Uranyl Adsorption onto Hydrous Ferric Oxide—A Re-Evaluation for the Diffuse Layer Model Database

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The diffuse layer model (DLM) database of Dzombak and Morel was developed to quantify the adsorption of dissolved species onto the hydrous ferric oxide (HFO) surface, and contained numerous surface complexation reactions, including surface complexation reactions for uranyl (UO₂⁺²) consisting of Hfo_sUO₂⁺ and Hfo_wUO₂⁺. However, these constants were not based upon experimentally obtained data, but rather were derived from linear free energy relationships (LFER) using log KMOH values. When compared to experimental data, the LFER-derived constants for uranyl were shown to overestimate adsorption by a factor of 10 in some cases. At least 14 uranyl HFO data sets have been previously published and were used to re-estimate constants by coupling the geochemical computer code PHREEQC with UCODE_2005, an automated parameter optimization program. Five uranyl-bearing surface complexation reactions were initially evaluated; the constants were optimized by allowing UCODE to incrementally vary selected log Kx values until the best fit to the experimental data was obtained. Assumptions consistent with the original DLM were retained. Changes to the KMOH and Kint values for uranyl monocarbonate and uranyl dicarbonate surface complexes, will update and correct the uranyl sorption reactions in this widely used database.

Introduction

Predicting the fate and mobility of uranium in groundwater is important in the licensing and decommissioning of uranium mills and associated tailings management facilities. Under oxidizing conditions, uranyl [U(VI)] is the dominant form of uranium, and most uranyl-bearing minerals (such as schoepite) are relatively soluble (1). Consequently, models used to describe the behavior of uranyl in groundwater rely predominantly upon adsorption processes. Thus, accurate sorption constants for the modeling of uranium are critical to uranium processing facility environmental assessments.

A significant amount of experimental work has been performed to quantify and describe the behavior of uranyl in these systems (2–9). During the past 25 years, numerous surface ionization and complexation models, and resultant databases, have been developed that describe trace metal adsorption onto surfaces such as hydrous ferric oxide (HFO) or ferrihydrate, as well as goethite, quartz, and clays. One database that has achieved a large degree of usage was developed by Dzombak and Morel (10) (D&M). In their seminal work, previously published adsorption data sets were evaluated and surface complexation reactions were defined assuming that a diffuse layer model (DLM) described the charge potential relationships on the HFO surface. The model developed from their effort was based upon a series of well-considered parameters, such as surface site densities and surface areas. The utility of this database is evident in its inclusion in numerous modeling packages such as PHREEQC, MINTEQA2, and Geochemist’s Workbench (11–13).

The original constants provided with the D&M database that quantified the adsorption of the uranyl ion (UO₂⁺²) onto HFO were not based upon fitting experimental results, but rather used correlations between the constant for the formation of various metal hydroxides (MeOH⁺), and surface complexation constants for cation complexation on strong (Hfo_sOH) and weak (Hfo_wOH) surface sites. Using their linear free energy relationship (LFER), and a log KMOH of 8.2 for the UO₂(OH)⁺ complex, D&M calculated log K values for Hfo_sUO₂⁺ (log K¹INT of 5.2) and Hfo_wUO₂⁺ (log K²INT of 2.8).

Hfo_sOH + UO₂⁺² = Hfo_sUO₂⁺ + H⁺ K¹INT
Hfo_wOH + UO₂⁺² = Hfo_wUO₂⁺ + H⁺ K²INT

As part of a solute transport model developed for licensing a uranium mill tailings facility, the LFER-derived parameters were initially compared to two different sets of experimental data. Unfortunately, the LFER-derived constants show poor agreement with these two data sets (Figures 1 and 2). The D&M model parameters tended to overpredict the amount of adsorption under low-pH conditions and under-predict the amount of adsorption under high-pH conditions. The failure of the uranyl surface complexation constants developed by D&M to agree with experimental data may be related to the fact that the ions used to develop the LFER correlation were all simple mononuclear cations whereas uranyl is an oxygen-bearing polynuclear cation. Additionally, the log KMOH value of 8.2 for the UO₂(OH)⁺ complex, which was obtained

FIGURE 1. Comparison of Hsi’s (2) experimentally derived measurements of uranyl uptake onto HFO to DLM calculations using LFER-derived constants of D&M uranyl surface complexation reactions (model fits shown by dashed lines); based upon 10⁻³ m U(VI) sorbed onto 0.15 (triangles) and 1 g/L (lined X’s) of ferrihydrate in a 0.1 NaNO₃ solution with no carbonate.
from Baes and Mesmer (14), is no longer the generally accepted value for this reaction. The revised value, following the convention used by D&M, is now 8.8 (1, 15). Using the updated constant would increase the log $K_{\text{int}}$ to 5.9 and log $K_{\text{int}}$ to 3.5. These values would further increase the extent of uranyl sorption and move the adsorption edge to even lower pH values. This suggests that for these adsorption experiments, the polynuclear uranyl ion achieves a greater relative stability in solution when compared to the simpler mononuclear cations. Reduced adsorption relative to the mononuclear cations may also be caused by a steric effect. Finally, the original DLM database did not include surface complexation constants for uranyl carbonate surface complexes. Much work has demonstrated the importance of these constants when uranyl adsorption is evaluated in carbonate-bearing waters (1–9).

Although other models have been developed to describe adsorption of uranyl onto HFO, their assumptions summarized in the Supporting Information (SI) are not consistent with assumptions in the original D&M model. For example, Hsi and Langmuir (2, 3) used a triple layer model (TLM), but because the underlying assumptions between various models are so different the TLM parameters cannot be easily converted to the DLM (16). Some models claim to fit within the DLM framework, but do not provide a fully defensible connection with the rest of the DLM database. Work performed primarily by Waite and Payne (4–6) and Morrison, Spangler, and Tripathi (8) used different site densities than those cited in the original DLM. Morrison, Spangler, and Tripathi also eliminated the electrostatic terms. While the importance of individual attempts to produce updated constants should not be discounted, none of them readily fit into the internally consistent D&M database that has proven to be a valuable resource in surface complexation and solute transport modeling. The primary purpose of this work is to provide corrections to the DLM database for uranyl adsorption, while maintaining the basic tenets such as surface site densities with those presented by D&M in 1990 (10). Also, we have maintained the original conventions related to strong and weak site definitions, mainly that high affinity (strong sites) model only cation sorption. Work using extended X-ray adsorption fine structure (EXAFS) (6) suggests that at least some uranyl surface complexes are bidendate, forming bonds with two oxygens within an iron centered octahedron. Several geochemical modeling codes, including PHREEQC (11), can accommodate bidendate complexes within the DLM framework, but it requires some exceptions to the charge and elemental balance checking routines to function properly; specifically the no_check option must be included to define bidendate type surface complexes in PHREEQC. Because this effort was primarily designed to fix issues with the DLM database we opted to keep the definitions of surface complexes as simple as possible and to keep the number of surface complexes to a minimum. For consistency with the original database compilation we assumed that the surface complexes are monodendate. The uranyl surface complexes defined in this work are similar to the three surface complexes defined by Wazne et al. (7), which were selected based upon a combination of zeta potential and Fourier transform infrared spectroscopic measurements.

Materials and Methods

An evaluation of the published uranyl complexation reactions in solution was undertaken as the first step in this study. Various database compilations were examined and it was decided to use the WATEQ4F database as our primary source of thermodynamic data for this work. The evaluation indicated that the WATEQ4F database is generally available and is likely to be used in any initial model of uranyl sorption. However, to evaluate the sensitivity of the surface complexation coefficients to other database compilations additional fits were obtained using the NEA database (15).

The D&M assumptions regarding site density [weak sites (Hfo_wOH) at 0.2 mol/mol Fe; strong sites (Hfo_sOH) at 0.005 mol/mol Fe], and surface acidity constants (log $K_{\text{int}}$ of 7.29 and log $K_{\text{int}}$ of –8.93), were the same for both strong and weak sites (10); a surface area of 600 m$^2$/g and a formula weight of 89 g/mol were used to complete the definition of the HFO surface (10). For the simulations that included carbonate, two additional surface complexation reactions were included:

$$\text{Hfo}_\text{wOH} + \text{CO}_3^{2-} + \text{H}^+ = \text{Hfo}_\text{wOCO}_2^- + \text{H}_2\text{O}$$

$\log K_{\text{Hfo}_\text{wOCO}_2^-} = 12.78 \pm 0.48$

$$\text{Hfo}_\text{wOH} + \text{CO}_3^{2-} + 2\text{H}^+ = \text{Hfo}_\text{wOCO}_2^-\text{H} + \text{H}_2\text{O}$$

$\log K_{\text{Hfo}_\text{wOCO}_2^-\text{H}} = 20.37 \pm 0.20$

The log $K_{\text{int}}$ values were reported by Appelo et al. (17) and are consistent with the initial assumption of the DLM developed by D&M. The log $K_{\text{int}}$ values for these two reactions were not adjusted as part of this evaluation.

The inverse modeling program UCODE_2005 (18) was used to optimize the fit of the surface complexation constants to the experimental data. This program was originally developed to optimize estimates of parameters used to model groundwater flow. However, UCODE_2005 is designed to be a universal inverse modeling code, so when coupled with PHREEQC, it can be used to model reactions in solution (19) or surface complexation reactions. The PHREEQC input file consisted of a series of models representing each individual data point. Because the starting and final concentrations for
the various data sets cover several orders of magnitude, concentrations were converted to log values for purposes of residual calculation and optimization.

It should be noted that many of the previous attempts to estimate equilibrium constants used FITEQL (20). These programs employ similar optimization methods. The main difference between FITEQL and UCODE is that UCODE uses the PHREEQC code to perform the solution reaction calculations, while FITEQL is a self-contained program designed to calculate equilibrium constants. One of the primary advantages of the approach incorporated as part of this study is the ability of PHREEQC to model a variety of experimental conditions in one input file including systems that are open to CO2 gas, and others that are closed systems (using total carbonate concentrations); additionally, changes in total uranium concentrations and sorbent amounts can also be readily handled by PHREEQC. FITEQL is not able to model different partial pressures of CO2 gas simultaneously, let alone different total U concentrations or changes in sorbent concentrations.

During parameter optimization, UCODE_2005 runs PHREEQC many times in succession, each time incrementally varying the input parameters so as to minimize the sum of squared, weighted residuals (SOSR). The maximum fractional parameter change was 0.05. As part of the procedure, UCODE_2005 calculates the slope of the objective function (sensitivity) of each parameter. The residuals and sensitivities are used by UCODE_2005 to produce a better estimate of the parameter(s). The program minimizes the SOSR until convergence is reached. After each run, the residuals and parameters are compared to user-set convergence criteria to determine if convergence has been achieved. If the simulation has not met the convergence criteria, new parameter estimates are calculated, and a new iteration is performed. Convergence was attained when the estimated parameters changed by less than one percent over two iterations. Once convergence is reached, UCODE_2005 calculates a series of statistical measurements of fit and produces a summary of the iterations completed.

Table 1 provides a summary of the data used in the evaluation. In most cases, data were scanned and the individual data points were digitized from the publication figures to obtain the pH and reported concentrations for each data set. Data from Payne (5, 6) were taken from tabulations in an appendix in his dissertation.

UCODE_2005 allows weighting of data points based on objective or subjective judgments. We decided to weight all data points as equally reliable (weight of 1), except in the case of two high-pH data points from Hsi (2). During optimization, it was discovered that inclusion of these two data points resulted in unrealistic parameter estimates. These points are discussed below. Therefore, the data points were all but eliminated from the simulations by assigning them an extremely low weighting compared to the other points. Initially, a “bulk” fitting procedure was attempted that employed UCODE to simultaneously match all the data to the four primary surface complexation constants. However, depending upon the starting values selected for the uranyl carbonate surface complexes either the uranyl monocarbonate (Hfo_wOUO2(CO3)2−) or dicarbonate surface complex (Hfo_wOUO2(CO3)2−) dominated the upper pH region and the other complexation constant dropped in value by several orders of magnitude; this had been previously noted in earlier work (21). It was felt that the two uranyl carbonate surface complexes provided a better overall approach to fit the data. As a result, a stepwise optimization procedure was adopted. The steps undertaken were (1) optimize strong and weak site uranyl surface complexation constants, (2) evaluate uranyl hydroxide surface complex on weak sites, (3) optimize uranyl monocarbonate surface complex on weak sites, (4) optimize uranyl dicarbonate surface complex on weak sites, and (5) use additional data sets as a fit robustness check.

(1) Estimation of Hfo_sOUO2− and Hfo_wOUO2− Complexation Reactions. The two data sets of Hsi (2) prepared without carbonate were used to estimate the $K_{1\text{int}}$ and $K_{2\text{int}}$ values. Most of the data points had final pH values less than 7.0, so the data provided a good representation of the low-pH adsorption edge. The two data points with the highest pH values were removed because they were far above the low-pH adsorption edge, and they do not appear to represent complexation related to the $K_{1\text{int}}$ and $K_{2\text{int}}$ reactions. The data presented by Hsi were reported as final uranium concentrations in solution, rather than percentages, with ranges of 2–4 orders of magnitude. Both data sets used an initial uranyl concentration of $1 \times 10^{-3}$ mol/L. One data set used an HFO concentration of 1 g/L ferrihydrite, while the second data set used a lower HFO concentration of 0.15 g/L ferrihydrite. Uranyl surface complexation constants for the strong and weak sites (i.e., the $K_{1\text{int}}$ and $K_{2\text{int}}$ reactions) were simultaneously fit to the two data sets. In the initial re-evaluation of the data a trial and error visual fit of the 1 g/L ferrihydrite data set produced an excellent fit using a log $K_{1\text{int}}$ value of 4.15 and log $K_{2\text{int}}$ value of 2.05 (21). Using the UCODE_2005/PHREEQC setup, and the two data sets, changed the values to 3.736 and 2.534 respectively. Use of two data sets with different HFO concentrations provides a more robust and defensible fit than the previous fit to a single data set. These parameters are poorly constrained individually because of the similarity of the mass action equations for $K_{1\text{int}}$ and $K_{2\text{int}}$ (Table 2), but they do help the overall fit by steepening the

### Table 1. Summary of Experimental Data Conditions Used in This Evaluation

<table>
<thead>
<tr>
<th>researcher (group or publication)</th>
<th>series number</th>
<th>U(VI) total M</th>
<th>carbonate amount</th>
<th>carbonate condition</th>
<th>electrolyte (M)</th>
<th>number of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hsi, 1981; Hsi and</td>
<td>1</td>
<td>$1.0 \times 10^{-5}$</td>
<td>1 g/L ferrihydrite</td>
<td>no carbonate</td>
<td>0.1 NaNO3</td>
<td>29</td>
</tr>
<tr>
<td>Langmuir, 1985</td>
<td>2</td>
<td>$1.0 \times 10^{-5}$</td>
<td>0.15 g/L ferrihydrite</td>
<td>no carbonate</td>
<td>0.1 NaNO3</td>
<td>11</td>
</tr>
<tr>
<td>Morrison, Spangler and Tripathi, 1995</td>
<td>3</td>
<td>$1.0 \times 10^{-5}$</td>
<td>1 g/L ferrihydrite</td>
<td>closed 0.01 M (IV)</td>
<td>0.1 NaNO3</td>
<td>12</td>
</tr>
<tr>
<td>Tripathi, 1995</td>
<td>4</td>
<td>$1.0 \times 10^{-5}$</td>
<td>1 g/L ferrihydrite</td>
<td>closed 0.001 M (IV)</td>
<td>0.1 NaNO3</td>
<td>15</td>
</tr>
<tr>
<td>Wazne et al., 1994;  Payne, 1999</td>
<td>5</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1 mmol/L Fe [0.089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-3.5}$ atms CO2(g)</td>
<td>0.1 NaNO3</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>$1.0 \times 10^{-6}$</td>
<td>20 mmol/L Fe [1.78 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-3.5}$ atms CO2(g)</td>
<td>0.1 NaNO3</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1 mmol/L Fe [0.089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-3.5}$ atms CO2(g)</td>
<td>0.1 NaNO3</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>8</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1 mmol/L Fe [0.089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-3.5}$ atms CO2(g)</td>
<td>0.1 NaNO3</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1 mmol/L Fe [0.089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-2.0}$ atms CO2(g)</td>
<td>0.1 NaNO3</td>
<td>15</td>
</tr>
<tr>
<td>Morrison, Spangler and Tripathi, 1995</td>
<td>10</td>
<td>$1.0 \times 10^{-5}$</td>
<td>1.0 g/L Fe(OH)3</td>
<td>closed 0.001 M (IV)</td>
<td>0.1 NaNO3</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>2000 µg/L (8.4 × $10^{-6}$)</td>
<td>0.52 g/L Fe(OH)3</td>
<td>closed 0.0196 M (IV)</td>
<td>0.1 NaNO3</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>12</td>
<td>$4.2 \times 10^{-6}$</td>
<td>1.42 × $10^{-3}$ M Fe [0.126 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-3.7}$ atms CO2(g)</td>
<td>0.01 NaNO3</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1.00 × $10^{-4}$ M Fe [0.0089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-1.7}$ atms CO2(g)</td>
<td>0.005 NaNO3</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>14</td>
<td>$1.0 \times 10^{-6}$</td>
<td>1.00 × $10^{-3}$ M Fe [0.0089 g/L Fe(OH)3]</td>
<td>open $1.0 \times 10^{-1.7}$ atms CO2(g)</td>
<td>0.005 NaNO3</td>
<td>7</td>
</tr>
</tbody>
</table>

* Open systems use fixed carbon dioxide pressures specified in the table, while closed systems use a total carbonate [Ca(IV)] concentration for all pH values.
TABLE 2. Summary of UCODE_2005 Generated Results to Determine Uranyl Surface Complexation Constants onto HFO

<table>
<thead>
<tr>
<th>reaction</th>
<th>optimized log $K$</th>
<th>95% confidence interval</th>
<th>no. of observations</th>
<th>no. of data sets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ + H$_2$O $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$ + 2H$_2$O</td>
<td>3.792 WATEQ4f</td>
<td>38</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$ + CO$_2$</td>
<td>3.294 WATEQ4f</td>
<td>38</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>2.534 WATEQ4f</td>
<td>81</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>3.584 WATEQ4f</td>
<td>81</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>3.49 WATEQ4f</td>
<td>277</td>
<td>12</td>
<td>1</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>4.85 WATEQ4f</td>
<td>40</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>3.74 WATEQ4f</td>
<td>14</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Hfo$_w$OH + UO$_2$$^2^+$ + CO$_3$$^2^-$ $\rightarrow$ Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$</td>
<td>2.49 WATEQ4f</td>
<td>233</td>
<td>14</td>
<td>2</td>
</tr>
</tbody>
</table>

The importance of the Hfo$_w$OUO$_2$(CO$_3$)$_2$$^2^-$ surface complex is slight at best. It is discussed mainly for completeness of presentation, and for the rare occasion that it is required for a high-pH noncarbonate solution. It relies upon the fitting to only two uncertain data points and inclusion of the surface complex in any model tends to result in poorer overall fits, which would necessitate refitting of the other parameters. We do not recommend that this reaction be included in any general compilation database.

(3) Estimation of Hfo$_w$OUO$_2$(CO$_3$)$_3$$^2^-$ and (4) Hfo$_w$OUO$_2$(CO$_3$)$_3$$^2^-$ Complexation Reactions. Most of the experimental setups for carbonate-bearing solutions were performed at or near atmospheric CO$_2$ pressures of $10^{-15}$ atm (Table 1). A few experimental setups were run under different effective pressures, either because they represent closed systems (those not open to a fixed CO$_2$ pressure) or were run at higher CO$_2$ pressures. No attempt was made to try and adjust CO$_2$ pressures to compensate for possible changes caused by degassing.

Initial evaluation of the uranium and carbonate systems (21) indicated that models including either a uranyl monocarbonate or a uranyl dicarbonate surface complex could both separately provide acceptable fits to most of the experimental data. UCODE_2005 calculations were initially performed that allowed for the simultaneous adjustment of both uranyl carbonate surface complexes. The two reactions are

$$\text{Hfo}_w\text{OH} + \text{UO}_2^{2^+} + \text{CO}_3^{2^-} = \text{Hfo}_w\text{OUO}_2\text{CO}_3^- + \text{H}^+K_{3^\text{int}}$$

$$\text{Hfo}_w\text{OH} + \text{UO}_2^{2^+} + 2\text{CO}_3^{2^-} = \text{Hfo}_w\text{OUO}_2(\text{CO}_3)_2^- + \text{H}^+K_{3^\text{int}}$$

These initial simulations generally resulted in the program selecting one reaction and increasing the log $K$ value (either $K_{3^\text{int}}$ or $K_{4^\text{int}}$), and reducing the other constant, often to near zero. Even with all the data used in the estimates, UCODE_2005’s selection of the uranyl monocarbonate over the uranyl dicarbonate surface complex depended upon the initial conditions. This is related to the nature of the high pH desorption edge, which is controlled by a combination of factors including, point of zero charge, and the dominance of uranyl carbonate complexes, such as UO$_2$(CO$_3$)$_3$$^2^-$ in solution.
Ultimately, it was decided to include both reactions, but to estimate the reaction constants separately by continuing the stepwise approach used to evaluate the $K_{1\text{int}}$, $K_{2\text{int}}$, and $K_{3\text{int}}$ reaction constants.

To estimate the log $K_{4\text{int}}$ value, data were selected with pH values less than 6.33 from the initial 10 data sets that contained carbonate. The low-pH data were used because uranyl monocarbonate surface complex would dominate in lower pH systems, this set of calculations essentially corrects for the presence of a uranyl carbonate surface complex. The optimization was performed twice: once with $K_{4\text{int}}$ and once without. In each case, $K_{1\text{int}}$, $K_{2\text{int}}$ and $K_{3\text{int}}$ (when included) were fixed at their previously optimized values, and only $K_{4\text{int}}$ was estimated.

To estimate the uranyl dicarbonate surface complexation constant value (log $K_{5\text{int}}$), all 217 data points from the first 12 data sets (i.e., not including the two sets from Fox et al. (9) listed in Table 1) were used. This optimization was also performed twice: once with $K_{5\text{int}}$ and once without. In each case, the log $K_{1\text{int}}$, $K_{2\text{int}}$, $K_{3\text{int}}$, and $K_{4\text{int}}$ (if included) values were fixed at their optimized values, and only $K_{5\text{int}}$ was estimated. These fitting calculations essentially fit to the high pH desorption edges, which as mentioned previously is actually fairly insensitive to the selection of the specific uranyl and carbonate bearing surface complex. Figure 4 shows the final fit when compared to one example data set. The figure also includes the distribution of the four selected uranyl-bearing surface complexes. Other fits are included in the SI.

(5) Fit Robustness Check. Finally, to test the robustness of the optimized fits, two previously unused data sets (the two Fox et al. (9) data sets in Table 1) were appended to the previously used data compilation. Because these data sets only included carbonate system data with pH > 6.33, only $K_{4\text{int}}$ was re-evaluated. This final simulation used all 233 data points from the 14 data sets. The optimized $K_{4\text{int}}$ value was identical to the one estimated using the previous simulations, providing additional confidence in the optimized values obtained from earlier simulations.

Previously we had demonstrated (21) that the two carbonate surface complexes (Hfo_wOCO$_2^-$ and Hfo_wOCO$_3^-$) had little impact on the extent of uranyl adsorption. Waite et al. (6) also made a similar observation. This is probably because most of the experimental conditions were limited to the relatively low atmospheric value of $10^{-3.5}$ atmospheres for CO$_2$ gas. These two complexes become more significant at higher partial pressures of CO$_2$ gas and in some solute transport model scenarios.

Table 2 summarizes the optimized fit results for both the WATEQ4F and NEA database model sets. In addition, Table 2 provides three metrics describing the uncertainty associated with the fits: (1) 95% confidence interval ranges, (2) average residual, and (3) average magnitude of residual. These summary statistics are automatically generated by UCODE_2005. Smaller 95% confidence interval ranges generally indicate less uncertainty associated with the optimized result. Average signed residuals and residual magnitudes indicate how well the model fits the data; thus, both metrics should be close to zero if there is a good fit to data. Differences in the UCODE_2005 selected constants between the two databases are not statistically different (Figure 5).

For comparison, the same 14 experimental data sets were simulated using the original two D&M constants plus the two carbonate surface complexes (see SI). The resulting average residual (0.2) was approximately an order of magnitude larger than the values listed in Table 2. The average residual magnitude was also larger (0.5). Thus, the new constants result in a significantly improved fit to the experimental data.

Discussion

Figure 6 compares the model-predicted concentrations to the measured concentrations. Overall the agreement between the modeled and experimental data is good with the exception of a few outliers, which we attribute to setup of the original measurements. In addition, much of the data was obtained from plots and tables that show percent adsorbed, rather than final concentrations in solution, and data presented in this fashion can produce reporting limit issues. This has resulted in generally poorer fits in the middle pH range where adsorption is maximized. Examination of the individual fits (see SI) indicates that generally the better fits are for the adsorption and desorption edges, whereas mid-pH ranges tend to show poorer agreement. Reporting limit truncation is probably responsible for the five data points whose measured values are $1.0 \times 10^{-6}$ moles per kilogram of water (mol/kgw), which represents 99.9% adsorption of an initially $1.0 \times 10^{-6}$ mol/kgw solution.
that the experimental efforts show a consistency that sets developed by five different research groups indicates the overall data set of 233 points as represented in 14 data sets between the final model selected parameters and uranyl sorption in carbonate-bearing systems. The agreement with this database, and improves the fitting of complexes, and limiting high affinity sites to cation retained, such as using only monodentate type surface original DLM as possible certain assumptions were to the original DLM database as it applies to uranyl.

FIGURE 6. Scatter plot of DLM predicted concentrations of U(VI) with experimentally obtained data (measured concentrations). The figure includes all 233 points from 14 data sets and represents the combined work of five different research groups. Modeled results (predicted concentrations) used the four major uranyl surface complexation reactions defined in this study (\(K_1^{4\text{int}}\) through \(K_4^{4\text{int}}\)) as calculated with the WATEQ4F database. The series numbers 1–14 correspond to the data sets listed sequentially in Table 1.

This study was primarily designed to provide corrections to the original DLM database as it applies to uranyl adsorption. To maintain as much consistency with the original DLM as possible certain assumptions were retained, such as using only monodentate type surface complexes, and limiting high affinity sites to cation adsorption reactions. Inclusion of uranyl carbonate surface complexes into the original DLM database corrects an oversight with this database, and improves the fitting of uranyl sorption in carbonate-bearing systems. The agreement between the final model selected parameters and the overall data set of 233 points as represented in 14 data sets developed by five different research groups indicates that the experimental efforts show a consistency that supports the general application of this revised model in describing uranyl adsorption.

The modeling presented in this paper has shown that the previously published and widely used uranyl sorption constants in the original DLM compilation result in unrealistic predictions of uranium fate and mobility in the environment. This is environmentally significant because the previous constants tend to overpredict uranium sorption under low-pH conditions. Consequently, resultant models were not environmentally conservative and could result in inaccurate predictions. The re-evaluation conducted here corrects that problem.

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Supporting Information Available
Additional details are available. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited


