Assessment of Uranyl Sorption Constants on Ferrihydrite – Comparison of Model Derived Constants and Updates to the Diffuse Layer Model Database

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Abstract. Surface complexation constants for uranyl (UO_2^{+2}) sorption onto hydrous ferric oxide (HFO) using a diffuse layer model (DLM) developed with the Dzombak and Morel correlation are demonstrated to provide poor fits to two independently derived laboratory datasets. Alternative surface complexation reactions based upon geochemical modeling provided better matches to the data and still follow the underlying principles of the DLM as used in databases associated with several geochemical modeling programs.

Introduction

In 1990, David Dzombak and Francois Morel (D&M) (Dzombak and Morel, 1990) published a compilation of surface complexation reactions for hydrous ferric oxide (HFO). In their seminal work, previously published data sets were re-evaluated and surface complexation reactions were defined assuming that a diffuse layer model (DLM) best described the charge potential relationships on the surface. The model developed from their effort presupposed a series of well defined parameters such as surface site densities, and surface area assumptions. The database that was developed from these significant efforts has been used in numerous programs including MINTEQA2 (Allison et al. 1991), PHREEQC (Parkhurst and Appelo 1999) and Geochemist's Workbench (Bethke 1996). Because the USEPA provides MINTEQA2 to outside users, that program and its associated databases have developed a perceived or tacit approval by many regulatory agencies.

As part of the efforts to increase the number of components in the database, D&M developed a linear free energy relationship (LFER) to estimate surface complexation reaction constants for several species that were not evaluated using laboratory developed data, these included uranyl, tin, palladium, plutonium (as

PuO_2^{+2}) and manganese. The authors developed a relationship between the formation constant for various metal hydroxides ($MeOH^+$), and known surface complexation constants for strong (Hfo_sOH) and weak (Hfo_wOH) sites. Then new constants were developed for surface complexes not evaluated using experimentally derived measurements. Using the LFER and a log K of 8.2 for the $UO_2(OH)^+$ complex, D&M calculated log K values for Hfo_sOUO$_2^+$ (log K^1_{int} of 5.2) and Hfo_wOUO$_2^+$ (log K^2_{int} of 2.8). Unfortunately, comparison of the estimated surface complexation constants to two independent experimentally derived datasets indicates that the constants overestimate the extent of adsorption, particularly at low pH conditions.
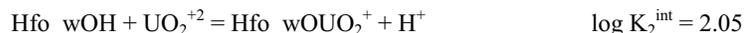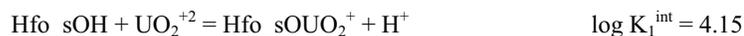
The primary purpose of this work is to provide corrections to the DLM database for uranyl adsorption, while maintaining the basic conditions, such as surface site densities, with those presented by D&M in 1990. Work using EXAFS (Payne 1999) suggests that the uranyl surface complexes are of a bidendate nature. This paper assumes that the surface complexes are monodendate for consistency with the other surface complexes in the DLM database.

Comparison to experimental data

Experimental data from different published sources were used. Fits were prepared using PHREECQ. The method was primarily trial and error, where visual fits were compared between experimental and modeled data. Goodness of fit was evaluated by a root mean square type objective function.

Prior to performing the fitting calculations, an evaluation of the published uranyl complexation reactions in solution was undertaken. The evaluation indicated that the WATEQ4f.dat database, included in the PHREEQC distribution package, was consistent with generally accepted complexes and their stability constants. Figure 1 shows the distribution of UO_2^{+2}, uranyl hydroxide and uranyl carbonate complexes developed from this database.

Figure 2 shows data prepare by Hsi (Hsi 1981, Hsi and Langmuir 1985), and compares it to a model using the original LFER derived constants. Examination of Figure 2 indicates that the original DLM constants have a tendency to over-predict the extent of adsorption, in some cases by a factor of 10. The data developed by Hsi used an initial U(VI) concentration of 1×10^{-5} m and 1 g/L amorphous ferric hydroxide, total carbonate was zero. The second set of lined data (open diamonds) show the final fit using two surface complexation reactions:

$$Hfo\_sOH + UO_2^{+2} = Hfo\_sOUO_2^+ + H^+ \qquad \log K_1^{int} = 4.15$$

$$Hfo\_wOH + UO_2^{+2} = Hfo\_wOUO_2^+ + H^+ \qquad \log K_2^{int} = 2.05$$

The problem with the D&M constants becomes more evident when compared to other datasets. Failure to match one dataset may be related to experimental technique. Failure to match two independent datasets suggests a problem with the LFER estimation method. Figure 3 shows the model compared to experimental da-
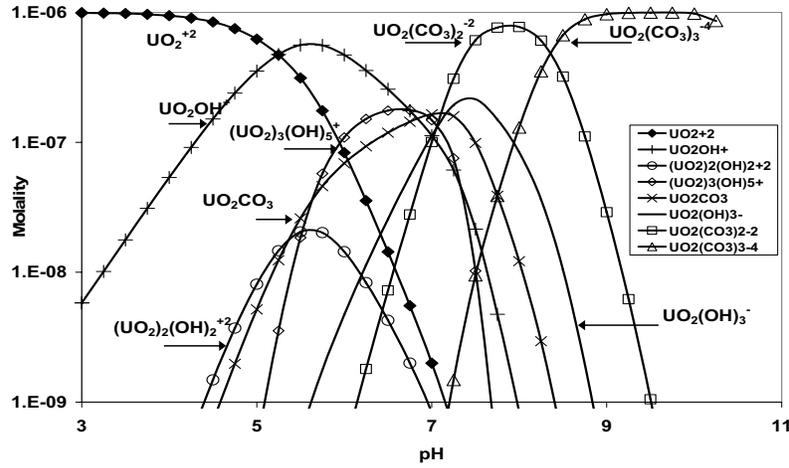

Fig.1. Distribution of uranyl species for a solution containing 10^{-6} M U(VI) and a carbon dioxide pressure of $10^{-3.5}$ atmospheres.
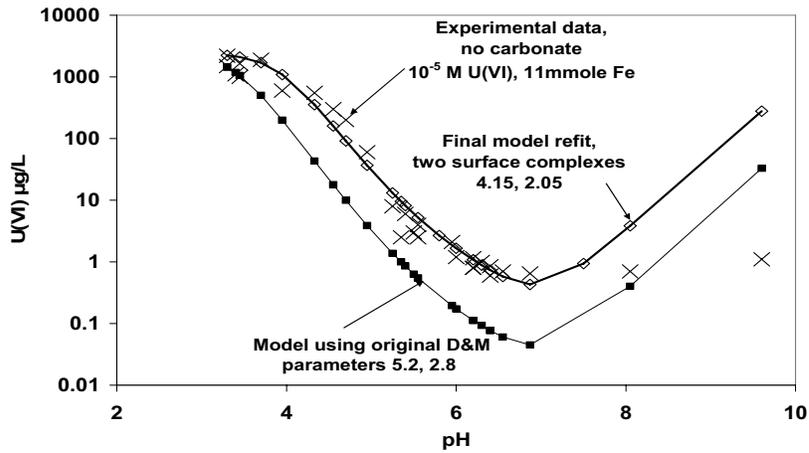

Fig.2. Comparison Hsi's (1981) of experimentally derived measurements of uranyl uptake onto amorphous ferric hydroxide (X's) to DLM calculations using LFER derived constants presented by D&M (thin line and small filled square) and our model fit (thicker line open diamonds).

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ta developed by T. E. Payne for 10^{-6} m U(VI) onto 1 mmole Fe (precipitated as HFO). The experiments were open to the atmosphere; consequently, the partial pressure of carbon dioxide was set to $10^{-3.5}$ atmospheres. Again, the LFER derived values tend to over estimate adsorption at low pH values. The model also tends to underestimate adsorption at high pH conditions.

To obtain his fits, Payne modified several tenets of the D&M DLM. He increased the surface site density from 0.2 moles of weak sites/mole Fe to 0.875 moles/mole Fe. In the original model D&M assigned a site density for strong sites of 0.005 moles/mole Fe, Payne decreased it to 0.0018 moles/mole Fe. The overall increase in surface site concentrations impacts the surface charge/surface potential features of the model. Payne noted that his modifications required subsequent adjustments of other reactions, notable the surface ionization reactions involving the K_{a1}^{int} and K_{a2}^{int} constants. These changes limit the ability to apply his model to systems that contain other competing cations such as nickel or zinc. In general, the effects are small but can raise questions about internal consistency. One final feature of the Payne model is its assumption that the strong sites could form uranyl carbonate surface complexes. Uranyl carbonate complexes are either neutral or negatively charged. The original rationale for including strong sites in the DLM was to provide a means to model high affinity cation adsorption, which generally took place under low pH conditions. Because these assumptions changed the underlying assumptions of the D&M DLM we decided to recalculate uranyl sorption in accordance with the original requirements stated in D&M (1990).
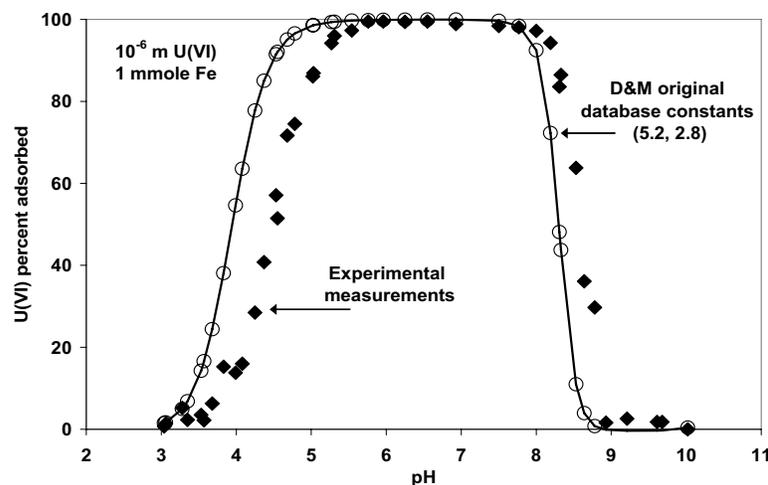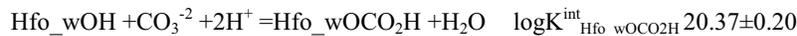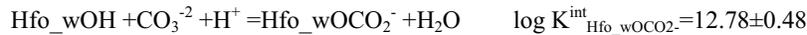

Fig.3. Comparison of Payne's (1999) experimental data (filled diamonds) to model based upon D&M uranyl surface complexation reaction (open circles with line); based upon 10^{-6} m U(VI) sorbed onto 1mmole of HFO in a 0.1 NaNO$_3$ solution, CO$_2$ at $10^{-3.5}$ atmospheres.

To refit the Payne experimental data, our work used the surface site density assumptions in the D&M version of the DLM (proportions of 0.2 and 0.005). Initially a third reaction was added to allow for a uranyl carbonate surface complex. The added reaction was:

$$Hfo\_wOH + UO_2^{+2} + CO_3^{-2} = Hfo\_wOUO_2CO_3^- + H^+ \quad \log K^{int}_{Hfo\_wOUO2CO3-} = 10.05$$

Figure 4 compares Payne's experimental data at a U(VI) concentration of 10^{-6} m, and 1 mmole of Fe to three different model fits. The first fit was the simplest and included the three uranyl surface complexes described above. Based upon the values obtained from the Hsi data (Figure 3), we selected a log K_1^{int} value of 4.15, log K_2^{int} of 2.05 and a log $K^{int}_{Hfo\_wOUO2CO3-}$ of 10.05.

The original DLM database, as presented in PHREEQC, did not include surface complexation reactions between surface sites and carbonate, consequently the first models did not include surface complexation reactions with carbonate. Appelo et al. (2002) reported surface complexation reaction constants for carbonate suitable for the D&M database. The reactions are defined below.

$$Hfo\_wOH + CO_3^{-2} + H^+ = Hfo\_wOCO_2^- + H_2O \qquad \log K^{int}_{Hfo\_wOCO2-} = 12.78 \pm 0.48$$

$$Hfo\_wOH + CO_3^{-2} + 2H^+ = Hfo\_wOCO_2H + H_2O \quad \log K^{int}_{Hfo\_wOCO2H} \, 20.37 \pm 0.20$$

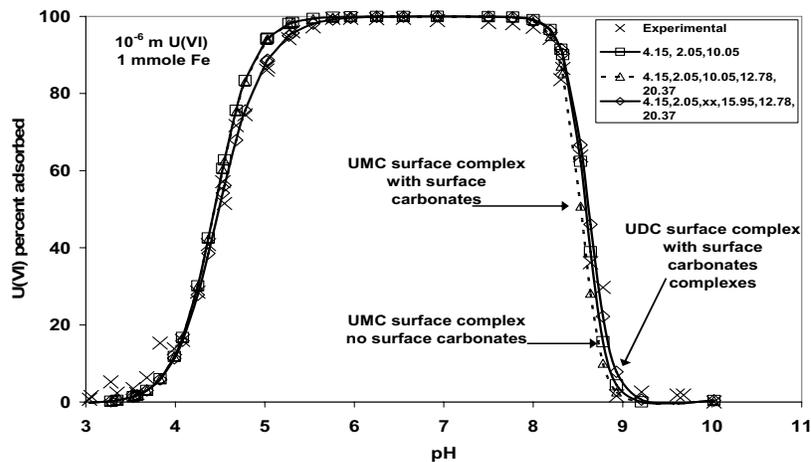These reactions in addition to the uranyl surface complexation reactions were

Fig.4. Comparison of Payne's (1999) experimental data (X's) with DLM fit assuming three surface complexation reactions for uranyl (line with squares); based upon 10^{-6} m U(VI) sorbed onto 1mmole of HFO in a 0.1 NaNO₃ solution with a partial pressure of CO₂ of $10^{-3.5}$ atmospheres. The figure also includes another model with two surface carbonate complexes (dashed line with triangles). A final model (line with diamonds) replaced the uranyl monocarbonate (UMC) surface complex (2nd model) with a uranyl dicarbonate (UDC) surface complex.

included in a second set of model calculations. Several simulations indicated that the impact of the carbonate surface complexes was minimal.

Finally, a third model was developed that included a uranyl dicarbonate (UDC) surface complex. The UDC surface complexation reaction was defined as:

$$Hfo\_wOH + UO_2^{+2} + 2CO_3^{-2} = Hfo\_wOUO_2(CO_3)_2^{-3} + H^+ \quad Log\ K^{int}_{UDC} = 15.95$$

The third model replaced the uranyl monocarbonate (UMC) surface complex with a uranyl dicarbonate (UDC) surface complex. The final model included the simple carbonate surface complexes. A value of 15.95 was selected as the best value for the log $K^{int}_{Hfo\_wOUO2(CO3)2-3}$. The constant was adjusted primarily to improve the fit in the higher pH range, but replacing the UMC surface complex with the UDC complex also resulted in a better fit in the lower pH ranges (4.5 to 6.0).

Figure 5 shows the distribution of uranyl surface complexes for two of the models shown in Figure 4. Under low pH conditions, the strong site is the dominant retainer of U(VI). The selection of either the UMC or UDC surface complex significantly impacts the distribution of the two uranyl surface complexes.

Payne expanded his experimental work to other conditions by increasing the amount of sorbent phase or increasing the initial concentration of uranium. Figure 6, shows the fit when the amount of U remains at 10^{-6} m, and the iron is increased to 20 mmole. These experiments have the lowest loadings of U. The log K_1^{int} value of 4.15, and log K_2^{int} of 2.05 remained the same, but for the first model the log $K^{int}_{Hfo\_wOUO2CO3-}$ was adjusted to 11.05 for this data set. For the model with the
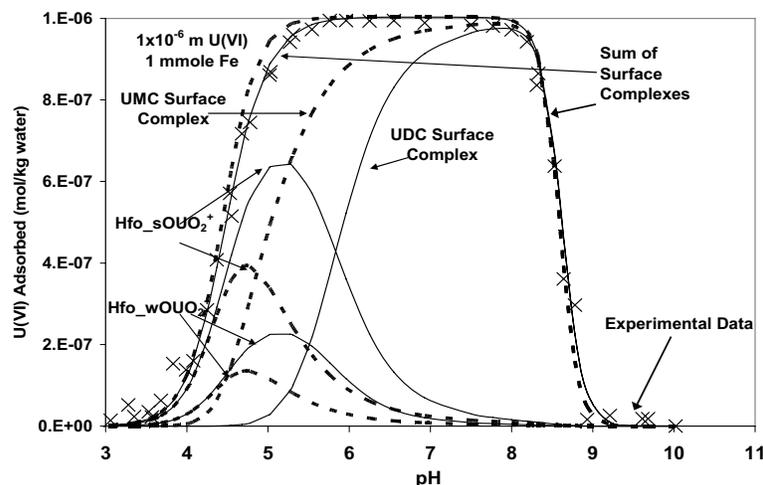

Fig.5. Distribution of uranyl-bearing surface complexes. The UMC model surface complexes are represented by thick dashed lines. The UDC model based surface complexes are represented by thin solid lines; experimental data from Payne (1999).

UDC surface complex, the selected log $K^{int}_{Hfo\_wOUO2(CO3)2-3}$ value was 16.4.

The effects of increasing the uranyl concentration to 10^{-5} or 10^{-4} m, while retaining HFO at 1mmole, are shown on Figures 7 and 8.

In both models, we have preserved the log K_2^{int} value at 2.05. For the 10^{-5} m
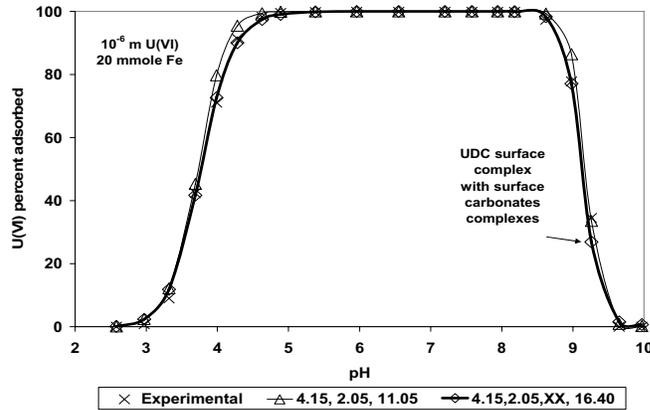

Fig.6. Comparison of experimental data (X's) comparing UMC and UDC surface complexes DLM fits. The model with UMC surface complex is represented by thin line with triangles. The UDC surface complex model also included carbonate surface complexes (thick line with diamonds). Experimental conditions from Payne (1999), based upon 10^{-6} m U(VI) sorbed onto 20 mmole of HFO in a 0.1 NaNO$_3$ solution CO$_2$ at $10^{-3.5}$ atmospheres.
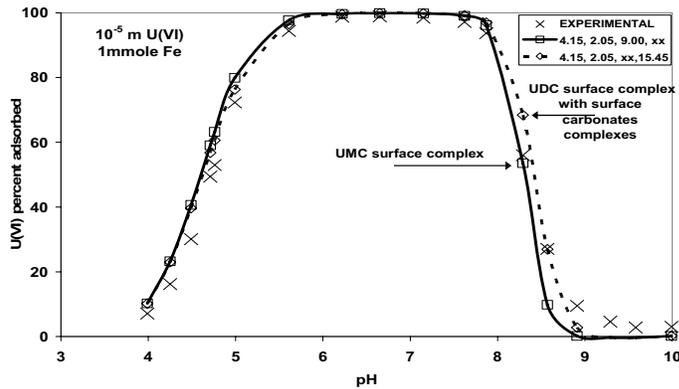

Fig. 7. Comparison of experimental data (X's) with two DLM simulations. The model fit with the UMC surface complex is represented by a solid line with squares. The fit with the UDC surface complex model also included carbonate surface complexes (dashed line with diamonds). Experimental conditions from Payne (1999) based upon 10^{-5} m U(VI) sorbed onto 1 mmole of HFO in a 0.1 NaNO$_3$ solution, CO$_2$ at $10^{-3.5}$ atmospheres.

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U(VI) measurements we have retained both the log K_1^{int} and the K_2^{int} values at 4.15 and 2.05, respectively.

At a loading of 10^{-4} m U(VI) (Figure 8), the final constants were 3.70 for log K_1^{int}, 2.05 for the log K_2^{int} value and log $K^{int}_{Hfo\_wOUO2CO3-}$ was adjusted to 8.2. The model with the UDC surface complex used a log $K^{int}_{Hfo\_wOUO2(CO3)2-3}$ value of 15.0. The change in the log K_1^{int} for these experimental conditions is not surprising. At the 10^{-4} m loading, the less than 5 percent of U(VI) is sorbed onto strong sites (Figure 8) the model is not sensitive to the parameter, therefore a difference of nearly half a log unit is not unexpected. The role of the strong and weak uranyl surface complexes is reversed when compared to lower loadings (Figure 4).

Figure 8 also included another model that used the log $K^{int}_{Hfo\_wOUO2(CO3)2-3}$ developed from the 10^{-6} U(VI) 20 mmole Fe dataset, that value was 16.4 (see Figure 6). This simulation was run to demonstrate that acceptable fits can be obtained using the largest value for the UDC surface complex. Although the comparison to the higher pH range is not as good as models that use a smaller value, the 16.4 value actually improves the fit from pH 5.5 to 7.0.

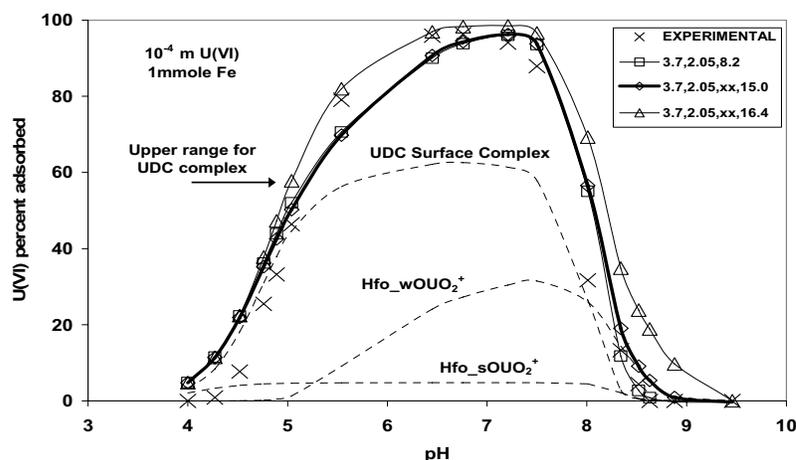Table 1 summarizes the model conditions and selected surface complexation

Fig.8. Comparison of experimental data (X's) with DLM fits assuming three surface complexation reactions for uranyl. The fit with the UMC surface complex is represented by a thin line with squares. The UDC surface complex model also included carbonate surface complexes (thick line with diamonds), the distribution of uranyl bearing surface complexes (thin dashed lines) for the UDC model is also included. A model using the maximum value for the UDC surface complex (line with triangles) was included to show sensitivity of model. Experimental conditions (Payne, 1999) based upon 10^{-4} m U(VI) sorbed onto 1 mmole of HFO in a 0.1 Na-NO$_3$ solution CO$_2$ at $10^{-3.5}$ atmospheres.

constants derived from this study. Of greatest concern is the variation in log $K^{int}_{Hfo\_wOUO2CO3-}$ as the proportion of available U(VI) to sorption sites changes. The UMC surface complex models have a spread of 2.85 log units. Initially, it was thought that some of this variation could be explained by including the surface carbonate complexes. However, their inclusion had no effect on the selected values. A strong correlation between the log of the site loading value, defined as U(VI) as moles/mmoles Fe, to the selected log $K^{int}_{Hfo\_wOUO2CO3-}$ value was noted. The variation in the value of the UMC surface complex was the reason that the additional models with the UDC surface complex were prepared. Replacement of the UMC with the UDC surface complex reduced the spread to about 1.4 log units. Figure 8 demonstrates that the variation in the UDC surface complex does not have a significant effect on the overall fit, and that an average value of about 15.7 would provide a good starting point for most models.

Table 1. Summary of initial model parameters, experimental conditions and final surface complexation constants.

Data Source	U(VI) mol/L	Fe mmoles	Carb.	Log K_1^{int}	Log K_2^{int}	Log K^{int}_{UMD}	Log K^{int}_{UDC}
D&M LFER	NA	NA	NA	5.2	2.8	NA	NA
Hsi, 1981	1.E-5	11 (1gm/L)	Ct = 0.0	4.15	2.05	NA	NA
	1.E-6	20	$10^{-3.5}$ atms	4.15	2.05	11.05	16.40
Payne, 1999	1.E-6	1	$10^{-3.5}$ atms	4.15	2.05	10.05	15.95
	1.E-5	1	$10^{-3.5}$ atms	4.15	2.05	9.0	15.45
	1.E-4	1	$10^{-3.5}$ atms	3.7	2.05	8.2	15.0

Conclusions

This work has demonstrated that the constants for uranyl adsorption onto HFO (or ferrihydrite) provided in the D&M diffuse layer database are in error and tend to over estimate the extent of uranyl sorption particularly for low pH conditions. Furthermore, D&M did not consider the importance of uranyl carbonate surface complexes in their initial compilation. The original intent of this work was to develop a set of simple surface complexation constants to describe uranyl adsorption using the DLM. This has been partially accomplished. New constants have been provided (Table 1), but the role of the uranyl carbonate surface complexes has not been fully resolved. Satisfactory models can be constructed with either the UMC or UDC surface complex. We favor the model that uses the UDC surface complex, but we are performing more simulations to better resolve this issue.

These corrections will improve applications such as solute transport calculations. The errors in the previously published values were as much as an order of magnitude in the amount predicted to be adsorbed. The failure to include carbo-

nate complexation reactions was also a major shortcoming of the original work. The corrections will result in significant differences among the predicted mobility of uranium in solute transport models. Under low pH, carbonate-free conditions, which are common in some acid rock drainage environments, the calculated distribution coefficient of uranyl will be reduced in some cases by nearly a factor of 10. These new constants indicate less sorption of U(VI) than previously indicated and consequently these new estimates will under certain conditions tend to be more protective of the environment.

Future work will refine these fits using an alternative solver/fitting program such as UCODE (Poeter et al. 2005) and provide better estimates of errors. The additional work will re-evaluate the relationships involving the behavior of the uranyl surface carbonate surface complex. Also surface complexation models based upon the bidendate surface complexes identified by Payne will be developed, but will use the site density conventions of the original diffuse layer model. The bidendate models may provide a better means to handle the variations in the uranyl carbonate complexation constants.

References

Allison, J.D., Brown, D.S., and Novo-Gradac, K.J., 1991, MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems, Version 3.0 User's Manual: U.S. Environmental Protection Agency Report EPA/600/3-91/021, 106 p.

Appelo, C.A.J., Van der Weiden, M.J.J., Tournassat, C. and Charlet, L., 2002, Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environ. Sci. Technol. V. 36, p. 3096 -3103.

Bethke, C.M., 1996, Geochemical Reaction Modeling: Oxford University Press, New York, 397 p.

Dzombak, D.A., and Morel, F.M.M., 1990, Surface complexation modeling - hydrous ferric oxide: New York, John Wiley and Sons, 393 p.

Hsi, C.-K.D., 1981, Sorption of Uranium (VI) by iron oxides. Ph.D. Dissertation, Colorado School of Mines, pp. 154.

Hsi, C.-K.D. and Langmuir, D. 1985, Adsorption of uranyl onto ferric oxyhydroxides: applications of a surface complexation site binding model. Geochimica et Cosmochimica Acta, 49, p. 2423-2432.

Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQE (version 2) - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigation Report 99-4259, 312 p.

Payne, T.E. (1999), Uranium (VI) interactions with mineral surfaces: controlling factors and surface complexation modeling, Ph.D. Dissertation, University of New South Wales, pp. 332.

Poeter, E.P., Hill, M.C., Banta, E.R., Mehl, S., and Christensen, S., 2005. UCODE_2005 and six other computer codes for universal sensitivity analysis, calibration and uncertainty evaluation. USGS Techniques and Methods 6-A11. Reston, Virginia.

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