Sensitivity of Database Selection in Modeling the Transport of Uranium

John J. Mahoney

Mahoney GeochemicalConsulting,892 S. Newcombe Way, Lakewood, Colorado, 80226, USA,jmahoney@mahoneygeochem.com

Abstract Reactions defined in geochemical databases can directly influence conclusions drawn from fate and transport models. Unfortunately, many of these "off-the-shelf" databases contain numerous and significant errors. An appreciation of the historical development of these databases can help in selecting realistic values, and produce more accurate models. Recently, errors in the diffuse layer database for uranyl sorption onto ferrihydrite have been identified and corrections published; but dissemination of this information has been limited and users must make corrections themselves. Comparisons between solute transport models using the older and revised databases result in significant differences, which can affect costs and performance criteria.

Keywords Uranium surface complexation, database, PHREEQC, PHAST for Windows, transport modeling

Introduction

In the 35 years since Donald Langmuir published his summary on uranium solution – mineral equilibria (Langmuir 1978) there have been numerous changes to the distribution of the dissolved species and to the surface ionization and complexation models (SICM)that describe adsorption of uranium onto mineral surfaces such as hydrous ferric oxide (HFO). These changes produce significant differences in the modeled extent of adsorption of uranium, and the predicted mobility of uranium in the subsurface. Of notable importance is that because database derived differences can change retardation factors they can also alter model estimated amounts of uranium in a system.

Corrections to the Diffuse Layer Model

It was not until 1990, when Dzombak and Morel (1990)published their database compilation on the diffuse layer model,and their values were incorporated into the MINTEQA2 database (Allison *et al.* 1990) that the surface ionization and complexation model became widely accepted as an important attenuation process. Unfortunately, and in spite of the availability of data to prepare a robust set of diffuse layer model reactions for uranium adsorption onto HFO, Dzombak and Morel did not estimate parameters from published data. Rather they proposed a Linear Free Energy Relationship (LFER) to estimate surface complexation constants for uranyl sorption. Previously, Hsi and Langmuir (1985) had prepareda triple layer model (Fig. 1), and provided laboratory measurements that could have been used to define diffuse layer model surface complexation constants for uranyl sorption, but Dzombak and Morel took an alternative approach.

When compared to experimental data, it became apparent that the values obtained from the original D&M LFER were clearly wrong (Mahoney and Jakubowski 2008). The D&M LFER overestimated sorption for uranium by a factor of about 10 for non-carbonate systems. Furthermore, the failure of the Dzombak and Morel (1990) compilation to consider uranyl hydroxide or uranyl carbonate surface complexation reactions was another shortcoming.To be fair, it was never intended that their compilation should become the industry

History of Uranium Surface Ionization and Complexation Model Database
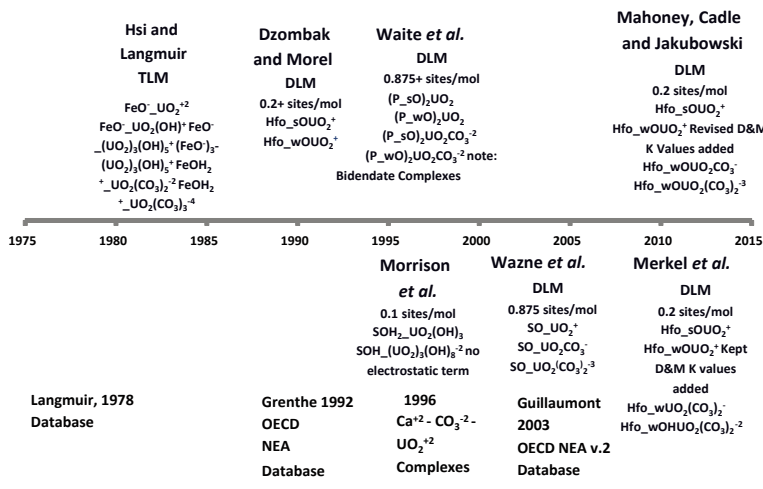**(Hydrous Ferric Oxide)**

Fig. 1. *Timeline showing the changes in uranium surface complexation models and solution complexation databases.*

standard for uranium sorption, but it filled a need for a set of readily useable parameters to describe sorption of many trace metals, including uranium, and was in a database that had some apparent acceptance by researchers in the USEPA's Center for Exposure Assessment Modeling.

To correct some of these oversights, other groups performed additional laboratory work and published new models. Unfortunately, these models were constructed independently from the original D&M framework, which limited their utility in complicated problems where simultaneous (competitive) adsorption reactions might be critical to a better understanding of the dominant geochemical processes. The models were specific to uranium only, and other surface complexation reactions would require different model parameters. Morrison *et al.* (1995) used a smaller site density than defined by Dzombak and Morel (1990), and to simplify the computational load eliminated the electrostatic terms. Waite *et al.* (1994) and Payne (1999) produced excellent fits to their data, but they used a different site density and changed the surface hydrolysis reactions (pK_{a1}^{int} and pK_{a2}^{int}), preventing a direct import into the previously codified compilations in MINTEQA2 and PHREEQC. Wazne (2003)

used the Waite *et al.* (1994) site density, but selected a different set of surface reactions. Even more recently, Merkel *et al.* (2008) used the original Dzombak and Morel (1990) uranyl surface complexes with two reactions for uranyl carbonate surface complexes. These reactions were listed in his textbook (2nd edition), but there was no discussion or documentation about the two additional surface complexation reactions involving carbonate.

Ultimately these parameters were corrected (Fig. 2), and the results published (Mahoney *et al.* 2009). The effort used PHREEQC (Parkhurst and Appelo 1999) coupled with UCODE (Poeter *et al.* 2005); and drew data from five different research groups that represented 14 different experimental conditions and 214 different data points. The following surface complexation reactions were selected to describe uranium (as uranyl) adsorption onto HFO, based upon constants in the WATEQ4F.DAT (first value) and the updated NEA databases:

- Hfo_sOH + UO_2^{+2} = Hfo_sOUO$_2^+$ + H^+
  Log K_1 = 3.735, NEA = 3.792

- Hfo_wOH + UO_2^{+2} = Hfo_wOUO$_2^+$ + H^+
  Log K_2 = 2.534, NEA = 2.507,

- $Hfo\_wOH + UO_2^{+2} + CO_3^{-2} =$
  $Hfo\_wOUO_2CO_3^- + H^+$
  Log $K_{Hfo\_wOUO2CO3-}$= 9.014, NEA = 9.150

- $Hfo\_wOH + UO_2^{+2} + 2CO_3^{-2} =$
  $Hfo\_wOUO_2(CO_3)_2^{-3} + H^+$
  Log $K_{Hfo\_wOUO2(CO3)2-3}$ = 15.24, NEA = 15.28

In addition to the uranyl adsorption reactions, two additional reactions (Appelo *et al.* 2002) were added to the database. These reactions are defined below:

- $Hfo\_wOH + CO_3^{-2} + H^+ =$
  $Hfo\_wOCO_2^- + H2O$
  Log K_{Hfo_wOCO2-} = 12.78
- $Hfo\_wOH + CO_3^{-2} + 2H^+ =$
  $Hfo\_wOCO_2H + H2O$
  Log K_{Hfo_wOCO2H} = 20.37

Fig. 2 *Comparison of Dzombak and Morel (1990) uranyl sorption model (dashed lines) onto HFO with refit model of Mahoney et al. (2009) solid lines. Diamonds represent 0.15 g/L of HFO X's represent 1.0 g/L HFO. Total U was 1.0×10^{-5} mol/kg of water.*

Other Database Updates

Around the same time as the revised surface complexation constants were published, there were several papers that further demonstrated the existence of divalent uranyl carbonate complexes, specifically $CaUO_2(CO_3)_3^{-2}$, $Ca_2UO_2(CO_3)_3^o$ and $MgUO_2(CO_3)_3^{-2}$ in solution (Dong and Brooks 2006). Updating the surface complexation database with the new constants tended to increase uranyl sorption in carbonate bearing waters. Including the ternary complexes generally lessened the extent of uranyl adsorption, so in calcite bearing systems there is often some offsetting.

Impacts to Solute Transport Models

In solute transport models, surface complexation is directly related to retardation of the solute. Consequently selection of database parameters will have a profound influence on model conclusions. Fig. 3 shows the results of a series of PHREEQC calculations for various SICM parameters under different scenarios. The figure shows uranium breakthrough curves using the PHREEQC transport model. There were 20 cells in the model and 80 shifts for a total of 4 pore volumes. The calculations
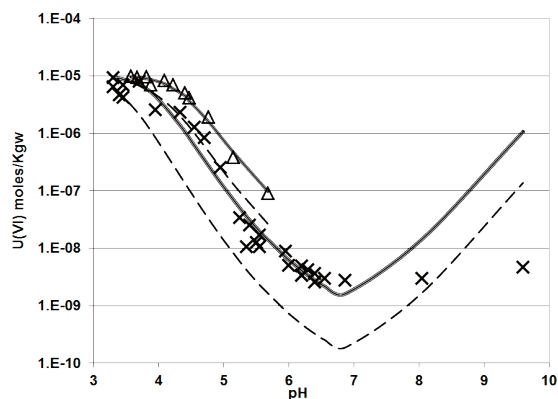
in Fig. 3 do not include calcium, so the ternary complexes are not considered. The original Dzombak and Morel (1990) parameters overestimated uranium surface complexation in non-carbonate bearing waters, (middle of the set of curves – solid lines). For comparison, models that use only the first two revised surface complexation constants (K_1, and K_2) were prepared (dashed lines), those models reduced the amount of surface complexation and so in this transport model they show greater mobility and less retardation. However, most groundwaters contain carbonate and all four reactions plus the complexes $Hfo\_wOCO_2^-$ and Hfo_wOCO_2H are required. Inclusion of the updated surface complexation constants increases the overall retardation of uranium (short dashes). The two Hfo_carbonate complexes compete for sites and reduce uranyl sorption slightly.

Other model scenarios are summarized in Table 1. Both open systems with fixed partial pressures and a closed system [calcite only, no fixed $CO_2(g)$] scenario were examined; some scenarios included calcite. To estimate the sensitivity of database assumptions on mobility, additional comparisons, with and without the
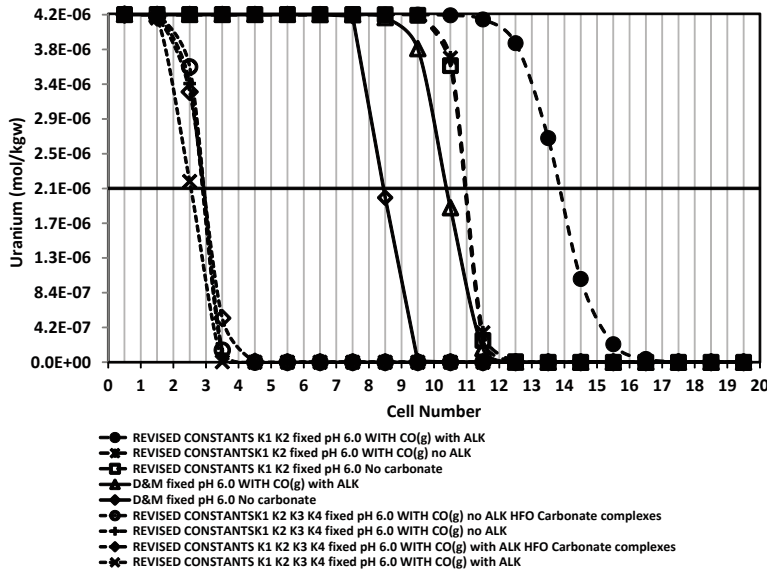
Fig. 3 Solute transport models (breakthrough curves) for uranium onto HFO using different SICM models and assumptions about the presence or absence of carbonate species.

ternary complexes, were also performed. Inclusion of the ternary complexes tends to decrease the retardation factor. Notice how greatly retardation values change up and down a column, as different database assumptions are evaluated.

Changes in retardation factors can produce another unintended consequence and in certain PHREEQC based models more uranium can be added to the modeled system than may have been intended. The "-equilibrate surface with solution" option in PHREEQC will add uranium to a surface until

it is equilibrated with the defined solution. A comparison of uranium transport models showed that inclusion of the newer database assumptions decreased bulk distribution coefficients by a factor of 2.5. Specifically, a three dimensional transport model run in PHAST (Parkhurst *et al.* 2010) and using the original Dzombak and Morel (1990) parameters (WATEQ4F.dat database provided with version 2 of PHREEQC) without the ternary complexes calculated a distribution coefficient of 50. The program required that the surface contain 50 ppm for every 1 ppm of uranium in solu-

MODEL	Fixed pH =6.0			Calcite Included		
	No CO_3^{-2}	$CO_2(g)$ =-3.5	$CO_2(g)$ =-2.0	No fixed $CO_2(g)$	$CO_2(g)$ =-3.5	$CO_2(g)$ =-2.0
D&M $K_1 K_2$	8.5	8.5	7.6	2.34 (1)	2.74 (1)	1.47 (1)
Revised $K_1 K_2$	7.6	7.6	5.7	1.56 (1)	1.18 (1)	1.1 (1)
$K_1 K_2 K_3 K_4$	NA (7.6)	26	32	11.76 (1.7)	12.5 (2.74)	10 (4.1)
$K_1 K_2 K_3 K_4$ HFO Carbonate	NA(7.6)	26	26	10.25 (1.7)	11.1 (1.96)	5 (1.1)

Table 1 Retardation factors for different surface complexation model assumptions for different scenarios. Values in parentheses represent NEA database with ternaries, the pH was allowed to float in the calcite scenarios, values were around 7.9 to 8.1.

tion. Whereas, the same model based upon the four surface complexation constants plus the updated NEA database (Grenthe *et al.* 1992, Guillaumont *et al.* 2003) with the ternary complexes produced a distribution coefficient of 18. For evaluation of performance and cleanup costs these two different starting points will greatly impact any cost estimates and feasibility evaluations.

Conclusions

The importance in selecting database parameters that represents realistic quantifiable reactions cannot be underestimated. Geochemical modelers must understand the impact that selection of such reactions can have on model conclusions. In many cases, the selection of these parameters can have a much greater impact than defining other model conditions such as carbonate minerals and the partial pressure of carbon dioxide gas. Database selection will impact conclusions from solute transport models, and potentially affect the permitting of new facilities. This historical review has shown that the extent of uranium plume migration is not always caused by the geologic setting, but in some cases by historically changing database parameters.

References

Allison JD, Brown DS, Novo-Gradac KJ (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 CAJ, Van der Weiden MJJ, Tournassat C, Charlet L (2002) Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environ. Sci. Technol., 36, 3096–3103.

Dong W, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environ. Sci. Technol. vol. 40, 4689–4695.

Dzombak DA, Morel FMM (1990) Surface complexation modeling – hydrous ferric oxide: New York, John Wiley and Sons, 393 p.

Grenthe I, Fuger J, Konings RJM, Lemire RJ, Muller AJ, Nguyen-Trung C, Wanner H (1992) Chemical Thermodynamics of Uranium. 2004 reprint available from NEA OECD. 735 p.

Guillaumont R, Fanghanel T, Neck V, Fuger J, Palmer D, Grenthe I, Rand M H (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium; Elsevier B.V. Amsterdam. 960 p.

Hsi CKD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site binding model. Geochim. Cosmochim. Acta, vol. 49, 1931–1941.

Langmuir D (1978) Uranium solution mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta, vol. 42(6), 547–569.

Mahoney JJ, Cadle SA, Jakubowski RT (2009) Uranyl adsorption onto hydrous ferric oxide – a re-evaluation for the diffuse layer model database. Environ. Sci. and Technol. vol. 43, no. 24, 9260–9266. DOI 10.1021/es901586w.

Mahoney JJ, Jakubowski RT (2008) Assessment of uranyl sorption constants on ferrihydrite – Comparison of model derived constants and updates to the diffuse layer model database. in Merkel, B.J. and Hasche-Berger, A., eds., Uranium, Mining and Hydrogeology; Springer, Berlin, p.919 – 928.

Merkel BJ, Planer-Friedrich B (2008) Groundwater Geochemistry, a practical guide to modeling of natural and contaminated aquatic systems. 2nd Ed. Nordstrom DK, Springer, Berlin, 230 p.

Morrison SJ, Spangler RR, Tripathi VS, (1995) Adsorption of uranium(VI) on amorphous ferric oxyhydroxide at high concentrations of dissolved carbonate(IV) and sulfur(VI). J. Contam.Hydrol.17, 333–346.

Parkhurst DL, Appelo CAJ, (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.

Parkhurst DL, Kipp KL, Charlton SR, (2010) PHAST Version 2—A program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions: U.S. Geological Survey Techniques and Methods 6–A35, 235 p.

Payne TE (1999) Uranium (VI) interactions with mineral surfaces: controlling factors and surface complexation modeling. Ph.D. Dissertation, University of New South Wales, Sydney, NSW.

Poeter EP, Hill MC, Banta ER, Mehl S, Christensen S (2005) UCODE_2005 and Six Other Computer Codes for Universal Sensitivity Analysis, Calibration and Uncertainty Evaluation; Techniques and Methods 6-A11; USGS: Reston, VA, 2005.

Waite TD, Davis JA, Payne TE, Waychunas GA, Xu N (1994) Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochim. Cosmochim. Acta,57, p. 2251–2269.

Wazne M, Korfiatis GP, Meng X (2003) Carbonate effects on hexavalent uranium adsorption by iron oxyhydroxide. Environ. Sci. Technol., 37, 3619–3624.