Uranium^{VI} sorption behavior on silicate mineral mixtures

James D. Prikryl*, Alka Jain, David R. Turner, Roberto T. Pabalan

Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78238-5166, USA

Abstract

Uranium^{VI} sorption experiments involving quartz and clinoptilolite, important mineral phases at the proposed US nuclear waste repository at Yucca Mountain, NV, were conducted to evaluate the ability of surface complexation models to predict U^{VI} sorption onto mineral mixtures based on parameters derived from single-mineral experiments. The experiments were conducted at an initial U^{VI} aqueous concentration of $\sim 2.0 \times 10^{-7}$ mol $\cdot$ l^{-1} (0.1 mol $\cdot$ l^{-1} NaNO$_3$ matrix) and over the pH range ~ 2.5 to ~ 9.5. The U^{VI} solutions were reacted with either quartz or clinoptilolite only, or with mixtures of the two minerals. The experiments were carried out under atmospheric pCO$_2$(g) conditions (in loosely capped containers) or under limited pCO$_2$(g) (in capped containers or in a glove box).

Data from sorption experiments on quartz at atmospheric pCO$_2$ conditions were used to derive U^{VI} binding constants for a diffuse-layer surface complexation model (DLM). The DLM was then used with surface area as a scaling factor to predict sorption of U^{VI} onto clinoptilolite and clinoptilolite/quartz mixtures under both atmospheric and low pCO$_2$ conditions. The calculations reproduced many aspects of the pH-dependent sorption behavior. If this approach can be demonstrated for natural mineral assemblages, it may be useful as a relatively simple method for improving radionuclide transport models in performance-assessment calculations. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Uranium; Sorption; Surface complexation; Clinoptilolite; Quartz; Mineral mixture

* Corresponding author. Tel.: +1-210-522-5667; fax: +1-210-522-5184.
E-mail address: jprikryl@swri.edu (J.D. Prikryl).

1. Introduction

The potential release of radionuclides as dissolved constituents in groundwater is a primary concern in performance assessments of proposed high-level nuclear waste (HLW) geologic repositories. Sorption onto mineral surfaces is an important mechanism for reducing radionuclide concentrations along groundwater flow paths and retarding radionuclide migration to the accessible environment. However, the dependence of sorption on aqueous solution properties (e.g., pH, radionuclide concentration, ionic strength, and complexing ligands) and sorptive phase characteristics (e.g., composition, surface area, and sorption site density) makes prediction of radionuclide retardation and transport difficult in natural geologic systems that are mineralogically and chemically heterogeneous. Recent sorption studies on a variety of mineral separates indicate that sorption of U^{VI} and Np^{V} through a surface complexation mechanism is important where the chemistry of the system favors the formation of hydroxy complexes in the aqueous phase, and that the magnitude of sorption is controlled primarily by the number of available sorption sites, which may be indirectly determined from surface area measurements (Pabalan and Turner, 1997; Bertetti et al., 1998; Pabalan et al., 1998; Turner et al., 1996). Because rocks are multimineralic phases, an important uncertainty in predicting sorption in natural systems is the effect of the heterogeneity of the geologic materials.

In this study, experimental and surface complexation modeling studies were conducted to investigate the sorptive behavior of U^{VI} onto clinoptilolite, quartz, and binary mixtures of both minerals. Clinoptilolite and quartz are common sorptive mineral phases present in the rock matrix and in fractures at the proposed Yucca Mountain HLW repository (Bish and Chipera, 1989). The mineralogic and surface characteristics of clinoptilolite and quartz are distinct and could potentially influence U^{VI} sorption. The study was designed to determine whether model parameters derived from data on single minerals can be used successfully to predict U^{VI} sorption onto mineral mixtures.

2. Experimental

2.1. Mineral preparation and characterization

Clinoptilolite was prepared from a clinoptilolite-rich tuff from Death Valley Junction, CA (Minerals Research, Clarkson, NY). The tuff was crushed and sieved to obtain material in the 100–200 mesh (0.150–0.074 mm) size range. Clinoptilolite was pretreated to remove mineral impurities such as soluble salts, carbonates, and iron oxides using a procedure described in Pabalan (1994). The purified clinoptilolite was converted to Na-form by ion exchange with 3 mol·l^{-1} NaCl solutions at 90°C for about 2 weeks. The measured external surface area (gas adsorption N_2-BET method, Coulter SA3100 surface-area analyzer) of the clinoptilolite is 11.9 ± 0.08 m$^2 \cdot$ g^{-1}.

Quartz was prepared from a quartz sand (Wedron #510) obtained from Wedron Silica (Wedron, IL). The quartz was sieved to isolate the 60–100 mesh (0.250–0.149 mm) size range and pretreated in a similar manner to clinoptilolite to remove mineral

impurities. A fine-grained quartz fraction (0.044–0.004 mm) was then prepared for use in the sorption experiments by crushing the 60–100 mesh fraction, sieving to isolate the ≤ 325 mesh (≤ 0.044 mm) size range, and removing particles < 4 μ m in size by density separation via centrifugation. The measured surface area of the fine-grained quartz was 0.31 ± 0.01 m$^2 \cdot$ g^{-1}.

XRD analysis and optical examination indicated that the pretreated minerals were greater than 99% by volume clinoptilolite or quartz. For the mineral mixture experiments, clinoptilolite and quartz were mixed with mass ratios (clinoptilolite to quartz) of 0.035, 0.35, and 0.7. The measured surface areas of these mixtures were 0.61 ± 0.03, 2.94 ± 0.03, and 4.58 ± 0.03 m$^2 \cdot$ g^{-1}, respectively. These measured surface areas are slightly less than the values calculated based on the mass of clinoptilolite and quartz in the mixture, probably due to particle agglomeration that reduced the surface area available for N$_2$ gas adsorption.[1]

2.2. Batch experiments

Batch experiments were conducted by reacting weighed amounts of the sorbent minerals (clinoptilolite, quartz, and clinoptilolite/quartz mixtures) with weighed quantities (~ 35 ml) of U^{VI} solutions in polycarbonate centrifuge tubes. The U^{VI} solutions used in the experiments ($\sim 2.0 \times 10^{-7}$ mol $\cdot$ l^{-1} U^{VI} in a 0.1 mol $\cdot$ l^{-1} NaNO$_3$ matrix) were prepared by diluting a ^{233}U standard obtained from Isotope Products (Burbank, CA). The amount of quartz in the quartz-only and clinoptilolite/quartz experiments was constant at 1.0 g, whereas the amount of clinoptilolite in the clinoptilolite-only and clinoptilolite/quartz experiments was varied (0.035, 0.35, or 0.7 g). The conditions of the various experiments are summarized in Table 1.

Experiments were conducted at room temperature ($22 \pm 2°C$) under conditions in equilibrium with atmospheric CO$_2$(g) (pCO$_2 = 10^{-3.5}$ atm) or at CO$_2$(g) pressures less than atmospheric (low-pCO$_2$). In experiments at atmospheric pCO$_2$, the solutions were in loosely capped containers to allow equilibration with atmospheric CO$_2$(g). In low-pCO$_2$ experiments, the U^{VI} solutions were in containers that were either tightly capped or placed in a controlled-atmosphere glove box containing zero-grade air (< 3 ppm CO$_2$).

The pH of the solutions, measured using a glass combination electrode (Orion-Ross), was adjusted to be in the range ~ 2.5 to ~ 9.5 by addition of HNO$_3$, NaHCO$_3$, or NaOH solutions. Experimental solutions were agitated using gyratory shakers for at least 10 days. After reaching equilibrium, the final pH of each solution was measured and the amount of U^{VI} sorbed on the mineral(s) was determined either from the difference in

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[1] In the draft version, the sentence included sample heterogeneity as another possible explanation of the difference in measured and calculated surface areas. The technical reviewer (P.B.) commented that if the samples were heterogeneous enough to affect the S_A measurements, it would also impact the sorption results. P.B. recommended that replicate analyses could resolve this issue. If replicates were analyzed and S_A values were within error range, then heterogeneity is not a factor. P.B. thinks that incorporating this explanation brings up much uncertainty, that it should be confirmed or removed. We opted to remove sample heterogeneity.

Table 1
Summary of experimental conditions[a]

Mineral sorbent	Clinoptilolite/quartz[b] mass ratio	Clinoptilolite M/V ratio $(g \cdot l^{-1})$	Quartz[b] M/V ratio $(g \cdot l^{-1})$	Initial U^{VI} concentration $(mol\ l^{-1})$	pCO_2 conditions
Clinoptilolite (0.7 g)	–	20	–	2.06×10^{-7}	Atmosphere
Clinoptilolite (0.7 g)	–	20	–	2.09×10^{-7}	Glove box
Quartz	–	–	28.6	2.03×10^{-7}	Atmosphere
Quartz	–	–	28.6	2.04×10^{-7}	Capped
Clinoptilolite/quartz	0.035	1	28.6	2.04×10^{-7}	Atmosphere
Clinoptilolite/quartz	0.35	10	28.6	1.92×10^{-7}	Atmosphere
Clinoptilolite/quartz	0.35	10	28.6	2.04×10^{-7}	Capped
Clinoptilolite/quartz	0.7	20	28.6	2.10×10^{-7}	Atmosphere
Clinoptilolite/quartz	0.7	20	28.6	2.03×10^{-7}	Glove box

[a] All experiments used a solution volume of 35 ml.
[b] The amount of quartz used was 1.0 g.

initial and final U concentration in solution or from the amount of U^{VI} desorbed from the solid phase with 0.1 M HNO_3. Uranium was analyzed by counting ^{233}U α-activity in an α–β discriminating liquid scintillation analyzer (Packard 2505 TR/AB) for a period of time such that the 2σ error of the sample activity was $\pm 3\%$.

3. Experimental results and discussion

Results of the U^{VI} sorption experiments are shown in Fig. 1 in terms of the distribution coefficient (K_d) vs. pH. The K_d was calculated from the equation:

$$K_d \left(ml \cdot g^{-1} \right) = \frac{\text{equilibrium amount of U sorbed}}{\text{equilibrium amount of U in solution}} \left(\frac{V}{M} \right) \tag{1}$$

where V is the solution volume (ml) and M is the solid mass (g). The use of K_d provides a means of normalizing sorption results with respect to the M/V ratio and of taking into account the decrease in U^{VI} solution concentration that occurs during the course of the experiment.

The data in Fig. 1 show that U^{VI} sorption on clinoptilolite, quartz, and clinoptilolite/quartz mixtures is strongly influenced by solution pH. In experiments conducted at atmospheric pCO_2 (Fig. 1A), U^{VI} sorption reaches a maximum at near-neutral pH (~ 6.0 to ~ 6.5) and decreases toward more acidic and more alkaline conditions. Under low-pCO_2 conditions (Fig. 1B), U^{VI} sorption increases with increasing pH up to about 6.0, then remains relatively constant with further increases in pH. Notably, the pH dependence of U^{VI} sorption is similar regardless of the relative proportion of clinoptilolite to quartz.

It is useful to compare the pH dependence of U^{VI} sorption with its aqueous speciation. The calculated relative stabilities of aqueous U^{VI} species in a 2.1×10^{-7} mol l^{-1} U^{VI} solution (0.1 mol$\cdot l^{-1}$ $NaNO_3$ matrix) are shown in Fig. 2. The U^{VI}
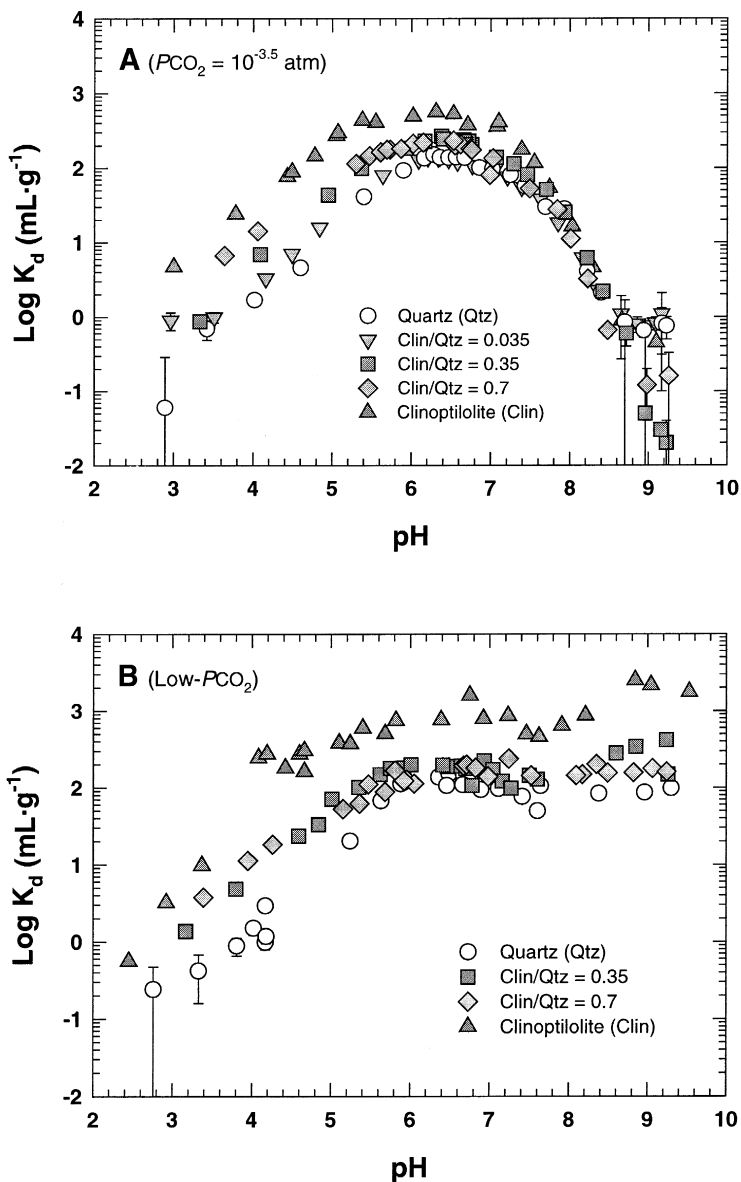
Fig. 1. Uranium[VI] sorption on clinoptilolite, quartz, and clinoptilolite/quartz mixtures under (A) atmospheric pCO_2 conditions ($pCO_2 = 10^{-3.5}$ atm) and (B) low-pCO_2 conditions. Experimental solutions had initial U[VI] concentrations of $\sim 2.0 \times 10^{-7}$ mol^{-1}. Error bars indicate 2σ uncertainties associated with the sorption data.

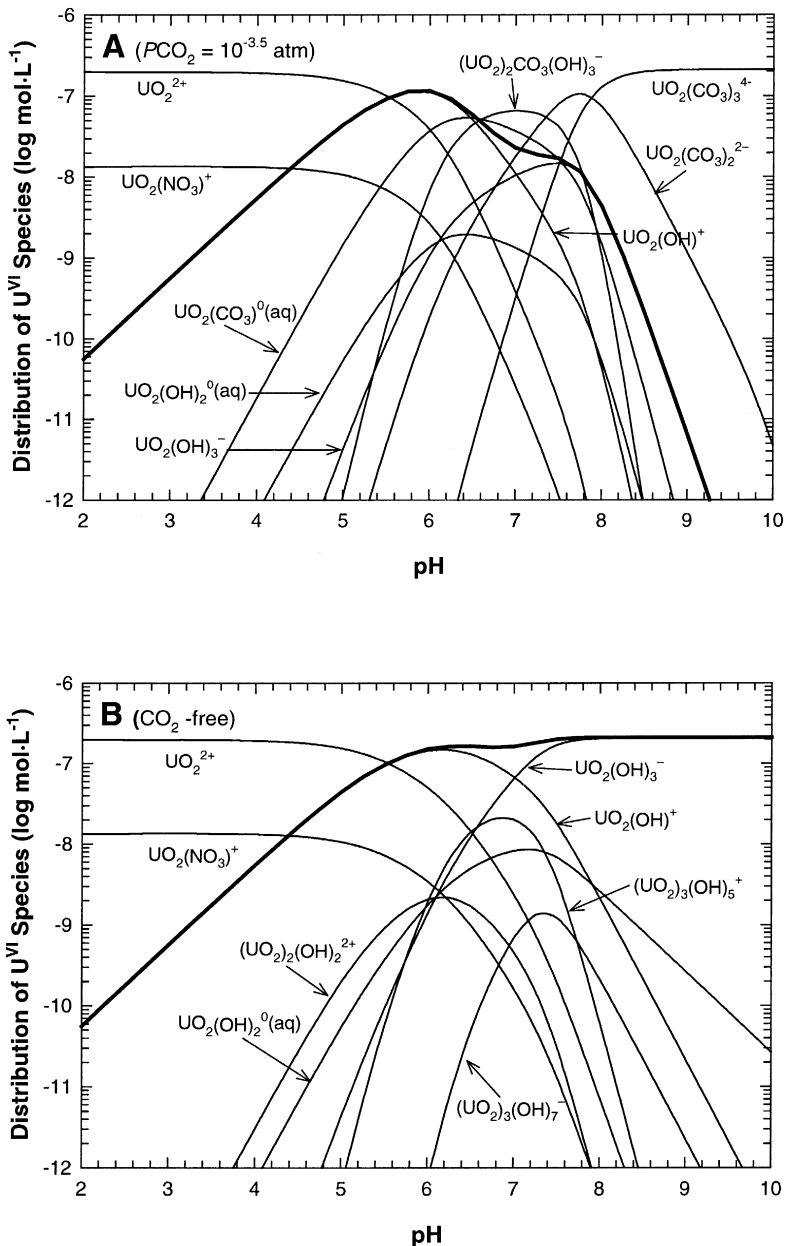Fig. 2. Calculated speciation of a 2.1×10^{-7} mol^{-1} U^{VI} solution (0.1 mol^{-1} NaNO$_3$ matrix) in equilibrium with atmospheric pCO$_2$ (pCO$_2 = 10^{-3.5}$ atm) (A) and in the absence of CO$_2$ (B). Some minor species are not shown. The heavy curves represent the total concentration of U^{VI} hydroxy complexes.

speciation was calculated using stability constants for U^{VI} aqueous species taken from the Nuclear Energy Agency (NEA) database (Wanner and Forest, 1992), except the value for the $UO_2(OH)_2^0(aq)$ species which was taken from Fuger (1992).

A comparison of Fig. 1A with Fig. 2A (atmospheric pCO_2 conditions) and Fig. 1B with Fig. 2B (low-pCO_2 conditions) indicates that U^{VI} sorption occurs in the pH range where U^{VI} hydroxy complexes predominate. In the absence of CO_2, U^{VI} hydroxy complexes dominate U^{VI} speciation at near-neutral and alkaline pH, coincident with the strong sorption of U^{VI} sorption on the mineral surface. Increased U^{VI} sorption at alkaline pH in carbonate-free systems has also been observed in other studies (e.g., Allard et al., 1980; Hsi and Langmuir, 1985; McKinley et al., 1995; Turner et al., 1996). The decreased sorption of U^{VI} sorbed at alkaline pH and atmospheric pCO_2 conditions has been correlated to the increased importance of aqueous U^{VI} carbonate complexes (Pabalan et al., 1998; Pabalan and Turner, 1997).

The U^{VI} sorption results indicate that the K_d values for U^{VI} sorption on clinoptilolite are greater than those on quartz by as much as an order of magnitude at some pHs (Fig. 1A and B). The K_d values for the clinoptilolite/quartz mixtures generally lie between the end-member mineral K_d values. Variations in K_d at near-neutral and alkaline pHs observed in the low-pCO_2 experiments may be due to CO_2 contamination in some solutions that resulted in formation of U^{VI} aqueous carbonate complexes.

The difference in sorption values at a particular pH for the different sorbents is a result of representing sorption in terms of K_d, which normalizes the amount of sorbed U^{VI} to the sorbent mass, not to the number of sorption sites on the mineral surface. The specific surface area, S_A, may be used as a relative index of the number of sorption sites on a mineral surface. Although it has not been demonstrated for trivalent and tetravalent actinides, data on U^{VI} and Np^V sorption on various minerals, including clinoptilolite and quartz, suggest that the magnitudes of sorption at a specific pH, initial actinide concentration, and pCO_2 are similar if normalized to an effective surface area (S_{EA}; $m^2 \cdot g^{-1}$) (Bertetti et al., 1998; Pabalan et al., 1998). For quartz, which is a nonlayered and nonporous mineral, S_{EA} can be assumed equal to S_A. For layered or porous minerals, such as clays and zeolites, interlayer or intracrystalline sites are not accessible for actinide sorption and surface areas determined, for example, by N_2-BET methods may overestimate the number of sorption sites for these minerals. For example, surface complex formation of U^{VI} on montmorillonite has been inferred to occur on hydroxylated edge sites (Zachara and McKinley, 1993), which have been estimated by potentiometric titration to account for only 10% of the specific surface area of the clay (Wanner et al., 1994). Assuming that surface complex formation of U^{VI} on clinoptilolite is similar to that on montmorillonite and that some sites are inaccessible to U^{VI} sorption, Pabalan et al. (1998) proposed an S_{EA} for clinoptilolite equal to 10% of its measured surface area.

The U^{VI} sorption data are replotted in Fig. 3 in terms of $K_{a'}$ (ml · m^{-2}), where $K_{a'}$ is K_d normalized to the mineral S_{EA} (i.e., $K_{a'} = K_d/S_{EA}$). Because one objective of this study is to predict sorption on mineral mixtures from end-member properties, the mineral mixture S_{EA} was calculated from the S_{EA} of clinoptilolite and quartz and their corresponding mass in the mixture. At atmospheric pCO_2 (Fig. 3A), U^{VI} sorption on clinoptilolite, quartz, and clinoptilolite/quartz mixtures is essentially equivalent when
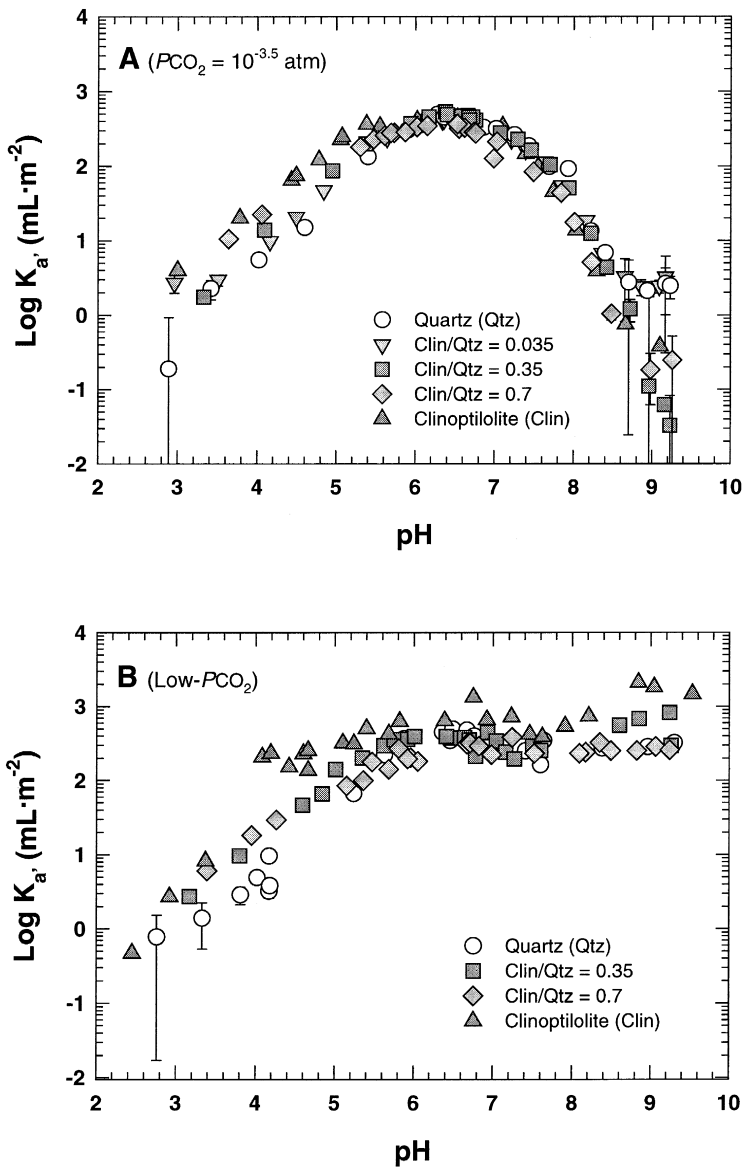
Fig. 3. Effect of surface area and normalization on U^{VI} sorption on clinoptilolite, quartz, and clinoptilolite/quartz mixtures for (A) atmospheric pCO_2 conditions ($pCO_2 = 10^{-3.5}$ atm) and (B) low-pCO_2 conditions. Sorption data are from Fig. 1(A) and (B), normalized to the sorbent effective surface area ($K_{a'} = K_d / S_{EA}$). Error bars indicate 2σ uncertainties associated with the sorption data.

recast in terms of $K_{a'}$. There is some scatter at low sorption values because of accumulated experimental uncertainties. Under low-pCO_2 conditions (Fig. 3B), there is a close correspondence in U^{VI} sorption data for the different mineral sorbents plotted in terms of $K_{a'}$. The trend of data points at neutral and alkaline pH in the low-pCO_2 experiments may have been affected by CO_2 contamination during adjustments of pH that required the addition of NaOH solution. The agreement between the $K_{a'}$ values for the various mineral sorbents indicates that S_{EA} is a useful parameter for comparing and estimating U^{VI} sorption on geologic media. Expressing sorption in terms of $K_{a'}$ is also consistent with the retardation expression developed by Freeze and Cherry (1979) for transport through fractured rock.

4. Surface complexation modeling

The diffuse-layer surface complexation model (DLM) is based on the assumption of analogous behavior between aqueous complex formation in the bulk solution and formation of surface complexes at the mineral–water interface. Additional terms are included in the mass action expressions for the surface reactions to account for electrostatic interactions near the mineral surface. Details of this modeling approach are given elsewhere (Davis and Kent, 1990).

For U^{VI}, a generalized reaction can be postulated for sorption onto an amphoteric site (represented here as $> XOH^0$) at the mineral surface:

$$> XOH^0 + pUO_2^{2+} + nH_2O \leftrightharpoons \left[> XOH_q - (UO_2)_p(OH)_n\right]^{2p+q-n-1}$$
$$+ (1 + n - q)H^+ \tag{2}$$
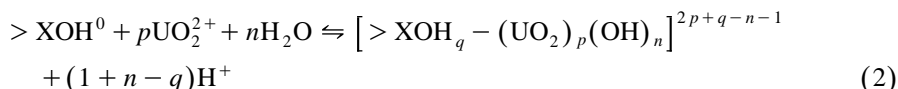
where q is the protonation state of the sorption site ($q = 0$, 1, or 2 for deprotonated, neutral, and protonated sites, respectively), and p and n are the reaction coefficients for UO_2^{2+} and H_2O, respectively. In the DLM approach, the model user postulates one or more surface reactions of the form given above, and mass action and mass balance constraints for the U^{VI}–H_2O–CO_2–mineral system are used to determine the appropriate binding constants (e.g., $K_{[> XOH_q - (UO_2)_p(OH)_n]}^{int}$). In general, a larger number of surface reactions provides a better fit to the sorption data. In the absence of detailed structural information on the mineral–water interface, the model with the fewest number of postulated surface reactions was preferred in this study.

The observed dependence of actinide sorption on pH and pCO_2 is a consequence of mass action effects and equilibrium chemistry in the U^{VI}–H_2O–CO_2–mineral system. From the point of view of using reactions as in Eq. (2) to model pH-dependent U^{VI} sorption, an increase in the activity of the UO_2^{2+} species drives the equilibrium reaction forward, increasing sorption. Competition by complexing ligands, such as carbonate, for the available U^{VI} reduces the aqueous activity of UO_2^{2+} and drives the reaction in the opposite direction, decreasing sorption.

In this study, binding constants for surface reactions on quartz were determined using the numerical optimization code FITEQL, Version 2.0 (Westall, 1982) based on data from experiments open to the atmosphere. It is important to note that the binding constants for the postulated surface reactions (Table 2) are determined in the context of

Table 2

DLM parameters and U^{VI} sorption binding constants determined from quartz-only, atmospheric pCO_2 sorption data using FITEQL, Version 2.0 (Westall, 1982)

DLM parameters	Quartz
Site density[a]	$2.3 \text{ sites} \cdot nm^{-2}$
Surface area[b]	$0.31 \text{ m}^2 \cdot g^{-1}$
Ionic strength	0.1 M NaNO_3
pCO_2	$10^{-3.5} \text{ atm}$
Surface/sorption reactions:	Log K
$> SiOH^0 \Leftrightarrow > SiO^- + H^+$	-7.06[c]
$> SiOH^0 + H^+ \Leftrightarrow > SiOH_2^+$	-1.24[c]
$> SiOH^0 + UO_2^{2+} \Leftrightarrow > SiO-UO_2^+ + H^+$	-0.30[d]
$> SiOH^0 + UO_2^{2+} + 3H_2O \Leftrightarrow > SiO-UO_2(OH)_3^{2-} + 4H^+$	-18.70[d]

[a] Davis and Kent (1990); Dzombak and Morel (1990).
[b] S_{EA} for quartz assumed to be equal to the total N_2-BET surface area.
[c] Sverjensky and Sahai (1996).
[d] This study.

the aqueous speciation reactions that make up the chemical equilibrium model and, therefore, are dependent on the thermodynamic data used to describe the U^{VI} system. Consistent with the aqueous speciation illustrated in Fig. 2, thermodynamic data from the NEA database (Wanner and Forest, 1992) and Fuger (1992) were used in the modeling study. Although quartz exhibits an overall negative surface charge over the pH range of the experiments, there are a finite number of undissociated sites that may contribute to uranyl sorption. Additional refinement of the modeling over a variety of experimental conditions to include features such as multidentate complexes, ion exchange, and competing cations/anions may help to clarify the nature of the surface complexes.

DLM-calculated K_ds for quartz sorption (atmospheric pCO_2) were cast in terms of $K_{a'}$ using the quartz N_2-BET surface area of $0.306 \text{ m}^2 \cdot g^{-1}$. $K_{a'}$ values were then used to predict K_d values for each of the different clinoptilolite/quartz mixtures (Fig. 4A). The quartz-based $K_{a'}$ was scaled using the S_{EA} calculated for each clinoptilolite/quartz mass ratio, assuming that the S_{EA} for clinoptilolite is 10% of its N_2-BET measured surface area. Similar calculations were done for comparison with the low-pCO_2 data (Fig. 4B). In that case, quartz K_ds for CO_2-free conditions were calculated using the DLM parameters derived from the atmospheric pCO_2 data and scaled to the S_{EA} of the mineral mixtures.

Although the agreement is not exact, the values calculated using S_{EA} as a scaling factor reproduce a number of the features observed in U^{VI} sorption onto clinoptilolite/quartz mixtures. The calculation predicts the slope of the increase in sorption over a pH range of 3 to ~ 6 (Fig. 4A), as well as the sorption maximum observed at a pH of about 6.5 and the sharp decrease in U^{VI} sorption at pH > 7. Scaling the quartz model based on the S_{EA} of the mineral mixtures correctly predicts the general increase in sorption as the clinoptilolite/quartz mass ratio increases. However, at pH < 5 and pH > 8.5, the amount of sorption is underpredicted for the mineral mixtures
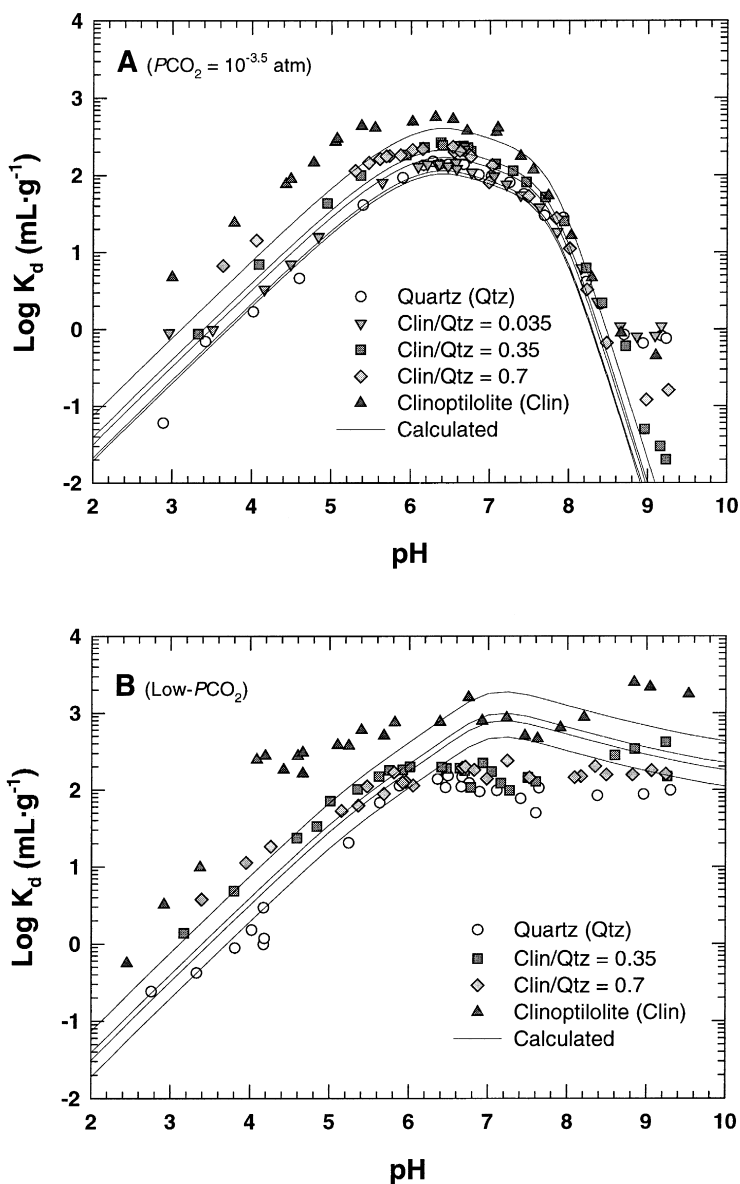
Fig. 4. Comparison of calculated and experimental results for (A) atmospheric pCO_2 ($pCO_2 = 10^{-3.5}$ atm) and (B) low-pCO_2 conditions. DLM parameters, listed in Table 2, were derived from experiments on quartz under atmospheric pCO_2 conditions, and were used to calculate quartz, clinoptilolite, and mineral mixture K_ds using surface area as a scaling factor.

and for the clinoptilolite end-member. Some of this underprediction is due to experimental uncertainty, whereas at low pH the disagreement is likely due to a clinoptilolite ion exchange process that is not included in the present model. Applying the DLM using parameters derived from the atmospheric pCO_2 data successfully predicted sorption trends at low-pCO_2 conditions, but the model simplicity resulted in a general overprediction of sorption at high pH values (Fig. 4B).

5. Conclusions

Similar pH-dependent trends in U^{VI} sorption behavior are observed for clinoptilolite, quartz, and mixtures of clinoptilolite and quartz. Uranium^{VI} sorption is enhanced under conditions that favor the formation of aqueous U^{VI} hydroxy complexes (e.g., near-neutral pH for atmospheric pCO_2 conditions and near-neutral and alkaline pH for low-pCO_2 conditions). Geochemical conditions that inhibit the formation of U^{VI} hydroxy complexes (e.g., low pH and formation of carbonate complexes) suppress U^{VI} sorption. When plotted in terms K_d, sorption values for the mineral mixtures at a specific pH, initial U^{VI} concentration and pCO_2 generally lie between those of the single minerals, suggesting that U^{VI} sorption is sensitive to changes in surface area or number of sorption sites. The results also indicate that for a specific pH, initial U^{VI} concentration, and pCO_2 the magnitude of U^{VI} sorption is essentially the same for the various mineral sorbents if normalized to an effective surface area.

Using quartz K_ds calculated with the DLM and using surface area as a scaling factor, sorption onto clinoptilolite and onto clinoptilolite/quartz mixtures was predicted. The scaled model reproduced many aspects of U^{VI} sorption onto mineral mixtures and eliminates the need to conduct separate DLM modeling for each mineral mixture. If this type of approach can be demonstrated for natural mineral assemblages, it suggests a relatively simple and effective method for improving radionuclide transport models used in performance assessment calculations.

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