solid SI(Gyp)	Infinite solid Ionic Str	Infinite solid pH	Infinite solid SI (Anhy)	Infinite solid SI(Gyp)
25	0.047	7.079	-0.175	0.000	0.044	7.065	-0.220	0.000
30	0.047	7.008	-0.153	0.000	0.044	6.994	-0.198	0.000
35	0.047	6.941	-0.126	0.000	0.044	6.926	-0.172	0.000
40	0.047	6.876	-0.096	0.000	0.044	6.861	-0.141	0.000
45	0.047	6.816	-0.061	0.000	0.043	6.800	-0.106	0.000
50	0.046	6.758	-0.023	0.000	0.043	6.742	-0.068	0.000
55	0.044	6.702	0.000	-0.019	0.043	6.688	-0.027	0.000
60	0.040	6.645	0.000	-0.064	0.041	6.634	0.000	-0.018
65	0.037	6.591	0.000	-0.112	0.037	6.580	0.000	-0.066
70	0.033	6.538	0.000	-0.162	0.033	6.527	0.000	-0.117
75	0.030	6.488	0.000	-0.216	0.030	6.488	0.000	-0.170

step	Temp	pH	pe	si_anhydri	si_gypsum
1	25	7.05556	10.6963	-0.2197	0
2	26	7.04052	10.6294	-0.2157	0
3	27	7.02567	10.5616	-0.2115	0
4	28	7.01101	10.4947	-0.2071	0
5	29	6.99653	10.4287	-0.2025	0
6	30	6.98225	10.3627	-0.1977	0
7	31	6.96815	10.2982	-0.1928	0
8	32	6.95423	10.2312	-0.1877	0
9	33	6.94049	10.1656	-0.1824	0
10	34	6.92694	10.1023	-0.1769	0
11	35	6.91356	10.0371	-0.1712	0
12	36	6.90035	9.97315	-0.1654	0
13	37	6.88732	9.90945	-0.1595	0
14	38	6.87446	9.84546	-0.1533	0
15	39	6.86177	9.79556	-0.147	0
16	40	6.84926	9.72057	-0.1406	0
17	41	6.8369	9.6582	-0.134	0
18	42	6.82472	9.59517	-0.1272	0
19	43	6.8127	9.53286	-0.1203	0
20	44	6.80084	9.47311	-0.1132	0
21	45	6.78914	9.40987	-0.106	0
22	46	6.7776	9.35425	-0.0986	0
23	47	6.76622	9.29331	-0.0911	0
24	48	6.75499	9.22761	-0.0835	0
25	49	6.74393	9.16567	-0.0757	0
26	50	6.73301	9.10933	-0.0678	0
27	51	6.72225	9.05762	-0.0597	0
28	52	6.71163	8.98913	-0.0515	0
29	53	6.70117	8.92936	-0.0432	0
30	54	6.69086	8.8697	-0.0347	0
31	55	6.68069	8.72595	-0.0261	0
32	56	6.67067	8.75469	-0.0174	0
33	57	6.66079	8.74328	-0.0085	0
34	58	6.65102	8.63024	0	-0.0004
35	59	6.6407	8.57368	0	-0.0095
36	60	6.6305	8.56629	0	-0.0187
37	61	6.62041	8.3714	0	-0.0281
38	62	6.61043	8.40499	0	-0.0375
39	63	6.60056	8.26016	0	-0.0471
40	64	6.5908	8.29443	0	-0.0567
41	65	6.58115	8.2874	0	-0.0665
42	66	6.5716	8.18397	0	-0.0764
43	67	6.56215	8.13385	0	-0.0865
44	68	6.55281	8.07777	0	-0.0966
45	69	6.54357	8.02477	0	-0.1068
46	70	6.53442	7.97015	0	-0.1171
47	71	6.52538	7.91745	0	-0.1276
48	72	6.51644	7.86354	0	-0.1381
49	73	6.50759	7.81126	0	-0.1488
50	74	6.49883	7.75629	0	-0.1595
51	75	6.49017	7.70579	0	-0.1704

step	Temp	pH	pe	si_anhydri	si_gypsum
1	25	7.05556	10.6963	-0.2197	0
6	30	6.98225	10.3627	-0.1977	0
11	35	6.91356	10.0371	-0.1712	0
16	40	6.84926	9.72057	-0.1406	0
21	45	6.78914	9.40987	-0.106	0
26	50	6.73301	9.10933	-0.0678	0
31	55	6.68069	8.72595	-0.0261	0
36	60	6.6305	8.56629	0	-0.0187
41	65	6.58115	8.2874	0	-0.0665
46	70	6.53442	7.97015	0	-0.1171
51	75	6.49017	7.70579	0	-0.1704

Output
PHREEQC, Version 2.6

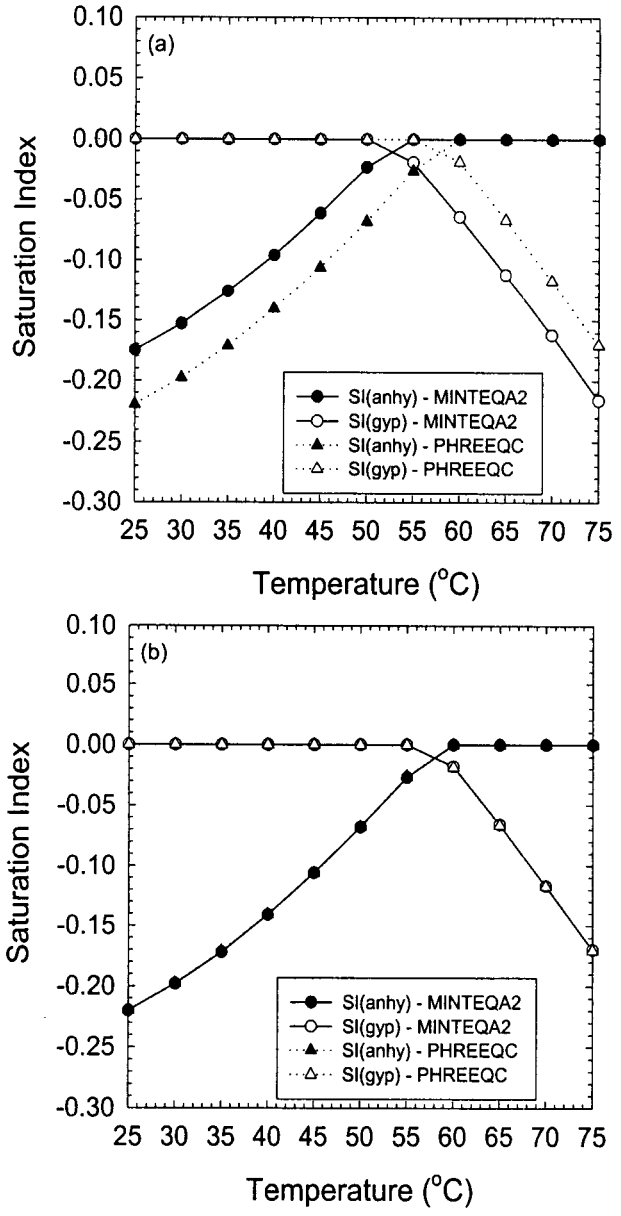
Comparison of Saturation Indexes (SI) Calculated by PHREEQC, Version 2.6 and PHREEQC, Version 2.6 for Anhydrite and Gypsum as a Function of Temperature.

	MINTEQA2, Version 4.02 (1 mol solid)			PHREEQC, Version 2.6		
T(°C)	pH	SI(Anhy)	SI(Gyp)	pH	SI(Anhy)	SI(Gyp)
25	7.08	-0.175	0.000	7.06	-0.220	0.000
30	7.01	-0.153	0.000	6.98	-0.198	0.000
35	6.94	-0.126	0.000	6.91	-0.171	0.000
40	6.88	-0.096	0.000	6.85	-0.141	0.000
45	6.82	-0.061	0.000	6.79	-0.106	0.000
50	6.76	-0.023	0.000	6.73	-0.068	0.000
55	6.70	0.000	-0.019	6.68	-0.026	0.000
60	6.65	0.000	-0.064	6.63	0.000	-0.019
65	6.59	0.000	-0.112	6.58	0.000	-0.067
70	6.54	0.000	-0.162	6.53	0.000	-0.117
75	6.49	0.000	-0.216	6.49	0.000	-0.170

5/6/03
DRJ

DRJ 05/06/2003

5/6/03
DB



Comparison of Saturation Indexes (SI) Calculated by PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 for Anhydrite and Gypsum as a Function of Temperature. (a) 1.0 mole anhydrite + 1.0 mole gypsum; (b) Assuming Infinite Gypsum (25° to 55°C), Infinite Anhydrite (60° to 75 °C) in MINTEQA2, Version 4.02 calculations.

Modified Database

The main code function to be checked in this section of the test plan is to ensure that the PHREEQC, Version 2.6 database modified to include Nuclear Energy Agency 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.

5/6/03

Speciation checks for uranium and neptunium were performed using MINTEQA2, Version 4.02 and PHREEQC, Version 2.6. Identical thermodynamic data from the Nuclear Energy Agency 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 CO_2 ($10^{-3.5}$ atm) and O_2 ($10^{-0.66}$ atm) conditions. Temperature was 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 PHREEQC, Version 2.6 database, and very simple solutions of 0.1 M $NaNO_3$ were used to minimize the effects of major ions such as Ca^{2+}, Mg^{2+}.

Comparison of the predicted speciation indicates good agreement between PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 for Np and U. With atmospheric oxygen ($P_{O2} = 10^{-0.66}$ atm), both codes calculate similar pe values for the system over the pH range. Not only is there good agreement for 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 $NpO_2(CO_3)_2^{2-}$ and $NpO_2(CO_3)_3^{2-}$ at pH > 8. There are minor differences that are most likely due to activity coefficient calculation, as discussed previously in Section 3.2. 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 $UO_2(OH)_2(aq)$ and $UO_2CO_3(aq)$. While PHREEQC, Version 2.6 assigns unity activity coefficients (i.e., $\gamma = 1$) to neutral species, MINTEQA2, Version 4.02 corrects for ionic strength effects using the relationship

$$\log \gamma = 0.1(\text{I.S.}) \tag{9}$$

where I.S. is the ionic strength of the solution. For the ionic strength used in the simulation (0.1 m $NaNO_3$), the activity coefficient for $UO_2(OH)_2(aq)$ and $UO_2CO_3(aq)$ is 1.02.

5/6/03

pH	pe	m_NpO2+	%_NpO2+	m_NpO2O	%_NpO2O	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	m_NpO2(C	%_NpO2(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		99.77
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		99.87
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		99.92
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		99.95
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		99.97
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		99.98
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		99.98
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		99.99
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		99.99
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		99.99
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		99.99
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		99.99
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		99.99
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		99.98
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		99.98
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		99.97
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		99.96
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		99.96
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		99.97
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		99.99
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		100.00
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		99.99
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		99.98
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		99.91
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		99.30

Np(V), PHREEQC, 2.6

pH	pe	m_UO2+2	%_UO2+2	m_UO2NO	%_UO2NC	m_UO2CC	%_UO2CC	m_UO2(C	%_UO2(C	m_UO2(C	%_UO2(C	m_(UO2)2	%_(UO2)2	m_UO2OH	%_UO2OH	m_UO2(OI	%_UO2(OI	m_UO2(OI	%_UO2(OI	m_UO2(OI	%_UO2(OI	m_UO2(OI	%_UO2(OI	m_(UO2)2	%_(UO2)2	m_(UO2)3	%m_(UO2)3(OH)5+	total
4.00	16.6157	9.11E-08	91.13	6.24E-09	6.24	3.26E-12	0.00	3.77E-18	0.00	8.73E-26	0.00	3.95E-18	0.00	2.61E-09	2.61	6.33E-12	0.01	2.59E-15	0.00	8.99E-25	0.00	6.69E-13	0.00	1.17E-18	0.00		100.00
4.25	16.3657	8.93E-08	89.30	6.12E-09	6.12	1.01E-11	0.01	3.70E-17	0.00	2.70E-24	0.00	6.75E-17	0.00	4.55E-09	4.55	1.96E-11	0.02	1.43E-14	0.00	8.81E-24	0.00	2.03E-12	0.00	1.96E-17	0.00		100.00
4.50	16.1157	8.62E-08	86.18	5.91E-09	5.91	3.08E-11	0.03	3.57E-16	0.00	8.25E-23	0.00	1.12E-15	0.00	7.81E-09	7.81	5.99E-11	0.06	7.76E-14	0.00	8.50E-23	0.00	5.98E-12	0.01	3.14E-16	0.00		100.00
4.75	15.8657	8.11E-08	81.08	5.56E-09	5.56	9.17E-11	0.09	3.36E-15	0.00	2.45E-21	0.00	1.76E-14	0.00	1.31E-08	13.06	1.78E-10	0.18	4.10E-13	0.00	8.00E-22	0.00	1.67E-11	0.03	4.65E-15	0.00		100.00
5.00	15.6157	7.32E-08	73.16	5.01E-09	5.01	2.62E-10	0.26	3.03E-14	0.00	7.01E-20	0.00	2.55E-13	0.00	2.10E-08	20.96	5.08E-10	0.51	2.08E-12	0.00	7.22E-21	0.00	4.31E-11	0.09	6.08E-14	0.00		100.00
5.25	15.3657	6.19E-08	61.93	4.24E-09	4.24	7.00E-10	0.70	2.56E-13	0.00	1.88E-18	0.00	3.25E-12	0.01	3.16E-08	31.55	1.36E-09	1.36	9.91E-12	0.01	6.11E-20	0.00	9.76E-11	0.20	6.55E-13	0.00		100.00
5.50	15.1157	4.78E-08	47.84	3.28E-09	3.28	1.71E-09	1.71	1.98E-12	0.00	4.58E-17	0.00	3.44E-11	0.07	4.33E-08	43.34	3.32E-09	3.32	4.30E-11	0.04	4.72E-19	0.00	1.84E-10	0.37	5.37E-12	0.02		100.00
5.75	14.8657	3.27E-08	32.73	2.24E-09	2.24	3.70E-09	3.70	1.36E-11	0.01	9.91E-16	0.00	2.87E-10	0.57	5.27E-08	52.74	7.19E-09	7.19	1.66E-10	0.17	3.23E-18	0.00	2.73E-10	0.55	3.06E-11	0.09		100.00
6.00	14.6157	1.91E-08	19.06	1.31E-09	1.31	6.81E-09	6.81	7.89E-11	0.08	1.82E-14	0.00	1.73E-09	3.46	5.46E-08	54.60	1.32E-08	13.24	5.42E-10	0.54	1.88E-17	0.00	2.92E-10	0.58	1.07E-10	0.32		99.99
6.25	14.3657	8.85E-09	8.85	6.06E-10	0.61	1.00E-08	10.01	3.66E-10	0.37	2.68E-13	0.00	6.63E-09	13.25	4.51E-08	45.08	1.94E-08	19.44	1.42E-09	1.42	8.73E-17	0.00	1.99E-10	0.40	1.91E-10	0.57		99.99
6.50	14.1157	3.16E-09	3.16	2.16E-10	0.22	1.13E-08	11.29	1.31E-09	1.31	3.02E-12	0.00	1.50E-08	30.01	2.86E-08	28.61	2.19E-08	21.94	2.84E-09	2.84	3.12E-16	0.00	8.03E-11	0.16	1.54E-10	0.46		99.99
6.75	13.8657	9.17E-10	0.92	6.28E-11	0.06	1.04E-08	10.37	3.80E-09	3.80	2.78E-11	0.03	2.25E-08	45.01	1.48E-08	14.78	2.01E-08	20.15	4.64E-09	4.64	9.05E-16	0.00	2.14E-11	0.04	6.73E-11	0.20		100.00
7.00	13.6157	2.34E-10	0.23	1.60E-11	0.02	8.35E-09	8.35	9.67E-09	9.67	2.24E-10	0.22	2.59E-08	51.88	6.69E-09	6.69	1.62E-08	16.22	6.64E-09	6.64	2.30E-15	0.00	4.39E-12	0.01	1.98E-11	0.06		100.00
7.25	13.3657	5.30E-11	0.05	3.63E-12	0.00	5.99E-09	5.99	2.20E-08	21.95	1.61E-09	1.61	2.38E-08	47.55	2.70E-09	2.70	1.16E-08	11.65	8.48E-09	8.48	5.23E-15	0.00	7.15E-13	0.00	4.11E-12	0.01		100.00
7.50	13.1157	9.89E-12	0.01	6.77E-13	0.00	3.53E-09	3.53	4.09E-08	40.94	9.49E-09	9.49	1.47E-08	29.38	8.95E-10	0.90	6.86E-09	6.86	8.89E-09	8.89	9.75E-15	0.00	7.86E-14	0.00	4.73E-13	0.00		100.00
7.75	12.8658	1.16E-12	0.00	7.91E-14	0.00	1.31E-09	1.31	4.79E-08	47.86	3.51E-08	35.13	3.57E-09	7.14	1.86E-10	0.19	2.54E-09	2.54	5.84E-09	5.84	1.14E-14	0.00	3.40E-15	0.00	1.34E-14	0.00		100.00
8.00	12.6158	7.02E-14	0.00	4.80E-15	0.00	2.51E-10	0.25	2.91E-08	29.08	6.77E-08	67.70	2.34E-10	0.47	2.01E-11	0.02	4.87E-10	0.49	2.00E-09	2.00	6.93E-15	0.00	3.96E-17	0.00	5.34E-17	0.00		100.00
8.25	12.3658	2.86E-15	0.00	1.95E-16	0.00	3.22E-11	0.03	1.18E-08	11.83	8.76E-08	87.60	6.86E-12	0.01	1.45E-12	0.00	6.25E-11	0.06	4.56E-10	0.46	2.82E-15	0.00	2.07E-19	0.00	6.37E-20	0.00		100.00
8.50	12.1158	9.79E-17	0.00	6.65E-18	0.00	3.47E-12	0.00	4.05E-09	4.05	9.59E-08	95.85	1.42E-13	0.00	8.81E-14	0.00	6.75E-12	0.01	8.75E-11	0.09	9.65E-16	0.00	7.64E-22	0.00	4.50E-23	0.00		100.00
8.75	11.8659	3.12E-18	0.00	2.11E-19	0.00	3.48E-13	0.00	1.29E-09	1.29	9.87E-08	98.69	2.54E-15	0.00	4.97E-15	0.00	6.76E-13	0.00	1.56E-11	0.02	3.08E-16	0.00	2.44E-24	0.00	2.55E-26	0.00		100.00
9.00	11.616	9.54E-20	0.00	6.34E-21	0.00	3.31E-14	0.00	3.95E-10	0.39	9.96E-08	99.60	4.11E-17	0.00	2.67E-16	0.00	6.43E-14	0.00	2.65E-12	0.00	9.40E-17	0.00	7.10E-27	0.00	1.24E-29	0.00		100.00
9.25	11.3663	2.75E-21	0.00	1.77E-22	0.00	2.92E-15	0.00	1.14E-10	0.11	9.99E-08	99.88	5.72E-19	0.00	1.34E-17	0.00	5.67E-15	0.00	4.19E-13	0.00	2.70E-17	0.00	1.80E-29	0.00	4.82E-33	0.00		99.99
9.50	11.1171	6.90E-23	0.00	4.09E-24	0.00	2.15E-16	0.00	2.85E-11	0.03	1.00E-07	99.95	5.60E-21	0.00	5.63E-19	0.00	4.16E-16	0.00	5.58E-14	0.00	6.78E-18	0.00	3.30E-32	0.00	1.10E-36	0.00		99.98
9.75	10.8697	1.22E-24	0.00	5.87E-26	0.00	9.82E-18	0.00	5.01E-12	0.01	9.99E-08	99.91	2.18E-23	0.00	1.52E-20	0.00	1.90E-17	0.00	4.75E-15	0.00	1.19E-18	0.00	2.61E-35	0.00	0.00E+00	0.00		99.91
10.00	10.6355	8.19E-27	0.00	2.23E-28	0.00	1.21E-19	0.00	3.27E-13	0.00	9.93E-08	99.30	6.56E-27	0.00	1.21E-22	0.00	2.32E-19	0.00	1.16E-16	0.00	7.53E-20	0.00	2.02E-39	0.00	0.00E+00	0.00		99.30

U(VI), PHREEQC, 2.6

pH	pe	m_NpO2+	%_NpO2+	m_NpO2OH	%_NpO2O	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	m_NpO2(C	%_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	99.98
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	99.99
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

Np(V), MINTEQA2, 4.02

pH	pe	m_UO2+2	%_UO2+2	m_UO2NC	%_UO2NC	m_UO2CO	%_UO2CC	m_UO2(C	%_UO2(C	m_UO2(C	%_UO2(C	m_(UO2)2	%_(UO2)2	m_UO2OH	%_UO2OH	m_UO2(OH	%_UO2(OH	m_UO2(OH	%_UO2(OH	m_UO2(OH	%_UO2(OH	m_(UO2)2	%_(UO2)2	m_(UO2)3	%m_(UO2)3(OH)5+	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	2.46E-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	2.26E-17	0.00	100.00
4.50	16.11	8.55E-08	85.46	6.34E-09	6.34	3.26E-11	0.03	3.76E-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	9.69E-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	0.02	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	3.13E-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	8.65E-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	8.53E-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-08	48.18	2.66E-09	2.66	1.14E-08	11.37	8.35E-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-08	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	0.00	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

U(VI), MINTEQA2, 4.02

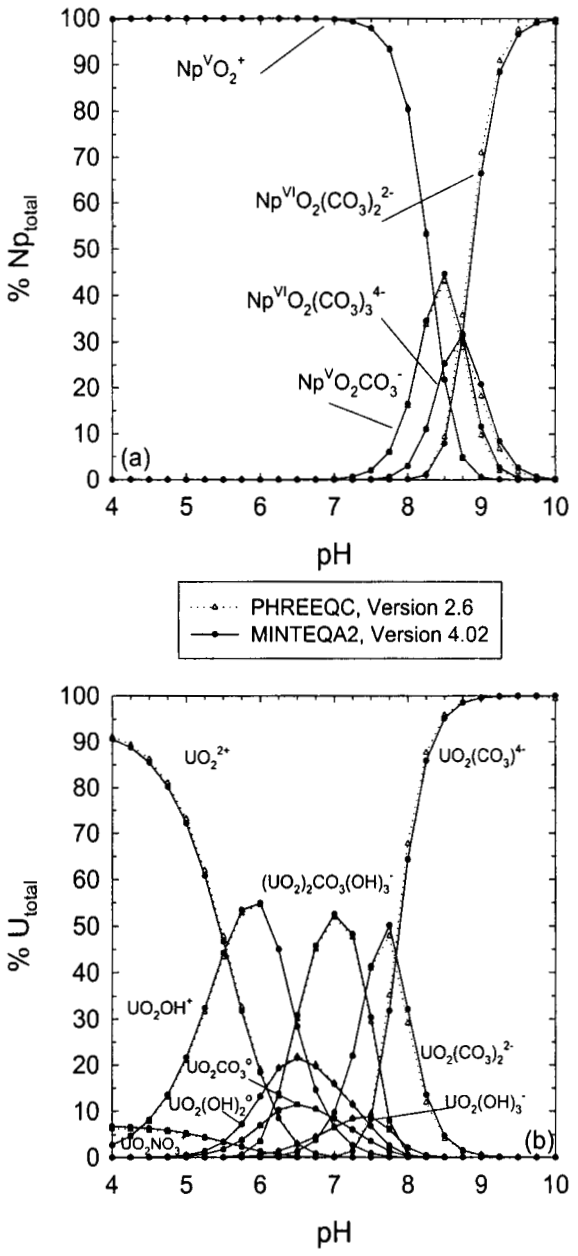
Comparison of PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 Results for Neptunium Speciation as a Function of pH. Np_{total} = 10^{-7} M, 0.1 M $NaNO_3$, T = 25 °C, $P_{CO2} = 10^{-3.5}$ atm, $P_{O2} = 10^{-0.66}$ atm. Both Np(V) and Np(VI) Are Present, as Indicated.

	Percent (%) of Total Neptunium							
pH	$Np^{V}O_2^{+}$ MINTEQA2	$Np^{V}O_2^{+}$ PHREEQC	$Np^{V}O_2CO_3^{-}$ MINTEQA2	$Np^{V}O_2CO_3^{-}$ PHREEQC	$Np^{VI}O_2(CO_3)_2^{2-}$ MINTEQA2	$Np^{VI}O_2(CO_3)_2^{2-}$ PHREEQC	$Np^{VI}O_2(CO_3)_3^{4-}$ MINTEQA2	$Np^{VI}O_2(CO_3)_3^{4-}$ PHREEQC
4.00	99.77	99.77	0.00	0.00	0.00	0.00	0.00	0.00
4.25	99.87	99.87	0.00	0.00	0.00	0.00	0.00	0.00
4.50	99.92	99.92	0.00	0.00	0.00	0.00	0.00	0.00
4.75	99.95	99.95	0.00	0.00	0.00	0.00	0.00	0.00
5.00	99.97	99.97	0.00	0.00	0.00	0.00	0.00	0.00
5.25	99.98	99.98	0.00	0.00	0.00	0.00	0.00	0.00
5.50	99.98	99.98	0.00	0.00	0.00	0.00	0.00	0.00
5.75	99.99	99.99	0.00	0.00	0.00	0.00	0.00	0.00
6.00	99.99	99.99	0.00	0.00	0.00	0.00	0.00	0.00
6.25	99.98	99.98	0.01	0.01	0.00	0.00	0.00	0.00
6.50	99.97	99.97	0.02	0.02	0.00	0.00	0.00	0.00
6.75	99.92	99.92	0.06	0.06	0.00	0.00	0.00	0.00
7.00	99.78	99.78	0.20	0.20	0.00	0.00	0.00	0.00
7.25	99.31	99.33	0.64	0.62	0.02	0.02	0.00	0.00
7.50	97.85	97.91	2.01	1.95	0.11	0.11	0.00	0.00
7.75	93.29	93.46	6.05	5.88	0.61	0.61	0.01	0.01
8.00	80.41	80.78	16.47	16.06	2.95	2.97	0.09	0.11
8.25	53.27	53.70	34.52	33.77	10.99	11.11	1.08	1.27
8.50	21.80	21.75	44.66	43.25	25.31	25.36	7.90	9.29
8.75	4.84	4.58	31.35	28.82	31.66	30.21	31.53	35.75
9.00	0.56	0.48	11.50	9.64	20.74	18.17	66.49	71.02
9.25	0.04	0.03	2.59	1.94	8.38	6.67	88.47	90.88
9.50	0.00	0.00	0.45	0.28	2.63	1.80	96.62	97.65
9.75	0.00	0.00	0.06	0.02	0.68	0.32	99.10	99.44
10.00	0.00	0.00	0.01	0.00	0.15	0.02	99.75	99.16

Comparison of PHREEQC, Version 2.6 and MINTEQA2, Version 4.02 Results for Uranium Speciation as a Function of pH. $U_{total} = 10^{-7}$ M, 0.1 M $NaNO_3$, T = 25 °C, $P_{CO2} = 10^{-3.5}$ atm, $P_{O2} = 10^{-0.66}$ atm. All Uranium Species are U(VI), the Dominant Uranium Species Over the Entire pH Range.

	Percent (%) of Total Uranium											
pH	UO_2^{2+} MINTEQA2	UO_2^{2+} PHREEQC	$UO_2(CO_3)_2^{-2}$ MINTEQA2	$UO_2(CO_3)_2^{2-}$ PHREEQC	$UO_2(CO_3)_3^{4-}$ MINTEQA2	$UO_2(CO_3)_3^{4-}$ PHREEQC	$(UO_2)_2CO_3(OH)_3^-$ MINTEQA2	$(UO_2)_2CO_3(OH)_3^-$ PHREEQC	UO_2OH^+ MINTEQA2	UO_2OH^+ PHREEQC	$UO_2(OH)_2(aq)$ MINTEQA2	$UO_2(OH)_2(aq)$ PHREEQC
4.00	90.56	91.13	0.00	0.00	0.00	0.00	0.00	0.00	2.71	2.61	0.01	0.01
4.25	88.67	89.30	0.00	0.00	0.00	0.00	0.00	0.00	4.72	4.55	0.02	0.02
4.50	85.46	86.18	0.00	0.00	0.00	0.00	0.00	0.00	8.09	7.81	0.06	0.06
4.75	80.22	81.08	0.00	0.00	0.00	0.00	0.00	0.00	13.51	13.06	0.18	0.18
5.00	72.15	73.16	0.00	0.00	0.00	0.00	0.00	0.00	21.60	20.96	0.52	0.51
5.25	60.78	61.93	0.00	0.00	0.00	0.00	0.01	0.01	32.36	31.55	1.38	1.36
5.50	46.67	47.84	0.00	0.00	0.00	0.00	0.07	0.07	44.19	43.34	3.36	3.32
5.75	31.72	32.73	0.01	0.01	0.00	0.00	0.62	0.57	53.41	52.74	7.22	7.19
6.00	18.33	19.06	0.08	0.08	0.00	0.00	3.65	3.46	54.89	54.60	13.20	13.24
6.25	8.44	8.85	0.37	0.37	0.00	0.00	13.78	13.25	44.96	45.08	19.23	19.44
6.50	2.99	3.16	1.32	1.31	0.00	0.00	30.76	30.01	28.32	28.61	21.54	21.94
6.75	0.86	0.92	3.80	3.80	0.02	0.03	45.72	45.01	14.56	14.78	19.70	20.15
7.00	0.22	0.23	9.66	9.67	0.19	0.22	52.50	51.88	6.58	6.69	15.83	16.22
7.25	0.05	0.05	21.95	21.95	1.39	1.61	48.18	47.55	2.66	2.70	11.37	11.65
7.50	0.01	0.01	41.31	40.94	8.26	9.49	30.34	29.38	0.89	0.90	6.77	6.86
7.75	0.00	0.00	50.14	47.86	31.72	35.13	7.95	7.14	0.19	0.19	2.60	2.54
8.00	0.00	0.00	32.11	29.08	64.31	67.70	0.58	0.47	0.02	0.02	0.53	0.49
8.25	0.00	0.00	13.52	11.83	85.84	87.60	0.02	0.01	0.00	0.00	0.07	0.06
8.50	0.00	0.00	4.72	4.05	95.17	95.85	0.00	0.00	0.00	0.00	0.01	0.01
8.75	0.00	0.00	1.53	1.29	98.45	98.69	0.00	0.00	0.00	0.00	0.00	0.00
9.00	0.00	0.00	0.48	0.39	99.52	99.60	0.00	0.00	0.00	0.00	0.00	0.00
9.25	0.00	0.00	0.15	0.11	99.85	99.88	0.00	0.00	0.00	0.00	0.00	0.00
9.50	0.00	0.00	0.04	0.03	99.96	99.95	0.00	0.00	0.00	0.00	0.00	0.00
9.75	0.00	0.00	0.01	0.01	99.99	99.91	0.00	0.00	0.00	0.00	0.00	0.00
10.00	0.00	0.00	0.00	0.00	100.00	99.30	0.00	0.00	0.00	0.00	0.00	0.00

5/6/03



Aqueous Speciation Predicted by PHREEQC, Version 2.6 (dotted line, open triangles) and MINTEQA2, Version 4.02 (solid line, filled circles) as a Function of pH. T = 25 °C, $P_{CO_2} = 10^{-3.5}$ atm $P_{CO_2} = 10^{-0.66}$ 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.

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Validation of FITEQL, Version 2.0

5/23/2003

DBS

SCOPE OF THE VALIDATION

FITEQL, Version 2.0 is an acquired code, originally developed by John Westall in the Department of Chemistry at Oregon State University. It has been broadly used in the geochemical and chemical communities to derive parameters for aqueous equilibria and sorption models (e.g., Dzombak and Morel, 1990). The software is used by staff at the Center for Nuclear Waste Regulatory Analyses (CNWRA) to provide technical assistance to the U.S. Nuclear Regulatory Commission (NRC) in its high-level waste program. The model most commonly used by CNWRA staff is the diffuse layer model (DLM). Other surface complexation models such as the constant capacitance and triple layer models are not commonly used and will therefore not be tested at this time. If a decision is made to use these models or other code capabilities, the software validation test plan will be modified and the FITEQL will be validated as necessary.

This work is intended to validate FITEQL, Version 2.0 for use in modeling geochemical equilibrium reactions as identified in the test cases described below. FITEQL, Version 2.0 is currently under configuration control in accordance with Technical Operating Procedure (TOP)-018.

DBS 05/23/2003

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TEST CASES

In this validation exercise, FITEQL, Version 2.0 was used to interpret a sorption data set with an electrostatic DLM approach, and the model results compared against the experimental data.

In addition to testing code function against experimental data, another part of the software validation is to test results from FITEQL, Version 2.0 against results from another geochemical speciation code such as MINTEQA2, Version 4.02 (EPA, 1999a,b). If the results are in agreement, this will build confidence in the capabilities of each code.

Comparison to Experimental Sorption Data

FITEQL, Version 2.0 was used to interpret experimental data for Np(V) sorption on hematite (Kohler et al., 1999). For the purposes of this validation, the modeling approach was simplified, to the extent possible, with a two-site electrostatic DLM invoking strong ($>XOH_s^0$) and weak ($>XOH_w^0$) sorption sites as described in Dzombak and Morel (1990). The sites were assumed to protonate and deprotonate according to the reactions:

$$>XOH^0 + H^+ = >XOH_2^+ \qquad \text{Log } K^+$$

$$>XOH^0 = >XO^- + H^+ \qquad \text{Log } K^-$$

Protonation (Log K^+) and deprotonation (log K^-) constants for both site types were assumed to be equal and set at values determined for the NEA sorption exercise, Test Case 1 (Turner, 2002b).

The Np(V)-hematite sorption data of Kohler et al. (1999) for CO_2-free atmosphere, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$, and $Np(V)_{total} = 1.24 \times 10^{-6}$ M was selected for optimization using FITEQL, Version 2.0 (Table 2). 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 $>XOH_s^0$ site type.

A single type of mononuclear, monodentate sorption reaction was assumed to form on both sorption sites:

$$>XOH_s^0 + NpO_2^+ = >XO_s\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOs\text{-}NpO2}$$

$$>XOH_w^0 + NpO_2^+ = >XO_w\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOw\text{-}NpO2}$$

FITEQL, Version 2.0 was used to solve for the binding constants (Log K values) for the postulated sorption reactions. Additional input data include the surface protonation/deprotonation constants and site concentrations determined from the potentiometric titration data and the NEA thermodynamic database (Lemire et al., 2001). Ionic strength corrections for the mass-based equilibria were determined using the Davies Equation as identified in Dzombak and Morel (1990, Table 2.13).

5/23/2003
CDB

Table 1. Input parameters for FITEQL, Version 2.0 and MINTEQA2, Version 4.02 simulations for Np(V) sorption on hematite.

Surface Species	Log K	T_{XOH} (mol sites/m^2)	Source
$>XOH_s^0 + H^+ = >XOH_2^+$	10.21	—	Turner (2002b)
$>XOH_s^0 = >XO^- + H^+$	-9.56	—	Turner (2002b)
$>XOH_s^0$	—	1.81E-07	Turner (2002b)
$>XOH_w^0 + H^+ = >XOH_2^+$	10.21	—	Turner (2002b)
$>XOH_w^0 = >XO^- + H^+$	-9.56	—	Turner (2002b)
$>XOH_w^0$	—	2.51E-06	Turner (2002b)
$>XOH_s^0 + NpO_2^+ = >XO_s\text{-}NpO_2^0 + H^+$	-0.44	—	This study
$>XOH_w^0 + NpO_2^+ = >XO_w\text{-}NpO_2^0 + H^+$	-3.62	—	This study

CDB 5/23/2003

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DRD

Validation Np(V)-hematite sorption. FITEQL, Version 2.0 input file for Np(V) sorption on hematite.

```
          1                                                          Neptunum
          1                                                             on
          1                                                          Hematite
          1                                                          1.6s\nm2
          1                                                          No CO2
         90                                                          I=0.10
          4          1          3          1                        np=1e-6
00001  -6.584 2.61E-7   xoh(str)                                     14.4m2/g
00002  -4.440 3.61E-6   xoh(weak)                                    0.1 g/l
00160  -2.0   0.00E00   psi0                                         00000095
00031  -5.91  1.24E-6   npo2+                                        00000098
00032   0.0   0.00E00   npo2(ads)                                    00000100
00050   0.0   0.00E00   h+                                           00000102
00003  -1.00  0.00E00   na+                                          00000104
00005  -1.00  0.00E00   clo4-                                        00000106
                                                                     00000110
00001    0.00  001  1                                                xoh(s)
00002    0.00  002  1                                                xoh(w)
00050    0.00  050  1                                                h+
00031    0.00  031  1                                                npo2+
00003    0.00  003  1                                                na+
00005    0.00  005  1                                                clo4-
03100  -11.30  031  1 050 -1                                         npo2oh
03101  -23.38  031  1 050 -2                                         npo2oh2
00100  -13.78  050 -1                                                h2o diss
01050    9.45  001  1 160  1 050  1                                  xoh2+(s)
01100  -10.13  001  1 160 -1 050 -1                                  xo-(s)
02050    9.45  002  1 160  1 050  1                                  xoh2+(w)
02100  -10.13  002  1 160 -1 050 -1                                  xo-(w)
03201    0.500 001  1 160  0 050 -1 031  1 032  1                    xos-npo2
03202   -3.250 002  1 160  0 050 -1 031  1 032  1                    xow-npo2
                                                                     00000174
                                                                     00000175
00002   014.4 0.100                                                  00000180
0.10   1.0                                                           00000185
          2          1                                               00000190
       3201                                                          00000195
       3202                                                          00000195
        001                                                          00000195
          9          1          1          0                        00000230
         32
1.00E-07
9.00E-08
1.90E-07
2.53E-07
1.90E-07
2.88E-07
4.08E-07
6.77E-07
7.60E-07
         50
-6.740
-6.870
-7.340
-7.360
-7.590
-7.860
-8.420
-9.210
-9.660
          1          1
         32       0.10   1.0E-09                                     10%error
         50       0.05   0.0E-00                                     +/- 0.02
```

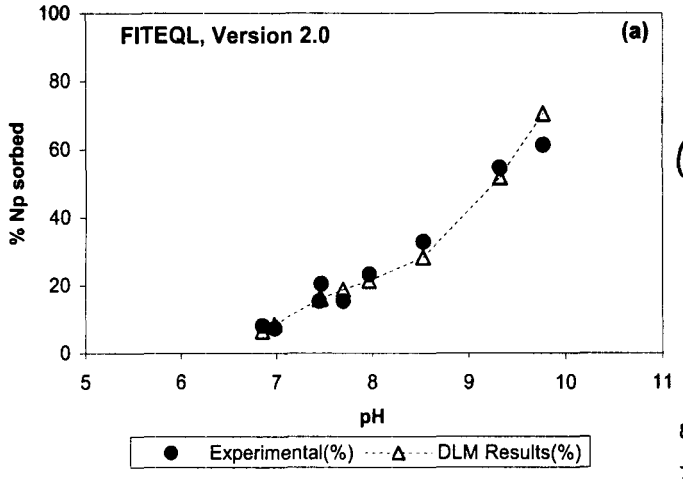
All Log K adjusted to I=0.1 m

Note: This input file is constructed to optimize on the experimental data and derive binding constants (log K) for the formation of XO(s)-NpO_2^0 (Species 3201) and XO(w)-NpO_2^0 (Species 3202). The numbers in the input file are seed values, not the final values determined by the optimization. Also, because the FITEQL calculation is concentration-based rather than activity-based, the Log K values for the chemical equilibrium model have been adjusted to compensate for the ionic strength of the solution (0.1 M $NaClO_4$) using the methods presented in Dzombak and Morel (1990, Table 2.13).

5/23/2003

Table 2. Comparison of sorption results calculated using FITEQL, Version 2.0 with Np(V)-hematite [specific area (A_{sp}) = 14.4 m^2/g] sorption data of Kohler et al. (1999). No CO_2, $Np(V)_{total}$ = 1.24 × 10^{-6} M, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$.

pH	Np(V) dissolved Experiment (M)	Np(V) dissolved FITEQL, Version 2.0 (M)	Np(V) sorbed Experiment (percent)	Np(V) sorbed FITEQL, Version 2.0 (percent)
6.85	1.14e-06	1.16e-06	8.1	6.4
6.98	1.15e-06	1.13e-06	7.3	8.5
7.45	1.05e-06	1.04e-06	15.3	15.9
7.47	9.87e-07	1.04e-06	20.4	16.1
7.70	1.05e-06	1.01e-06	15.3	18.8
7.97	9.52e-07	9.76e-07	23.2	21.3
8.53	8.32e-07	8.90e-07	32.9	28.2
9.32	5.63e-07	5.98e-07	54.6	51.8
9.77	4.80e-07	3.67e-07	61.3	70.4



Comparison of FITEQL, Version 2.0 results of experimental data

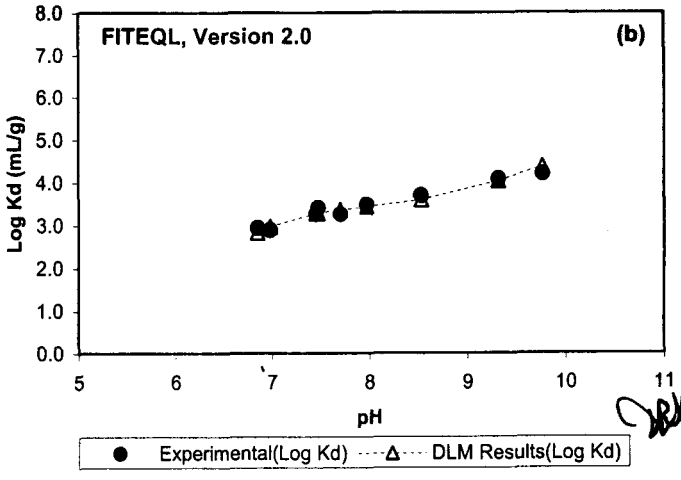


Figure 1. Comparison of sorption results calculated using FITEQL, Version 2.0 with Np(V)-hematite sorption data of Kohler et al. (1999). (a) percent Np(V) sorbed (b) Log K_d sorbed in mL/g.

Comparison to MINTEQA2, Version 4.02

The FITEQL-derived parameters from the data of Kohler et al. (1999) are suitable for use in the DLM model as implemented in MINTEQA2, Version 4.02. The calculated sorption results and aqueous speciation for the Np(V)-H_2O-hematite system were compared to both the experimental data and the model results produced using FITEQL, Version 2.0.

MINTEQA2, Version 4.02 includes surface complexation modeling capabilities that have previously been validated for use in CNWRA technical assistance activities (Turner, 2002a). To test FITEQL, Version 2.0 against MINTEQA2, Version 4.02, the same intensive properties (temperature, pressure) were used, with chemical reactions written in terms of the same component species. The same thermodynamic data (e.g., log K at 298 K) from the Nuclear Energy Agency (NEA) thermodynamic data base for neptunium (Lemire et al., 2001 were used in each code to ensure consistency.

DISCUSSION AND SUMMARY

FITEQL, Version 2.0 does a good job of matching the experimental data of Kohler et al. (1999) over most of the observed pH range. There is some variability in the experimental data that is not captured by the smooth curve calculated by FITEQL, Version 2.0. Results from FITEQL, Version 2.0 also match well with the sorption behavior calculated using MINTEQA2, Version 4.02. Small differences are likely due to differences in how the two codes calculate activity coefficients for the aqueous solution (0.1 M $NaClO_4$). 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):

$$\text{Goodness-of-Fit} = [\text{Log}\,(K_{d,model}/R_{d,experiment})]^2 \qquad [1]$$

Smaller values indicate a better prediction of the observed sorption behavior. The goodness-of-fit calculated using this measure for both FITEQL and MINTEQA2 results is typically small, in most cases ranging from 10^{-4} to 10^{-2} (Table 3). The goodness-of-fit parameters also compare well between the two codes, providing confidence that they are handling the geochemical and sorption equilibria in a comparable manner.

The model is chemically plausible with regard to Np(V) speciation. The dominant Np species is NpO_2^+ for pH up to about 8, and continues to be a significant species over the range of experimental conditions (Turner et al., 1998). The postulated surface reactions are also consistent with Extended X-Ray Absorption Fine Structure (EXAFS) data on Np(V)-sorption on goethite (Combes et al., 1992).

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Validation Np(V)-hematite sorption. MINTEQA2, Version 4.02 input file for Np(V) sorption on hematite. Sorption parameters from FITEQL, Version 2.0 optimization.

```
Np-Hematite Sorption Exp. 6: 0.1 g/L; I=0.1 M NaClO4
No CO2; Np=1.2E-6 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
 9 H+1                    ACTIVITY   mol/L
1 330   1.000
   6.85   6.98   7.45   7.47   7.70   7.97
   8.53   9.32   9.77
kohler99.123 8115520 8125520     552 5523300 5523301
4   1   7
1.000E-01   14.40 0.000 0.000 81
    330  0.000E+00   -5.00 y                    /H+1
    500  1.000E-01   -1.00 y                    /Na+1
    181  1.000E-01   -1.00 y                    /ClO4-
    552  1.240E-06   -5.91 y                    /NpO2+1
    813  0.000E+00    0.00 y                    /ADS1PSIo
    811  2.610E-07   -5.58 y                    /ADS1TYP1
    812  3.610E-06   -4.44 y                    /ADS1TYP2

  3   1
    330     5.0000     0.0000                   /H+1
  6   1
    813     0.0000     0.0000                   /ADS1PSIo

  2   6
8113300 xo(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   0.000   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8115520 xo(s)-npo2      0.0000   -0.4400   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8123300 xo(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   0.000   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   0.000   0
0  0.000   0   0.000   0   0.000   0
8125520 xo(w)-npo2      0.0000   -3.6200   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   0.000   0
0  0.000   0   0.000   0   0.000   0
```

Table 3. Comparison of Np(V)-hematite sorption results and Np(V) aqueous speciation calculated using FITEQL, Version 2.0 and MINTEQA2, Version 4.02. $Np(V)_{total} = 1.24 \times 10^{-6}$ M, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$, and, No CO_2.

	XO(s)-NpO_2^0		XO(w)-NpO_2^0		NpO_2^+		NpO_2OH^0		$NpO_2(OH)_2^-$		Goodness-of-Fit (Equation [1])	
pH	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL	MINTEQA2
6.85	7.89e-08	7.93e-08	1.05e-09	1.04e-09	1.16e-06	1.16e-06	3.20e-11	3.13e-11	1.46e-16	1.45e-16	1.10e-02	1.05e-02
6.98	1.04e-07	1.04e-07	1.60e-09	1.59e-09	1.13e-06	1.13e-06	4.22e-11	4.13e-11	2.60e-16	2.58e-16	5.70e-03	5.94e-03
7.45	1.90e-07	1.91e-07	6.48e-09	6.44e-09	1.04e-06	1.04e-06	1.14e-10	1.12e-10	2.08e-15	2.07e-15	3.19e-04	3.51e-04
7.47	1.93e-07	1.93e-07	6.86e-09	6.82e-09	1.04e-06	1.04e-06	1.19e-10	1.17e-10	2.28e-15	2.26e-15	1.56e-02	1.54e-02
7.70	2.20e-07	2.20e-07	1.28e-08	1.28e-08	1.01e-06	1.01e-06	1.96e-10	1.92e-10	6.36e-15	6.31e-15	1.12e-02	1.13e-02
7.97	2.39e-07	2.39e-07	2.58e-08	2.56e-08	9.75e-07	9.75e-07	3.54e-10	3.47e-10	2.13e-14	2.12e-14	2.25e-03	2.26e-03
8.53	2.55e-07	2.55e-07	9.53e-08	9.48e-08	8.89e-07	8.89e-07	1.17e-09	1.15e-09	2.56e-13	2.55e-13	9.21e-03	9.34e-03
9.32	2.60e-07	2.60e-07	3.83e-07	3.82e-07	5.93e-07	5.94e-07	4.82e-09	4.73e-09	6.50e-12	6.47e-12	2.36e-03	2.54e-03
9.77	2.60e-07	2.60e-07	6.13e-07	6.12e-07	3.59e-07	3.60e-07	8.22e-09	8.08e-09	3.13e-11	3.12e-11	3.12e-02	3.05e-02

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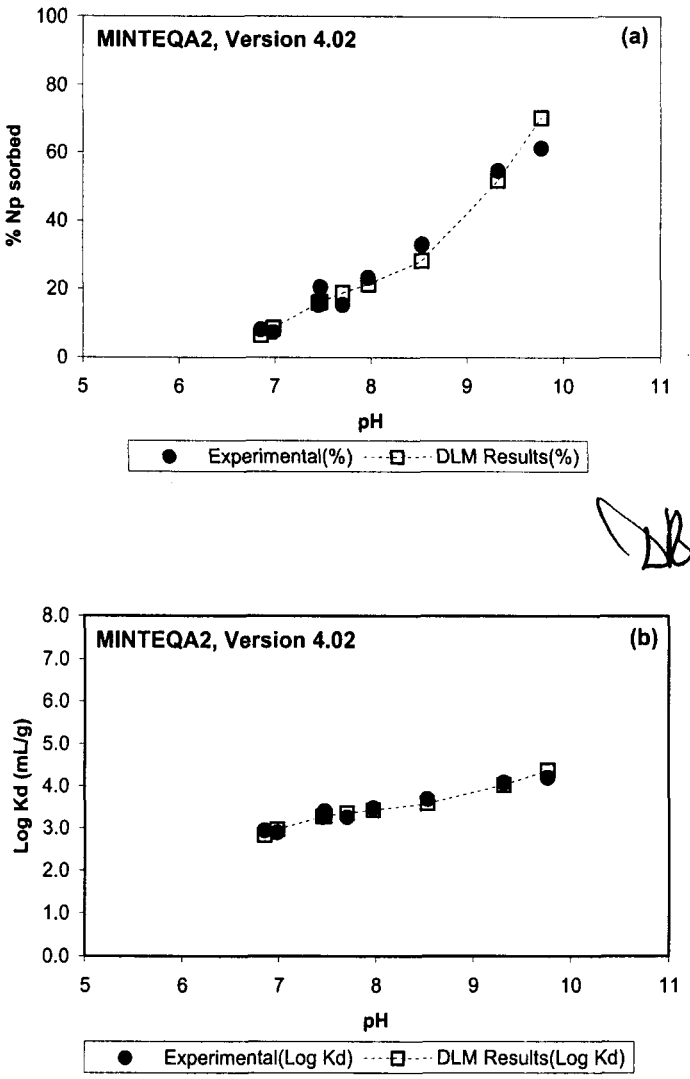

Figure 2. Comparison of sorption results calculated using MINTEQA2, Version 4.02 with Np(V)-hematite sorption data of Kohler et al. (1999). (a) percent Np(V) sorbed (b) Log K_d sorbed in mL/g.

MINTEQA2, Version 4.02 w/ FITEQL-derived parameters

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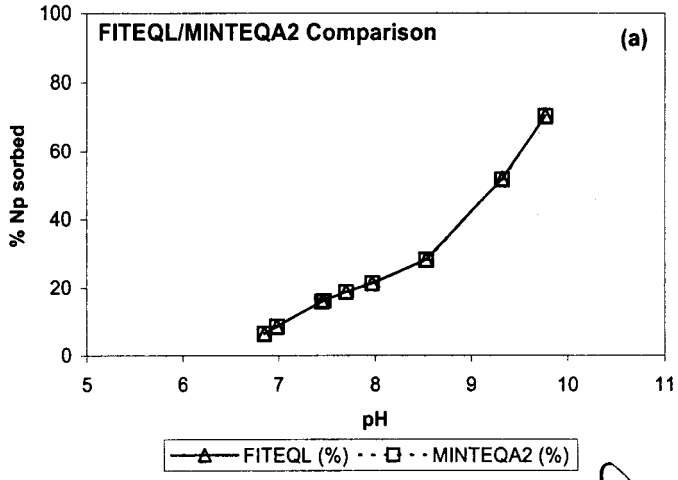

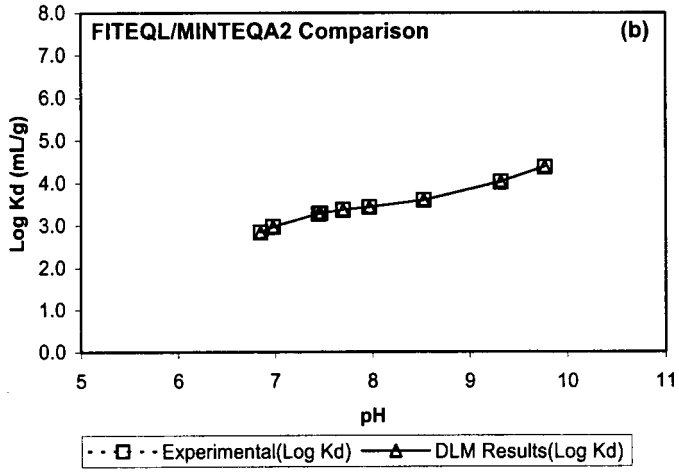

Figure 3. Comparison of Np(V)-hematite sorption sorption results calculated using FITEQL, Version 2.0 and MINTEQA2, Version 4.02. (a) percent Np(V) sorbed (b) Log K_d sorbed in mL/g.

Original Np sorption on hematite data

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.

Datapoint number	Hematite (grams/L)	Total Np concentration (moles/L)	$NaClO_4$ concentration (moles/L)	gas phase equilibrated with	final pH	final dissolved Np	% Np adsorbed	K_d (mL/g)
33.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	6.85	1.14E-06	8.06	877.19
34.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	6.98	1.15E-06	7.26	782.61
35.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	7.45	1.05E-06	15.32	1809.52
36.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	7.47	9.87E-07	20.40	2563.32
37.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	7.70	1.05E-06	15.32	1809.52
38.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	7.97	9.52E-07	23.23	3025.21
39.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	8.53	8.32E-07	32.90	4903.85
40.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	9.32	5.63E-07	54.60	12024.87
41.00	0.10	1.24E-06	0.100	air with <5 ppm CO_2	9.77	4.80E-07	61.29	15633.33

Kohler et al. (1999) data

FITEQL, Version 2.0 Results

DLM with EDL
FITEQL, Version 2.0

	M/V (g/L)	$NaClO_4$ concer	gas phase equilibrated with	Nptotal	pH	Exp Np-Dissolved(M	Exp Np-sorb(%)	Exp Kd(mL/g)	Exp Log Kd	Modeled Total Sorbed (M)	Modeled Np-Dissolved (M)	Modeled Total Sorbed (%)	Modeled Kd (mL/g)	Modeled Log Kd (mL/g)	Goodness of Fit (log(Kd/Rd))^2
33	0.10	0.100	air with <5 ppm CO_2	1.24E-06	6.85	1.14E-06	8.06	877.19	2.94	7.992E-08	1.160E-06	6.4	688.9	2.8	1.16E-02
34	0.10	0.100	air with <5 ppm CO_2	1.24E-06	6.98	1.15E-06	7.26	782.61	2.89	1.056E-07	1.134E-06	8.5	931.2	3.0	5.70E-03
35	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.45	1.05E-06	15.32	1809.52	3.26	1.987E-07	1.043E-06	15.9	1885.5	3.3	3.19E-04
36	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.47	9.87E-07	20.40	2563.32	3.41	2.000E-07	1.040E-06	16.1	1922.4	3.3	1.58E-02
37	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.70	1.05E-06	15.32	1809.52	3.26	2.328E-07	1.007E-06	18.8	2308.7	3.4	1.12E-02
38	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.97	9.52E-07	23.23	3025.21	3.48	2.646E-07	9.755E-07	21.3	2712.3	3.4	2.25E-03
39	0.10	0.100	air with <5 ppm CO_2	1.24E-06	8.53	8.32E-07	32.90	4903.85	3.69	3.500E-07	8.901E-07	28.2	3931.7	3.6	9.21E-03
40	0.10	0.100	air with <5 ppm CO_2	1.24E-06	9.32	5.63E-07	54.60	12024.87	4.08	6.425E-07	5.975E-07	51.8	10752.7	4.0	2.36E-03
41	0.10	0.100	air with <5 ppm CO_2	1.24E-06	9.77	4.80E-07	61.29	15633.33	4.20	8.729E-07	3.671E-07	70.4	23781.4	4.4	3.12E-02

	3201 >feo(s)-npo2 (M)	3202 >feo(w)-npo2 (M)	31 npo2+ (M)	3100 npo2oh (M)	3101 npo2(oh)2- (M)	Total Np (M)	3201 >feo(s)-npo2 (%)	3202 >feo(w)-npo2 (%)	31 npo2+ (%)	3100 npo2oh (%)	3101 npo2(oh)2- (%)	Total Np (%)
33	7.69E-08	1.05E-09	1.16E-06	3.20E-11	1.46E-16	1.240E-06	6.4	0.1	93.6	0.0	0.0	100.0
34	1.04E-07	1.60E-09	1.13E-06	4.22E-11	2.60E-16	1.240E-06	8.4	0.1	91.5	0.0	0.0	100.0
35	1.90E-07	6.48E-09	1.04E-06	1.14E-10	2.08E-15	1.240E-06	15.3	0.5	84.1	0.0	0.0	100.0
36	1.93E-07	6.86E-09	1.04E-06	1.19E-10	2.28E-15	1.240E-06	15.6	0.6	83.9	0.0	0.0	100.0
37	2.20E-07	1.28E-08	1.01E-06	1.96E-10	6.36E-15	1.240E-06	17.7	1.0	81.2	0.0	0.0	100.0
38	2.39E-07	2.58E-08	9.75E-07	3.54E-10	2.13E-14	1.240E-06	19.3	2.1	78.6	0.0	0.0	100.0
39	2.55E-07	9.53E-08	8.89E-07	1.17E-09	2.50E-13	1.240E-06	20.5	7.7	71.7	0.1	0.0	100.0
40	2.80E-07	3.83E-07	5.93E-07	4.82E-09	9.50E-12	1.240E-06	20.9	30.9	47.8	0.4	0.0	100.0
41	2.80E-07	6.13E-07	3.59E-07	8.22E-09	3.13E-11	1.240E-06	21.0	49.4	28.9	0.7	0.0	100.0

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~~FITEQL~~, MINTEQA2, Version 4.02 Results

DLM with EDL
MINTEQA2, Version 4.02

	M/V (g/L)	$NaClO_4$ concer	gas phase equilibrated with	Nptotal	pH	Exp Np-Dissolved(M	Exp Np-sorb(%)	Exp Kd(mL/g)	Exp Log Kd	Modeled Total Sorbed (M)	Modeled Np-Dissolved (M)	Modeled Total Sorbed (%)	Modeled Kd (mL/g)	Modeled Log Kd (mL/g)	Goodness of Fit (log(Kd/Rd))^2
33	0.10	0.100	air with <5 ppm CO_2	1.24E-06	6.85	1.14E-06	8.06	877.19	2.94	8.032E-08	1.160E-06	6.5	692.4	2.8	1.06E-02
34	0.10	0.100	air with <5 ppm CO_2	1.24E-06	6.98	1.15E-06	7.26	782.61	2.89	1.060E-07	1.134E-06	8.5	934.8	3.0	5.94E-03
35	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.45	1.05E-06	15.32	1809.52	3.26	1.970E-07	1.043E-06	15.9	1889.0	3.3	3.48E-04
36	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.47	9.87E-07	20.40	2563.32	3.41	2.002E-07	1.040E-06	16.1	1924.9	3.3	1.55E-02
37	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.70	1.05E-06	15.32	1809.52	3.26	2.328E-07	1.007E-06	18.8	2310.8	3.4	1.13E-02
38	0.10	0.100	air with <5 ppm CO_2	1.24E-06	7.97	9.52E-07	23.23	3025.21	3.48	2.645E-07	9.754E-07	21.3	2711.8	3.4	2.26E-03
39	0.10	0.100	air with <5 ppm CO_2	1.24E-06	8.53	8.32E-07	32.90	4903.85	3.69	3.496E-07	8.904E-07	28.2	3925.7	3.6	9.34E-03
40	0.10	0.100	air with <5 ppm CO_2	1.24E-06	9.32	5.63E-07	54.60	12024.87	4.08	6.412E-07	5.987E-07	51.7	10709.2	4.0	2.63E-03
41	0.10	0.100	air with <5 ppm CO_2	1.24E-06	9.77	4.80E-07	61.29	15633.33	4.20	8.718E-07	3.682E-07	70.3	23676.5	4.4	3.03E-02

	8115520 >feo(s)-npo2 (M)	8125520 >feo(w)-npo2 (M)	552 npo2+ (M)	5523300 npo2oh (M)	5523301 npo2(oh)2- (M)	Total Np (M)	8115520 >feo(s)-npo2 (%)	8125520 >feo(w)-npo2 (%)	552 npo2+ (%)	5523300 npo2oh (%)	5523301 npo2(oh)2- (%)	Total Np (%)
33	7.93E-08	1.04E-09	1.16E-06	3.13E-11	1.45E-16	1.240E-06	6.4	0.1	93.5	0.0	0.0	100.0
34	1.04E-07	1.59E-09	1.13E-06	4.13E-11	2.58E-16	1.240E-06	8.4	0.1	91.4	0.0	0.0	100.0
35	1.91E-07	6.44E-09	1.04E-06	1.12E-10	2.07E-15	1.240E-06	15.4	0.5	84.1	0.0	0.0	100.0
36	1.93E-07	6.82E-09	1.04E-06	1.17E-10	2.26E-15	1.240E-06	15.6	0.5	83.8	0.0	0.0	100.0
37	2.20E-07	1.28E-08	1.01E-06	1.92E-10	6.31E-15	1.240E-06	17.7	1.0	81.2	0.0	0.0	100.0
38	2.39E-07	2.56E-08	9.75E-07	3.47E-10	2.12E-14	1.240E-06	19.3	2.1	78.6	0.0	0.0	100.0
39	2.55E-07	9.48E-08	8.89E-07	1.15E-09	2.55E-13	1.240E-06	20.5	7.6	71.7	0.1	0.0	100.0
40	2.80E-07	3.82E-07	5.94E-07	4.73E-09	6.47E-12	1.240E-06	20.9	30.8	47.9	0.4	0.0	100.0
41	2.80E-07	6.12E-07	3.60E-07	8.08E-09	3.12E-11	1.240E-06	21.0	49.3	29.0	0.7	0.0	100.0

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