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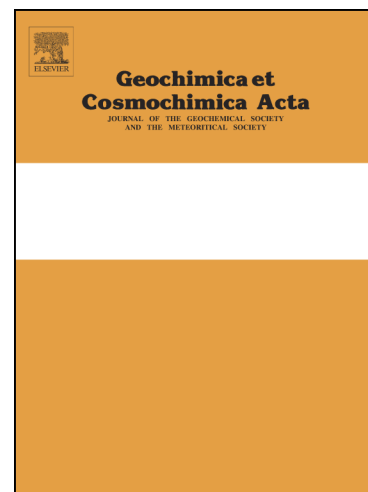
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Modeling uranium(VI) adsorption onto montmorillonite under varying carbonate concentrations: A surface complexation model accounting for the spillover effect on surface potential

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ABSTRACT

The prediction of U(VI) adsorption onto montmorillonite clay is confounded by the complexities of: (1) the montmorillonite structure in terms of adsorption sites on basal and edge surfaces, and the complex interactions between the electrical double layers at these surfaces, and (2) U(VI) solution speciation, which can include cationic, anionic and neutral species. Previous U(VI)-montmorillonite adsorption and modeling studies have typically expanded classical surface complexation modeling approaches, initially developed for simple oxides, to include both cation exchange and surface complexation reactions. However, previous models have not taken into account the unique characteristics of electrostatic surface potentials that occur at montmorillonite edge sites, where the electrostatic surface potential of basal plane cation exchange sites influences the surface potential of neighboring edge sites ('spillover' effect).

A series of U(VI) – Na-montmorillonite batch adsorption experiments was conducted as a function of pH, with variable U(VI), Ca, and dissolved carbonate concentrations. Based on the experimental data, a new type of surface complexation model (SCM) was developed for montmorillonite, that specifically accounts for the spillover effect using the edge surface speciation model by Tournassat et al. (2016a). The SCM allows for a prediction of U(VI) adsorption under varying chemical conditions with a minimum number of fitting parameters, not only for our own experimental results, but also for a number of published data sets. The model agreed well with many of these datasets without introducing a second site type or including the formation of ternary U(VI)-carbonate surface complexes. The model predictions were greatly impacted by utilizing analytical measurements of dissolved inorganic carbon (DIC) concentrations in individual sample solutions rather than assuming solution equilibration with a specific partial pressure of CO₂, even when the gas phase was laboratory air. Because of strong aqueous U(VI)-carbonate solution complexes, the measurement of DIC concentrations was even important for systems set up in the 'absence' of CO₂, due to low levels of CO₂ contamination during the experiment.

1. INTRODUCTION

Due to mining, milling and fuel processing operations, numerous sites have been contaminated with uranium in the past, with 38 proposed or final Superfund sites on the EPA National Priority List in the U.S. alone (NIH, 2016). In the future, the long-term storage of nuclear waste has the potential to create additional sources of uranium contamination affecting subsurface environments and drinking water resources. Chemically-induced, acute effects of uranium in humans, such as an inflammation of the kidneys (nephritis), have been reported (Hursh and Spoor, 1973), while chronic health effects and carcinogenicity are less well understood (World Health Organization, 2004). At this point in time, the World Health Organization has proposed a provisional guideline value of $15 \mu\text{g U L}^{-1}$ in drinking water (World Health Organization, 2004); the current U.S. EPA Maximum Contaminant Level (MCL) is set at $30 \mu\text{g U L}^{-1}$ (U.S. Environmental Protection Agency, 2001). A sound scientific understanding of uranium mobility is needed in order to evaluate risks to humans and the environment, to optimize the management of nuclear waste and to take appropriate remediation actions if necessary.

The most relevant factors controlling uranium transport in saturated porous media are uranium solubility in pore water solutions and uranium adsorption reactions to mineral surfaces. Uranium can exist at oxidation states of IV or VI, but U(VI) is the most relevant oxidation state in most surface waters and in oxic groundwaters (Choppin, 2006). In reducing environments, the low solubility of U(IV) mineral phases greatly decreases uranium mobility.

Numerous studies have demonstrated the impacts of pH, bicarbonate and calcium concentrations on U(VI) solution speciation, adsorption and transport behavior (Davis et al., 2004; Curtis et al., 2006; Fox et al., 2006; Hartmann et al., 2008; Yabusaki et al., 2008; Ma et al., 2010; Kerisit et al., 2010; Bradbury et al., 2011; Joseph et al., 2011). Potential changes in chemical solution conditions and contaminant solution speciation over time and space are especially relevant for uranium, given the long half-lives of uranium isotopes and complex transport pathways in engineered systems and the natural environment. For instance, in nuclear waste repositories, pore water pH is buffered at values between 7 and 8 in the bentonite backfill material of engineered barrier systems surrounding waste canisters and/or in the clay host-rock (Muurinen and Lehtikoinen, 1999; Bradbury and Baeyens, 2003; Wersin, 2003; Wersin et al., 2004; Tournassat et al., 2015c). However, more alkaline pH conditions are expected in close

proximity to steel canisters (pH 8 – 11) due to corrosion processes (Bildstein and Claret, 2015), as well as in cementitious leachates at bentonite-concrete boundaries (pH>13 for Ordinary Portland Cement and pH 9 – 11 for low alkali cement) due to the chemical degradation of cement (Savage et al., 1992; Gaucher and Blanc, 2006; Gaboreau et al., 2012b; Milodowski et al., 2016). Furthermore, dissolved calcium concentrations may also vary over time and space due to the progressive degradation of cement-based engineered barriers, the specific calcite contents in clay host rocks or changing concentrations in carbonate minerals along transport pathways (Hartmann et al., 2008; Gaboreau et al., 2012a; Adinarayana et al., 2013).

These chemical gradients in waste scenarios are important for the fate and transport of uranium, since U(VI) aqueous speciation is very complex. For instance, the uranyl cation (UO_2^{2+}) typically dominates speciation at low pH, while neutral and anionic U(VI)-hydroxyl and carbonate complexes become predominant at higher pH conditions. In a dilute U(VI) solution at pH 7 in the absence of carbonate, the predominant U(VI) species is the neutral $\text{UO}_2(\text{OH})_2^0$. In comparison, for the same solution in equilibrium with atmospheric CO_2 , the predominant species is the anion $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ (for a 1 μM solution). However, groundwater solutions are typically in equilibrium with partial pressures of CO_2 ($p\text{CO}_2$) at 1 % or greater, and may contain considerable concentrations of calcium due to the presence of carbonate minerals. At 1 % $p\text{CO}_2$, pH 7 and in the *absence* of Ca, U(VI) solution speciation is dominated by the anion $\text{UO}_2(\text{CO}_3)_2^{2-}$ (Fig. EA-1, Electronic Annex). For a comparable solution in equilibrium with calcite, the predominant U(VI) species is the neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ (Fig. EA-2, Electronic Annex).

Clay minerals are important minerals to consider in uranium contaminant transport because of the proposed use of bentonite or clay-rocks as a buffer material in engineered and natural barrier systems at future nuclear waste disposal sites (Tournassat et al., 2015b). Furthermore, there is the possibility that colloid-facilitated transport of uranium adsorbed on clay or bentonite particles may occur near granite waste repositories (Geckeis et al., 2004; Schäfer et al., 2004; Missana et al., 2008). Last, clay contents in soils and sediments are often high at uranium-contaminated sites (Grawunder et al., 2009; Graham et al., 2011).

Sodium-montmorillonite is the focus of this study because this mineral is the major component of bentonite in barrier systems. Montmorillonite is a smectite, a 2:1-layer-type dioctahedral phyllosilicate with a large specific surface area ($\sim 750 \text{ m}^2 \cdot \text{g}^{-1}$) and cation exchange capacity ($\sim 1 \text{ mol}_c \cdot \text{kg}^{-1}$). Each montmorillonite layer has a thickness of $\sim 1 \text{ nm}$ and carries

negative surface charges due to isomorphic substitutions of Al(III) for Si(IV) and Mg(II)/Fe(II) for Al(III) in its phyllosilicate framework (Brigatti et al., 2013). Due to its mineralogical structure, montmorillonite provides two types of surfaces and surface site types: (1) cation exchange sites, with a permanent surface charge, on basal planar surfaces, and (2) surface complexation sites, with variable surface charges as a function of pH, on edge surfaces of clay particles (Borisover and Davis, 2015).

Many research groups have investigated the surface speciation of adsorbed U(VI) on montmorillonite with EXAFS absorption spectroscopy (Dent et al., 1992; Chisholm-Brause et al., 1994; Giaquinta et al., 1997; Sylwester et al., 2000; Hennig et al., 2002; Catalano and Brown, 2005; Schlegel and Descostes, 2009; Marques Fernandes et al., 2012; Troyer et al., 2016). Analysis of the spectra obtained at various ionic strengths reveals the presence of U(VI) outer-sphere complexes at low pH and/or low ionic strengths, and of U(VI) inner-sphere complexes at other conditions. These interpretations of EXAFS data are in qualitative agreement with the duality of adsorption mechanisms on montmorillonite surfaces, i.e. cation exchange on basal planar surfaces at low pH/ionic strength and surface complexation on edge surfaces at other conditions, as also evinced by other spectrometric techniques for a range of different specifically adsorbed cations (Morris et al., 1994; Chisholm-Brause et al., 2001; Kowal-Fouchard et al., 2004; Wolthers et al., 2006).

The formation of inner-sphere bonds of U(VI) with surface groups at montmorillonite edge sites at neutral pH and high ionic strengths was deduced from the splitting of the U(VI) oxygen equatorial shell into two distinct contributions at ~ 2.3 Å and ~ 2.5 Å in EXAFS spectra. However, there is considerable uncertainty in the interpretation of second neighbor atoms involved in these surface complexes. Hennig et al. (2002) concluded that surface mononuclear bidentate complexes formed at aluminol sites. Schlegel and Descostes (2009) also proposed a U-Al shell, in agreement with Hennig et al. (2002). Additional Polarized-EXAFS (P-EXAFS) characterizations allowed them to conclude that the U complex was located on the particle edges and corresponded to a mononuclear bidentate complex. In contrast, Catalano and Brown (2005) suggested that the primary surface group second neighbors were Fe atoms, where Fe has substituted for Al in the octahedral sheets. In addition, Catalano and Brown (2005) fitted their data with a U-C shell and suggested that ternary uranyl-carbonato species formed at the surface in the presence of carbonate. However, more recently, Marques Fernandes et al. (2012) and

Troyer et al. (2016) concluded that it was not possible to conclusively distinguish between Fe, Al, and Si as second neighbor atoms in U(VI) EXAFS spectra. Furthermore, Marques Fernandes et al. (2012) did not find spectroscopic evidence for uranyl-carbonato complexes at the montmorillonite surface, despite the fact that their surface complexation model included the species. Troyer et al. (2016) were not able to confirm the presence of ternary uranyl-carbonato surface complexes from their EXAFS data either, but made a strong conclusion about the presence of such species from laser-induced fluorescence spectroscopy (LIFS) data. The LIFS results, however, were obtained at very high U(VI) equilibrium concentrations and U(VI)/clay ratios. The total U(VI) concentration was 100 μM and solid-to-liquid ratio was 0.2 $\text{g}\cdot\text{L}^{-1}$, leading to an equilibrium U(VI) solution concentration of ~ 70 μM . Although it is not known, these conditions might have favored the formation of uranyl carbonate complexes driven by a high total uranium-carbonate ratio.

An accurate prediction of uranium mobility in clay-rich environments is dependent upon the development of adsorption models that can capture: (1) the complex uranium solution and surface speciation as a function of chemical solution conditions, and (2) the complexity of montmorillonite and its implications for the conceptual description of adsorption processes. Surface complexation models (SCMs) have the ability to directly link U(VI) adsorption behavior with U(VI) solution speciation based on existing thermodynamic data, which allows the models to predict changes in adsorption as a function of chemical solution conditions over time and space. Several research groups have developed surface complexation models (SCMs) for the U(VI)-montmorillonite system (Pabalan and Turner, 1996; Turner et al., 1996; Hyun et al., 2001; Bradbury and Baeyens, 2005, 2011; Marques Fernandes et al., 2012). Surface complexation modeling studies predict that U(VI) adsorption decreases at alkaline pH when carbonate anions are present, due to the formation of strong aqueous uranyl-carbonato complexes (see Fig. EA-1, and see the aqueous speciation diagrams in Davis et al. (2004) and Fox et al. (2006)). However, the impact of the aqueous carbonate complexes on U(VI) sorption depends on whether these complexes adsorb on the clay surfaces or not. For example, in the model of Marques Fernandes et al., (2012), the authors found it necessary to include ternary uranyl-carbonato surface complexes to describe U(VI) adsorption onto montmorillonite in the presence of various concentrations of aqueous carbonate. Analogous U(VI) surface species have also been proposed on iron oxides and imogolite (Waite et al., 1994; Villalobos et al., 2001; Arai et al., 2007). For

U(VI) adsorption on montmorillonite, however, in the absence of clear spectroscopic evidence, the need to add such additional surface complexes was guided by the quality of the fit between the model and the data. This fitting criterion may however be impaired by inadequate hypotheses in the modeling exercise. For example, the model of Marques Fernandes et al., (2012) was a non-electrostatic model, which means that the ionic nature of the sorbent and its interaction with the electrostatic potential field surrounding the montmorillonite particles is inherently not included. Given the complex U(VI) solution speciation described above, it is important to take into account that the interactions of cationic, neutral or anionic U(VI) solution species with the surface electrostatic field is influenced by their charge. Hence, an electrostatic model is needed in order to test the importance of the electrostatic interactions in quantifying U(VI) adsorption. Furthermore, the electrostatic model is needed to test whether it is necessary to include ternary uranyl-carbonato surface complexes in the model.

Currently available electrostatic surface complexation models for montmorillonite have been mostly based on the classical surface complexation models for oxides. These models are based on the hypothesis that surface charges are homogeneously distributed on a flat and infinite surface, which is an invalid assumption for clay minerals for the following two reasons. First, the edge surface is very different from a flat infinite surface in terms of its dimensions: while its length could be considered to be infinite, its width is always limited to 1 nm for individual layers dispersed in an electrolytic solution. Second, the surface potential developed by the permanent charges of the basal surfaces interacts with the surface potential at the edge surfaces with pH-dependent charge (Secor and Radke, 1985; Chang and Sposito, 1994; Bourg et al., 2007; Tournassat et al., 2013, 2015a, 2016a). This unique feature, called the spillover effect, must be taken into account in the development of an electrostatic model for montmorillonite edge surfaces.

Given the current uncertainties associated with results from spectroscopic studies and the modeling needs described above, the goals of this study are:

- (1) to improve the current mechanistic understanding of uranium(VI) adsorption onto montmorillonite as a function of chemical conditions, with a specific focus on the role of dissolved inorganic carbon; and
- (2) to develop an electrostatic surface complexation model that accounts for the impacts of the electric-double-layer (EDL) spillover effect on U(VI) surface reactions.

2. MATERIALS AND METHODS

For the development of U(VI) surface complexation models, it is important to carefully characterize the compositions of experimental solutions, because various other solutes may affect U(VI) solution or surface speciation. Uranium(VI) adsorption onto Na-montmorillonite was investigated here as a function of total U(VI), dissolved carbonate, and calcium concentrations (Table 1). Experimental blanks, standards and sample suspensions were analyzed for U(VI), calcium and dissolved inorganic carbon (DIC), and monitored for elements that could indicate clay dissolution or inadequate solid-liquid phase separation (for U(VI) and Ca background values, see Electronic Annex; Si, Al, Fe, K, and Mg data not reported). In addition, analytical detection limits and experimental background values for DIC solution concentrations were determined as described in further detail below. Analysis of DIC concentrations in supernatant solutions was of particular importance in our experiments, given the relevance of carbonate for U(VI) speciation.

2.1. Materials

Glassware was cleaned by soaking in acid (10 % (v/v) HCl) over 12 to 24 h, followed by thorough rinsing with Nanopure water and air-drying. All aqueous solutions were prepared with Nanopure water (Barnstead ultrapure water system) using chemicals of reagent grade or better. Acids, bases and salt solutions used in adsorption experiments were of TraceSelect grade (Sigma Aldrich), in order to minimize calcium background concentrations in particular. Uranium(VI) solutions contained U-238, either from an in-house or a commercially available uranyl nitrate stock solution (1.30 mM stock provided by Drs. David Singer and Wayne Lukens at Lawrence Berkeley National Laboratory, or various dilutions of a 1000 µg U/mL Inorganic Ventures ICP-MS standard).

A well-characterized, standardized source clay (Na-montmorillonite, SWy-2, Clay Minerals Society) was selected as the sorbent. Since this material is known to contain considerable impurities of quartz (8 %), feldspars (16 %) and calcite (Chipera and Bish, 2001; Costanzo and Guggenheim, 2001; Mermut and Cano, 2001), it was pretreated to avoid uncontrolled impacts of calcite dissolution on U(VI) solution speciation during adsorption experiments. The major purification steps, which have been described in detail elsewhere (Tinnacher et al., 2016), included: (1) dissolution of calcite impurities in 1 M sodium

acetate/0.564 M acetic acid solution at pH 5, (2) conversion of the clay into its Na form, (3) separation of quartz and feldspar impurities from the $<2 \mu\text{m}$ clay fraction by centrifugation, and (4) oven-drying of the clay mineral phase at 45°C . Afterwards, clay stock suspensions of 10 or 20 g/L were prepared in Nanopure water, and exact solid concentrations determined by weighing volume fractions before and after drying at 45°C .

2.2. Experimental protocol for batch adsorption experiments

Uranium(VI) adsorption onto Na-montmorillonite was characterized as a function of pH, and total U(VI), DIC, and calcium concentrations (Table 1).

Table 1. Experimental conditions for U(VI) batch adsorption experiments

| Expt. # | Range of pH | Total U(VI) conc. ($\mu\text{mol}\cdot\text{L}^{-1}$) | Range of dissolved inorganic carbon (DIC) ($\text{mmol}\cdot\text{L}^{-1}$) | Range of Ca ($\mu\text{mol}\cdot\text{L}^{-1}$) ¹⁾ |
|---------|-------------|---|---|---|
| 1 | 4.1 – 9.0 | 0.11 | 0.023 – 5.62 | 6.7 - 8.5 |
| 2 | 4.0 – 10.0 | 0.96 | 0.01 – 72 | 6.4 - 1.9 |
| 3 | 4.2 – 9.0 | 2.6 | 0.025 – 5.15 | 9.1 - 13 |
| 4 | 4.0 – 8.0 | 0.98 | 0.013 – 0.87 | 2100 |
| 5 | 3.9 – 9.9 | 1.1 | 0.0082 – 0.062 | 7.7 - 9.8 |
| 6 | 4.0 – 10.2 | 0.81 | 0.31 – 127 | 10 - 27 |
| 7 | 4.0 – 8.3 | 0.98 | 0.026 – 34.4 | 10 - 13 |

¹⁾ Ca conc. in exp. 1 – 3 and 5 – 7 represent background values without any Ca additions (see Electronic Annex for details).

Batch adsorption experiments were conducted at room temperature ($22.5 - 23.5^\circ\text{C}$) at an ionic strength of 0.1 M, and a Na-montmorillonite concentration of $0.5 \text{ g}\cdot\text{L}^{-1}$ (except for experiment 7 with a solid concentration, m_s , of $0.24 \text{ g}\cdot\text{L}^{-1}$). pH values ranged from 3.9 to 10.2. The reaction time was 48.5 hours, which closely approached or was sufficient to reach steady-state conditions (see discussion of kinetic adsorption data in the Electronic Annex). This reaction time is comparable to reaction times of 20-72 hours used in other, similar studies (Chisholm-Brause et al., 1994; Hyun et al., 2001; Bradbury and Baeyens, 2005; Schlegel and Descostes, 2009). Total calcium concentrations varied from low micromolar background concentrations (see Electronic Annex) to the higher concentration of 2.1 mM in the experiment with added Ca.

The main steps in the batch adsorption experiments were: (1) pre-equilibration of Na-montmorillonite with a background electrolyte solution at specific pH and chemical solution conditions, (2) U(VI) adsorption equilibration with the mineral phase, and (3) sampling and analysis of supernatant fractions after removal of the solid phase by centrifugation. In the initial preparation of the solution/clay suspensions, aliquots of Nanopure water, Na-montmorillonite stock suspension, 1 M NaCl and 0.1M CaCl₂ solutions, and 1 M or 0.1 M NaHCO₃ solution were transferred into 50 mL polycarbonate centrifuge vials sample vials to yield the intended solid concentrations and aqueous compositions in the final sample volumes. The polycarbonate vials ('Oakridge centrifuge tubes') were chosen as sample vials to minimize U(VI) wall adsorption effects. The pH values were then adjusted to the intended values for the adsorption experiments with small volumes of HCl or NaOH.

During this initial preparation procedure, the solutions were exposed to one of three different gas phases: (1) atmospheric CO₂ in laboratory air (~0.04 %, 400 ppm), (2) CO₂-“free” atmosphere (in a glove box, filled with 93.3 % N₂/5.7 % H₂ gas mixture) and (3) elevated CO₂ atmospheres (intended to be 2 % CO₂/98 % N₂). In the CO₂-“free” experiment, the initial solutions used N₂-purged Nanopure water and were prepared in an anaerobic glove box purged with a 93.3 % N₂/5.7 % H₂ gas mixture. Two experiments involved exposure to elevated CO₂ atmospheres. In Experiment 6, the solutions were prepared in a disposable Sigma Aldrich glove bag purged with a 2 % CO₂/98 % N₂ gas mixture, but it was found subsequently that the purging of the glove bag was incomplete to remove all air (see Experimental Results section). Solutions in Experiment 7 were exposed in a COY glove box to the same gas mixture, but again it was found after the experiments that the glove box had been insufficiently purged with the gas mixture. After the preparation of the solutions, they were generally pre-equilibrated in closed sample vials by shaking for 12 to 24 h; however, in the case of Experiment 7 the vials were left open and exposed to the glove box atmosphere for 15 hours.

After pre-equilibration with the electrolyte solution, aliquots of acidified U(VI) stock solution were added to obtain the intended total U(VI) concentrations in the experiments. Because the U(VI) stock solution was acidic, it was necessary to add small amounts of NaOH immediately following the U(VI) addition to adjust the pH to the intended experimental value. The vials were then shaken for 48.5 hours. Afterwards, final pH values were recorded while minimizing gas exchange during the pH measurement (discussed further below). The sample

suspensions were centrifuged to remove particles larger than approximately 50 nm from solution, as calculated based on Stokes law (Beckman Coulter Allegra 64R, F0850 rotor, centrifugation at 26 900 g for 61 minutes). Aliquots of supernatant solution were collected and analyzed for metal concentrations by ICP-MS (Perkin-Elmer SCIEX ICP-Mass Spectrometer ELAN DRC II, after sample acidification with TraceSelect grade HNO₃ (2 % v/v)), and DIC concentrations on a Shimadzu TOC-V_{CSH}. Each experiment included experimental standards (in duplicate), in which the standards had the same volume of U(VI) stock solution added to a vial in the absence of the clay with pH adjusted to 2.0. In addition, electrolyte blanks (in duplicate) containing 0.1 M NaCl but no U(VI) or clay were used to determine calcium and uranium-238 background concentrations (see Electronic Annex).

The U(VI) adsorption results are reported as distribution coefficients (K_D values, in L·kg⁻¹) and fractions of U(VI) adsorbed ($f_{U(VI)ads}$ in %). Adsorbed U(VI) fractions and K_D values were computed based on concentration differences in supernatant solutions between experimental standards (C_{tot}) and samples (C_{eq}):

$$f_{U(VI)ads} = \frac{C_{tot} - C_{eq}}{C_{tot}} \times 100 = \frac{C_{ads}}{C_{tot}} \times 100 \quad (1)$$

$$K_D = \frac{C_{ads}}{m_s \cdot C_{eq}} \quad (2)$$

where m_s is the solid concentration in kg·L⁻¹.

The error bands were calculated as follows (Tournassat et al., 2013):

$$uC_{ads} = \sqrt{uC_{tot}^2 + uC_{eq}^2}; \Delta C_{ads} = k \times uC_{ads} \quad (3)$$

$$uf_{U(VI)ads} = 100 \cdot \sqrt{\left(\frac{uC_{eq}}{C_{tot}}\right)^2 + \left(\frac{C_{eq} \cdot uC_{tot}}{C_{tot}^2}\right)^2}; \Delta f_{U(VI)ads} = k \times uf_{U(VI)ads} \quad (4)$$

$$uK_D = \sqrt{\left(\frac{uC_{tot}}{m_s \cdot C_{eq}}\right)^2 + \left(\frac{C_{tot} \cdot uC_{eq}}{m_s \cdot C_{eq}^2}\right)^2}; \Delta K_D = k \times K_D \quad (5)$$

Where Δ values are the considered error bands, k is the coverage factor (taken at a value of $k=2$), C_{tot} , C_{eq} , uC_{tot} and uC_{eq} are the total concentration, the equilibrium concentration and their

associated uncertainties (we considered 2 % of the values) respectively. Uncertainty on m_s was neglected.

2.3. Analytical detection limits and background values for dissolved inorganic carbon

The Method Detection Limit (MDL) and Minimum Level (ML) were determined to be 0.051 and 0.161 mg·L⁻¹ DIC (4.2·10⁻⁶ and 1.3·10⁻⁵ mol·L⁻¹ DIC) for the specific setup of our DIC analysis, as described in detail in the Electronic Annex. The MDL represents the minimum DIC concentration that can be identified, measured and reported with a 99 % confidence that the concentration is greater than zero (U.S. EPA, 1995). The ML is defined as the smallest measured concentration of a constituent that may be reliably reported using a given analytical method. Potential DIC contributions from various sources in the CO₂-“free” batch adsorption experiment, performed in the 93.3 % N₂/5.7 % H₂ glove box environment, were quantified as described in detail in the Electronic Annex. Taking into account the offset due to DIC background concentrations in Milli-Q water (MQW), calibration curves showed linearity down to the lowest concentration standard at 0.025 mg·L⁻¹ (2.1·10⁻⁶ mol·L⁻¹) of added DIC.

3. EXPERIMENTAL RESULTS

3.1. Dissolved inorganic carbon in experimental solutions

Because U(VI) aqueous speciation is strongly dependent on the DIC concentration (Davis et al. (2004); Fox et al. (2006), and see Figs. EA-1 and EA-2), it was very important in these experiments to determine DIC directly rather than calculate its concentration based on an assumed equilibrium with a gas phase.

3.1.1. Detection limits and background contributions.

DIC background concentrations were similar for MQW before (0.121 mg·L⁻¹, 1.0·10⁻⁵ mol mg·L⁻¹) and after (0.125 mg·L⁻¹, 1.0·10⁻⁵ mol L⁻¹) purging with nitrogen gas. The handling of open sample vials in the glove box atmosphere (5 % H₂/95 % N₂) in the CO₂-“free” adsorption experiment, centrifugation of close vials under atmospheric CO₂ conditions, and refrigeration of closed vials outside the glove box prior to DIC analysis were each evaluated for their potential to increase measured DIC concentrations (see Electronic Annex for details).

Sample handling and centrifugation, which took place prior to supernatant sampling in the CO₂-“free” adsorption experiment, resulted in 0.344 and 0.277 mg·L⁻¹ DIC (2.9·10⁻⁵ and 2.3·10⁻⁵ mol·L⁻¹ DIC) concentrations during the test experiment. Storage of solutions in the refrigerator, which occurred after supernatant sampling in the adsorption experiments, resulted in a concentration of 0.331 mg·L⁻¹ DIC (2.8·10⁻⁵ mol·L⁻¹ DIC). Given the similarity of DIC contributions from these potential sources and the series of steps in the CO₂-“free” adsorption experiment, it can be assumed that these DIC concentrations are representative of typical DIC “contaminant” contributions to sample suspensions in our adsorption experiments. Furthermore, we can assume that measured DIC values represent DIC concentrations that were present in sample suspensions during the U(VI) sorption equilibration.

3.1.2. Measured DIC concentrations in batch adsorption experiments.

Final dissolved carbonate (DIC) concentrations in the U(VI) sorption experiments were the result of several contributions: 1) background concentrations from reagents (e.g., NaOH), 2) addition of NaHCO₃ during initial solution preparation, and 3) ingassing and outgassing of CO₂ during exposure to various gas phases during the preparation of solutions for the U(VI) sorption experiments. A summary of measured DIC concentrations in the adsorption experiments is provided in Figure 1.

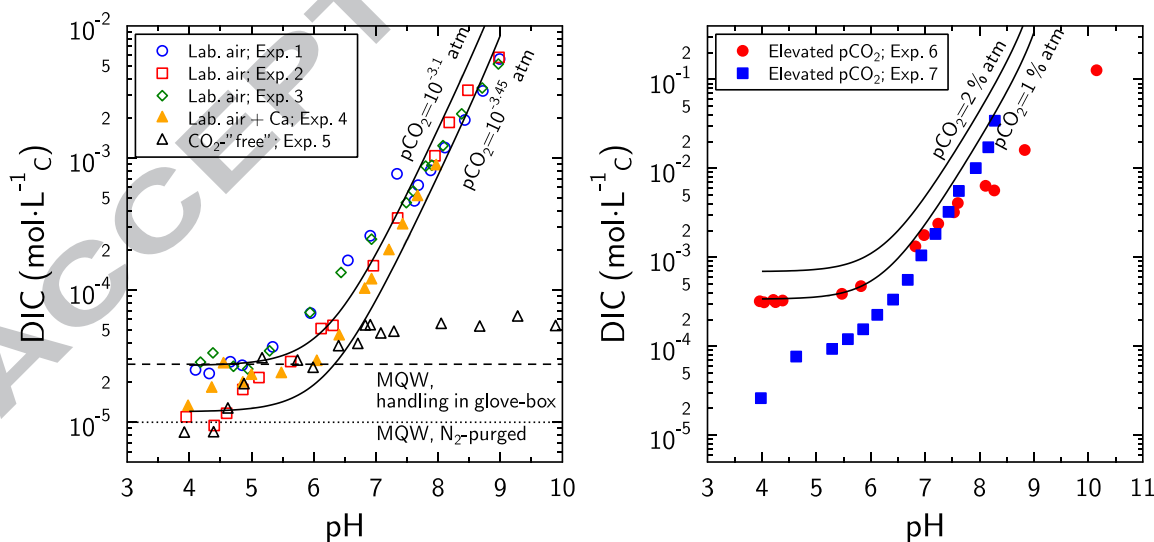


Figure 1. Measured DIC concentrations as a function of pH in the U(VI) sorption experiments and comparison with values computed for various partial pressures of CO₂. The calculations of DIC concentrations at given pCO₂ partial pressures were carried out using PHREEQC v.3 (Parkhurst and Appelo, 1999, 2013) with the THERMOCHEM database (Giffaut et al., 2014).

Experiments carried out in the presence of laboratory air (Experiments 1-4) resulted in measured DIC concentrations generally greater than the values expected for this pCO₂ ($\sim 10^{-3.45}$ atm) (Figure 1, left panel). This was likely due to additions of DIC with reagents, especially during the adjustments of pH with NaOH. Samples from the CO₂-“free” experiment (Experiment 5) had DIC concentrations similar to solutions observed under atmospheric conditions for pH < 6, suggesting CO₂ contamination during the experimental handling as described above. However, the samples at pH > 6 had DIC concentrations that were much lower than those under atmospheric conditions (Figure 1, left panel), demonstrating that the contaminant CO₂ ingassing to the solutions was likely flux-limited at higher pH.

In the experiments with elevated CO₂ in the gas phase, the DIC results (Figure 1, right panel) suggest that neither the gas bag (Experiment 6) or gas chamber (Experiment 7) was sufficiently purged with the 2% CO₂/98% N₂ gas to achieve the intended equilibration with the 2% partial pressure of CO₂. This was the case despite multiple purge volumes that were used to clear the bag and gas chamber in these experiments. In experiment 6, solutions up to a pH of 7.24 exhibited DIC concentrations that suggested equilibration with a gas phase composition closer to $\sim 1\%$ CO₂. Samples from supernatants at higher pH values had DIC concentrations consistent with even lower partial pressures of CO₂. This trend is most likely due to insufficient purging combined with a lack of fast CO₂ equilibration between the aqueous phase and the local atmosphere in the gas bag.

In experiment 7, the calculated low pCO₂ values at acidic pH suggest that the Coy gas chamber was not sufficiently flushed to achieve the target CO₂ partial pressure. Although the solutions contained added NaHCO₃ such that they would be equilibrated with a 2% CO₂ gas phase, DIC data indicate that some CO₂ outgassed from solutions into the chamber atmosphere, driven by a pCO₂ value lower than 2%.

Despite the problems equilibrating the solutions with the intended gas phases, DIC concentrations in the prepared solutions were constant in the U(VI) sorption experiments after

the closing of the centrifuge tubes (calculated partial pressures of CO_2 in the centrifuge tubes are given in Figure EA-6). By measuring DIC in all sample solutions, including those exposed to laboratory air, the equilibrium geochemical model determined the U(VI) aqueous speciation for each experimental data point rather than assuming a constant specific partial pressure of CO_2 in equilibrium with the aqueous phase. As will be discussed further below, this was very important in describing the observed U(VI) adsorption behavior in the SCM.

3.2. U(VI) Adsorption Behavior under Varying Chemical Conditions

3.2.1. Effect of variable DIC.

In experiments conducted in laboratory air (Experiments 1-4), U(VI)-montmorillonite K_D values varied over four orders of magnitude as a function of pH (Figure 2). At low pH, U(VI) adsorption is assumed to be limited due to its competition with protons at surface complexation sites (Stumm and others, 1992). At high pH, low uranium adsorption is attributed to increasing carbonate concentrations, leading to weakly sorbing or non-sorbing aqueous U(VI)-carbonate complexes (Hsi and Langmuir, 1985; Waite et al., 1994; Davis et al., 2004). In the CO_2 -“free” system, U(VI) adsorption is very similar at weakly acidic pH values to that observed for the laboratory air atmospheric CO_2 systems. Above pH 6.5, however, U(VI) adsorption was much stronger at very low concentrations of CO_2 than in the laboratory air systems. The increase in U(VI) adsorption at high pH under these conditions can be attributed to much lower concentrations of aqueous U(VI)-carbonate complexes that compete effectively with the edge site surface complexation reactions. The effect of aqueous carbonate complexes on U(VI) adsorption is further demonstrated by the U(VI) adsorption results in systems with elevated CO_2 concentrations (Experiments 6 and 7), where U(VI) adsorption decreased at pH values above 5.5 (Figure 2).

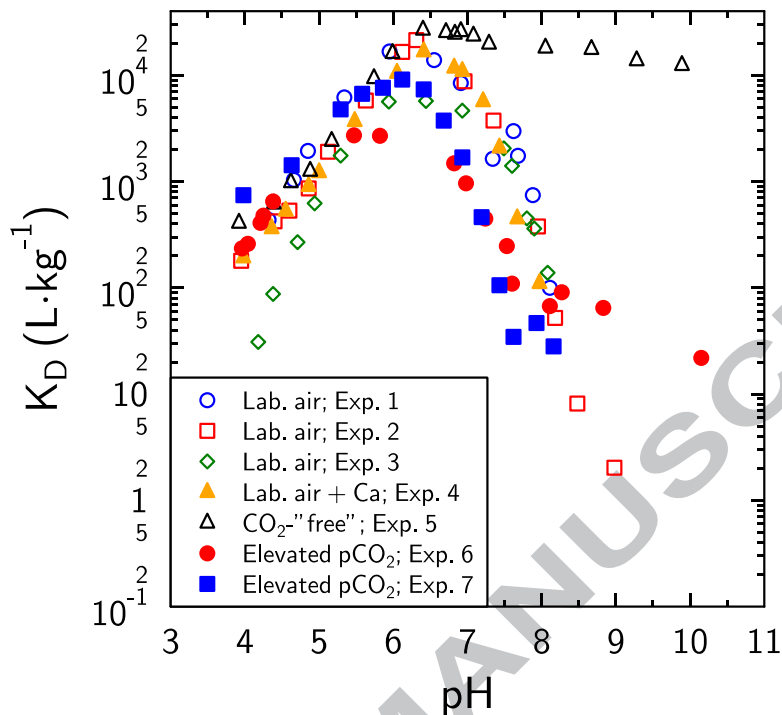


Figure 2. U(VI) adsorption as a function of pH under variable total U(VI), dissolved inorganic carbon (DIC), and Ca concentrations.

3.2.2. Effect of variable calcium concentrations.

Under laboratory air conditions, U(VI) adsorption appeared to be similar in the presence of 2.1 mM CaCl_2 compared to Ca background concentrations (Figure 2). However, upon closer inspection, the U(VI) K_D value appeared to be lower at pH~ 8 by approximately a half an order of magnitude (compare Exp. 2 and 4 with similar total U(VI) concentrations). Nonetheless, it is difficult to be certain of this effect because of differences in experimentally observed DIC concentrations. Calculations show that U(VI) aqueous speciation changes in this pH region in the presence of sufficient Ca because of the formation of aqueous ternary Ca-U(VI)-carbonate complexes at pH>7.5 (Figure 3). This effect is evaluated further in the modeling section, where calculations are made at a constant CO_2 partial pressure.

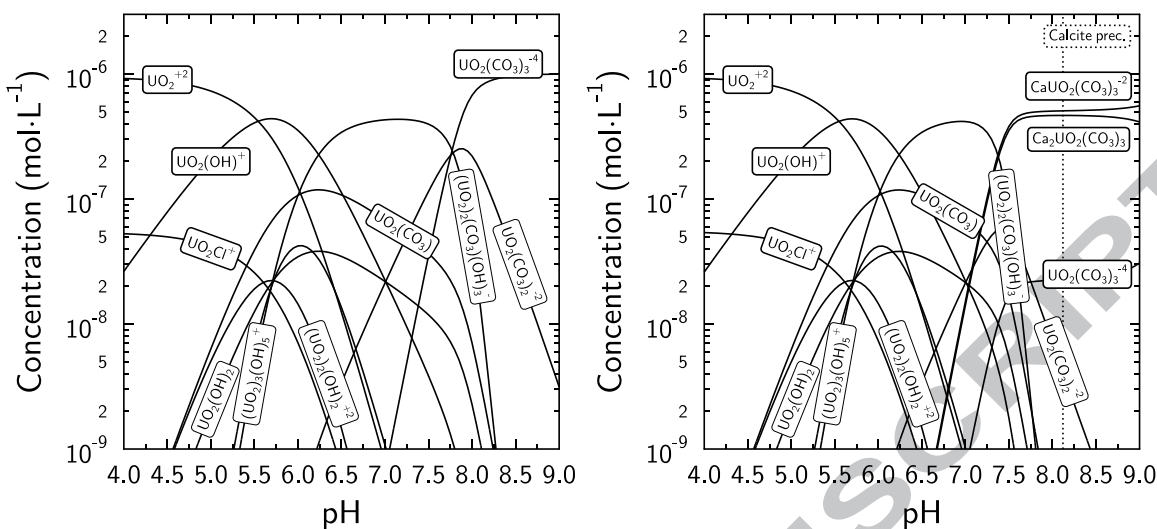


Figure 3. Calculated aqueous speciation of a 1 micromolar U(VI) solution in 0.1 M NaCl in equilibrium with atmospheric CO_2 ($\log \text{CO}_2 = -3.45$) in the absence (left) and presence of 2 mM Ca (right). Vertical axis is the negative log of the concentration of each U(VI) species.

4. MODELING AND DISCUSSION

4.1. Surface complexation modeling strategy

An analysis of the literature shows that considerable uncertainty remains on the nature of inner-sphere complexes on montmorillonite edge surfaces. Surface complexation modeling cannot elucidate the nature of clay atoms present on surface sites, i.e. decipher the contributions of aluminol, silanol and Fe-substituted sites. However, modeling allows for an estimation of the likelihood of a reaction, such as the adsorption of uranyl carbonate complexes, and an understanding of the effect of Ca- CO_3 -U(VI) solution complexes on the extent of U(VI) adsorption in calcium-rich environments. In the process, it is necessary to follow a parsimony rule, i.e. to build a model with the fewest adjustable parameters as possible in order to avoid correlations between fitting parameters. Accordingly, the chosen modeling strategy was based on a four-step approach, as follows. In a first step, U(VI) adsorption model parameters were fitted using experimental data from the CO_2 -“free” experiment. In a second step, we applied these parameters to predict the data obtained in the other experiments: a good match of the prediction

with experimental data would suggest that formation of ternary uranyl-carbonato surface complexes is not important, while an underestimation of the adsorption extent would indicate that a uranyl-carbonato surface complex must have formed (e.g., see the modeling approach of Waite et al. (1994)). In a third step, we applied the model to a large range of data obtained from the literature in order to test its robustness. In a fourth and final step, factors influencing U(VI) adsorption, such as $p\text{CO}_2$ or Ca^{2+} concentrations, are discussed on the basis of predictive calculations with the model. A summary of experimental U(VI) batch sorption data is provided in the Electronic Annex in order to allow other researchers to test their modeling concepts.

4.2. Surface complexation model for montmorillonite edge surfaces

The objective of the modeling work presented here was to develop a model that was as mechanistic as possible, but without adding too many fitting parameters. Accordingly, the speciation model for SWy-2 edge surfaces was directly taken from Tournassat et al. (2016a). This surface complexation model explicitly takes into account the spillover effect of the basal surface potential on the edge surface potential. This effect is typical for layered minerals with structural charges and renders classical surface complexation models developed for oxide surfaces incorrect for modeling clay mineral edge surface properties (Bourg et al., 2007; Tournassat et al., 2013, 2015a, 2016a).

Briefly, the negative surface charge created by the isomorphic substitutions in the montmorillonite lattice creates a negative electrostatic potential field that interacts with the electrostatic field created by the amphoteric edge surface sites (Secor and Radke, 1985; Chang and Sposito, 1994, 1996). Consequently, if the edge surface charge is zero, the edge surface potential remains negative. This effect can be adequately captured by setting the relationship between surface charge (Q_{edge} in $\text{C}\cdot\text{m}^{-2}$) and surface potential (ψ_{edge} in V) to:

$$\frac{F\psi_{edge}}{RT} = A_1 \operatorname{asinh}\left(A_2(Q_{edge} + A_3)\right) \quad (6)$$

where A_1 , A_2 , and A_3 are fitted parameters, F is the Faraday constant ($96\,485\text{ C}\cdot\text{mol}^{-1}$), R is the gas constant ($8.314\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and T is the temperature (K). For montmorillonite at $25\text{ }^\circ\text{C}$, Tournassat et al. (2013) refined the values of these parameters to: $A_1 = 1.4 - 1.2 \log I$, $A_2 = 11 + \log I$, and $A_3 = -0.02 \times (-\log I)^{1.60}$, where I refers to the ionic strength (unitless). This equation is comparable to the classic equation of the diffuse layer model (DLM) for oxides (Davis et al.,

1978) that is implemented in most geochemical calculation codes (Steefel et al., 2015), but that is not adapted to model the properties of clay edge surfaces (Tournassat et al., 2013, 2015a, 2016a):

$$\frac{F\psi}{RT} = 2 \operatorname{asinh}(B \cdot \sigma) \text{ with } B = \frac{1}{\sqrt{8\varepsilon\varepsilon_0RT \cdot 1000 \cdot I}} \quad (7)$$

where $\varepsilon\varepsilon_0$ is the dielectric constant for water. The site densities, stoichiometries and protonation/deprotonation constants were taken from Tournassat et al. (2016a). Site densities were calculated from crystallographic considerations and structural formulas; protonation/deprotonation constants were obtained from the predictions of first-principle molecular dynamics calculations (Liu et al., 2013, 2014, 2015a; b).

Edge surfaces with different crystallographic orientations exhibit amphoteric sites of different natures and with different site densities (Tournassat et al., 2016a). Two kinds of edge surfaces can be found in this model, corresponding to the AC and B chains that were first described by White and Zelazny (1988). The relative proportions of these two kinds of surfaces (AC and B) on SWy-2 particle edges and the total edge specific surface area ($\sim 14 \text{ m}^2 \cdot \text{g}^{-1}$) were fitted from titration curves. The value of the edge specific surface area that was fitted by Tournassat et al. (2016a) compared well with the value measured by the low-pressure gas adsorption method ($\sim 19 \text{ m}^2 \cdot \text{g}^{-1}$) (Duc et al., 2005). This value, however, was different from the SWy-2 N_2 -BET specific surface area value. Nitrogen-BET specific surface area measurements have been commonly used for the calibration of surface complexation models for clay minerals in the literature, even though these values are not representative of the edge specific surface area for the following reason. Nitrogen-BET measurements probe both edge and external basal surface areas of the particles, and the latter contribution always dominates over the first for montmorillonite particles (Tournassat et al., 2003, 2013, 2015a, 2016a; b).

None of the parameters of the above described surface model was changed during the modeling exercises, leaving only the speciation of U(VI) surface complexes and the related association constants as fitting parameters. Only U(VI) surface complexes on the B-chain surface type were considered in the model, in agreement with the results obtained with P-EXAFS on the orientation of the U(VI) surface complexes (Schlegel and Descostes, 2009; Marques Fernandes et al., 2012). In the absence of any supporting spectrometric evidence on the nature of the surface sites involved in U(VI)-specific adsorption, we hypothesized that the formation of U(VI) surface complexes took place on the most abundant, non-substituted $\text{Si}_\text{T}\text{-Al}_\text{Oc}\text{-Si}_\text{T}$ edge sites, where

subscripts T and Oc refer to the tetrahedral and octahedral sheets of the layer respectively (Table 2). Note that the influence of cation exchange reactions was negligible under our experimental conditions.

An in-house version of PHREEQC, which was modified to handle Eq. (6), was used to carry out the calculations, together with the database THERMOCHEM v. 9b0 for thermodynamic parameters of solute species (Giffaut et al., 2014). This database is available in various formats including PHREEQC format at the following address: <https://www.thermochimie-tdb.com/>.

Table 2. U(VI) surface complexation reactions on SWy-2 particle edges and related association constants used for modeling. The surface speciation model of Tournassat et al. (2016a) provides information on surface types and areas, site types and protonation/deprotonation constants. For the calculation of the sites stoichiometry, the following structural formula was considered: $(\text{Si}_{3.87}\text{Al}_{0.13})(\text{Al}_{1.52}\text{Mg}_{0.25}\text{Fe}^{\text{III}}_{0.224}\text{Fe}^{\text{II}}_{0.006})\text{Na}_{0.36}\text{O}_{10}(\text{OH})_2$ (Duc et al., 2005; Tournassat et al., 2016a).

| | | |
|--|---|--|
| Edge surface areas | Total | $14 \text{ m}^2 \cdot \text{g}^{-1}$ |
| | Edge surface of B type | $7 \text{ m}^2 \cdot \text{g}^{-1}$ |
| | | |
| Protonation/deprotonation reactions | Log K | |
| | $\text{Si}_T\text{-Al}_{\text{Oc}}\text{-Si}_T$ | $\text{Si}_T\text{-Fe}^{\text{III}}_{\text{Oc}}\text{-Si}_T$ |
| $>\text{SiteH}_4^+ = >\text{SiteH}_3 + \text{H}^+$ | -3.1 | -1.2 |
| $>\text{SiteH}_3 = >\text{SiteH}_2^- + \text{H}^+$ | -7 | -5.1 |
| $>\text{SiteH}_2^- = >\text{SiteH}^{2-} + \text{H}^+$ | -7 | -8.6 |
| $>\text{SiteH}^{2-} = >\text{Site}^{3-} + \text{H}^+$ | -8.3 | -8.6 |
| | | |
| | $\text{Si}_T\text{-Mg}_{\text{Oc}}\text{-Si}_T$ | $\text{Si}_T\text{-Fe}^{\text{II}}_{\text{Oc}}\text{-Si}_T$ |
| $>\text{SiteH}_4 = >\text{SiteH}_3^- + \text{H}^+$ | -10.8 | -6.6 |
| $>\text{SiteH}_3^- = >\text{SiteH}_2^{-2} + \text{H}^+$ | -10.8 | -10.2 |
| $>\text{SiteH}_2^{-2} = >\text{SiteH}^{-3} + \text{H}^+$ | -13.2 | -10.2 |
| $>\text{SiteH}^{-3} = >\text{Site}^{-4} + \text{H}^+$ | N.A. | -11.2 |
| | | |

| | | |
|---|---|-------|
| | $\text{Al}_T\text{-Al}_{\text{Oc}}\text{-Si}_T$ | |
| $>\text{SiteH}_4 = >\text{SiteH}_3^- + \text{H}^+$ | -4.9 | |
| $>\text{SiteH}_3^- = >\text{SiteH}_2^{-2} + \text{H}^+$ | -7 | |
| $>\text{SiteH}_2^{-2} = >\text{SiteH}^{-3} + \text{H}^+$ | -8.5 | |
| $>\text{SiteH}^{-3} = >\text{Site}^{-4} + \text{H}^+$ | -15.1 | |
| U(VI) adsorption reactions on $\text{Si}_T\text{-Al}_{\text{Oc}}\text{-Si}_T$ sites | | Log K |
| $>\text{SiteH}_3 + \text{UO}_2^{2+} = >\text{SiteH}_3\text{UO}_2^{2+}$ | | 4.8 |
| $>\text{SiteH}_3 + \text{UO}_2^{2+} = >\text{SiteHUO}_2 + 2 \text{H}^+$ | | -4.8 |
| $>\text{SiteH}_3 + \text{UO}_2^{2+} + 2 \text{H}_2\text{O} = >\text{SiteUO}_2(\text{OH})_2^{-3} + 5 \text{H}^+$ | | -25.3 |

4.3. Calibration of the U(VI) surface complexation model in the “absence” of CO_2

Carrying out all the steps of an adsorption experiment in the complete absence of CO_2 is very difficult. The DIC measurements indicate that carbonate was not fully excluded from the solutions despite the efforts to achieve this goal. Despite the observed carbonate contamination, the adsorption results from the CO_2 -“free” experiments were qualitatively similar to other literature data for carbonate-free systems (Bradbury and Baeyens, 2005; Marques Fernandes et al., 2012), i.e. showing a sharp increase in U(VI) adsorption from pH 4 to pH 6 and a limited decrease of U(VI) adsorption at pH > 6 (Figure 2).

While measured DIC concentrations are usually not considered in CO_2 -“free” U(VI) adsorption models in the literature, they were specifically taken into account in the model calculations discussed here. Only three edge surface reactions were necessary to reproduce the data (Figure 4 and Table 2). The effect of cation exchange was negligible because of the effective competition between Na^+ and UO_2^{2+} for cation exchange sites under our experimental conditions (0.1M NaCl background electrolyte). The calculation made with the same reference model parameters, but using a zero DIC value instead of the measured one, illustrates how sensitive the calculation is to the consideration of actual DIC values (dashed line in Figure 4). Even at the low DIC concentrations observed in the CO_2 -“free” experiment, dissolved carbonates provide highly competitive ligands for U(VI) complexation reactions relative to mineral surface sites.

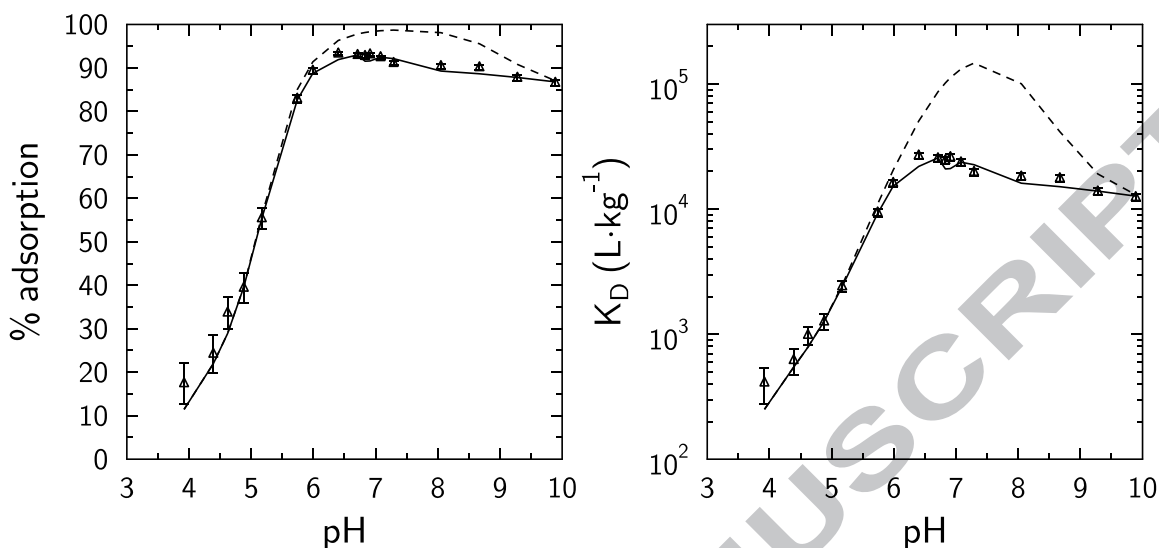


Figure 4. U(VI) adsorption results in the CO₂-“free” experiment (symbols: data; lines: model predictions) plotted as percentages of U(VI) adsorbed (left) and adsorption distribution coefficients (K_D , right). The reference model (solid line) was calculated taking into account individually measured DIC concentrations for each data point. The dashed line corresponds to a prediction using the same model parameters but while assuming zero DIC concentrations. Solid concentration = $0.52 \text{ g}\cdot\text{L}^{-1}$, total U(VI) concentration = $1.1\cdot 10^{-6} \text{ mol}\cdot\text{L}^{-1}$, $[\text{NaCl}]=0.1 \text{ mol}\cdot\text{L}^{-1}$.

4.4. Blind prediction of U(VI) adsorption in the presence of CO₂

The minimal set of adsorption parameters obtained from the fitting of CO₂-“free” adsorption data were directly used to predict the results of experiments carried out under laboratory air conditions (Experiments 1-3). The individually measured DIC concentrations were used to calculate the aqueous composition and U(VI) speciation. The blind prediction of U(VI) adsorption data was surprisingly good (Figure 5). Furthermore, in the experiment at $\text{U(VI)}_{\text{tot}} = 0.1 \text{ }\mu\text{M}$, the NaHCO₃ aliquot addition was twice of what it should have been for the sample at pH = 7.34, due to an experimental error (see point circled in left panel of Figure 5). The related decrease in U(VI) adsorption due to U(VI) aqueous complexation with carbonate

was perfectly reproduced by the model, without a need for including the formation of uranyl-carbonato complexes on the montmorillonite surface. This further supports doubts from spectroscopic studies on the existence of such ternary surface complexes (on montmorillonite) at atmospheric $p\text{CO}_2$ conditions. Furthermore, the experimental error in the NaHCO_3 addition for the sample at pH 7.34 also demonstrates that the solution was slow to re-equilibrate with the atmosphere outside of the closed sample vial, and confirms that the measured DIC values were constant during U(VI) sorption equilibration.

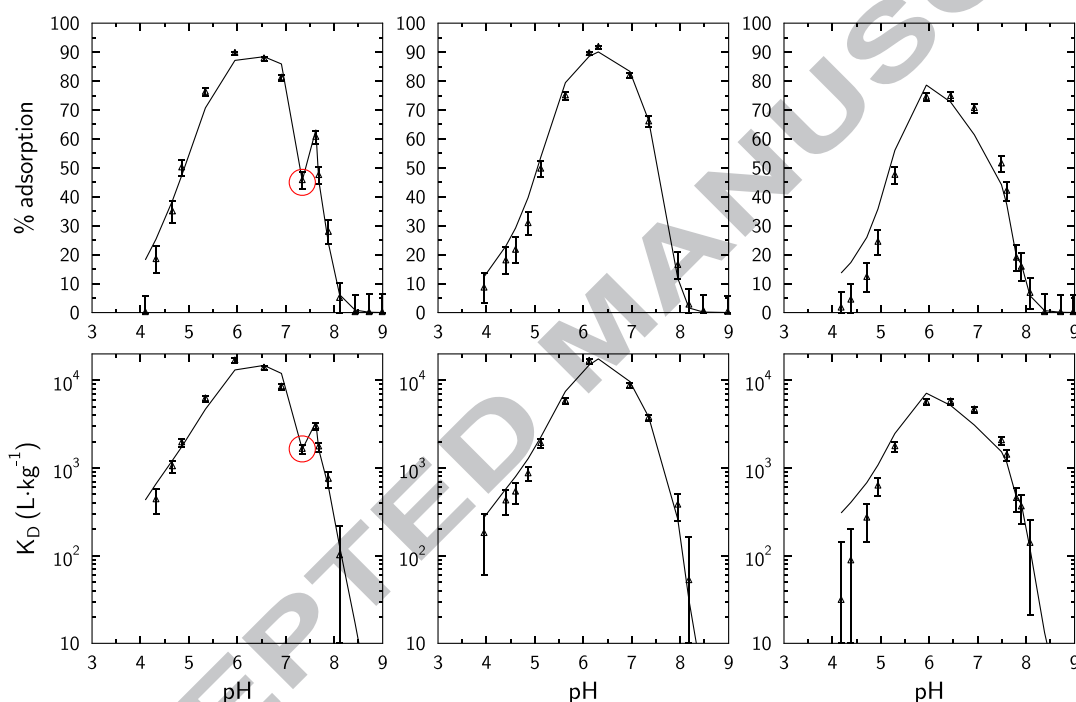


Figure 5. U(VI) adsorption results in laboratory air in a NaCl background electrolyte concentration of 0.1 M (symbols: data; line: model predictions). The model was calculated for each data point taking into account individually measured DIC concentrations. The solid concentration was $\sim 0.52 \text{ g}\cdot\text{L}^{-1}$. From left to right, the total U(VI) concentration was $1.1\cdot 10^{-7}$, $9.6\cdot 10^{-7}$, or $2.55\cdot 10^{-6} \text{ mol}\cdot\text{L}^{-1}$. NaHCO_3 aliquot addition was twice the intended amount for the sample at pH = 7.34 and $1.1\cdot 10^{-7} \text{ mol}\cdot\text{L}^{-1}$ U(VI) (circled experimental point in left panel).

The robustness of the model was further tested as a function of ionic strength, and, again, the model predicted the data well (Figure 6). Under the conditions of this experimental dataset, the influence of cation exchange reactions was negligible for $\text{pH} > 5$. The apparent effect of ionic strength on the extent of U(VI) adsorption is due to the changes in electrostatic potential as a function of ionic strength, as well as to small changes in pH values (see Figure 6 caption).

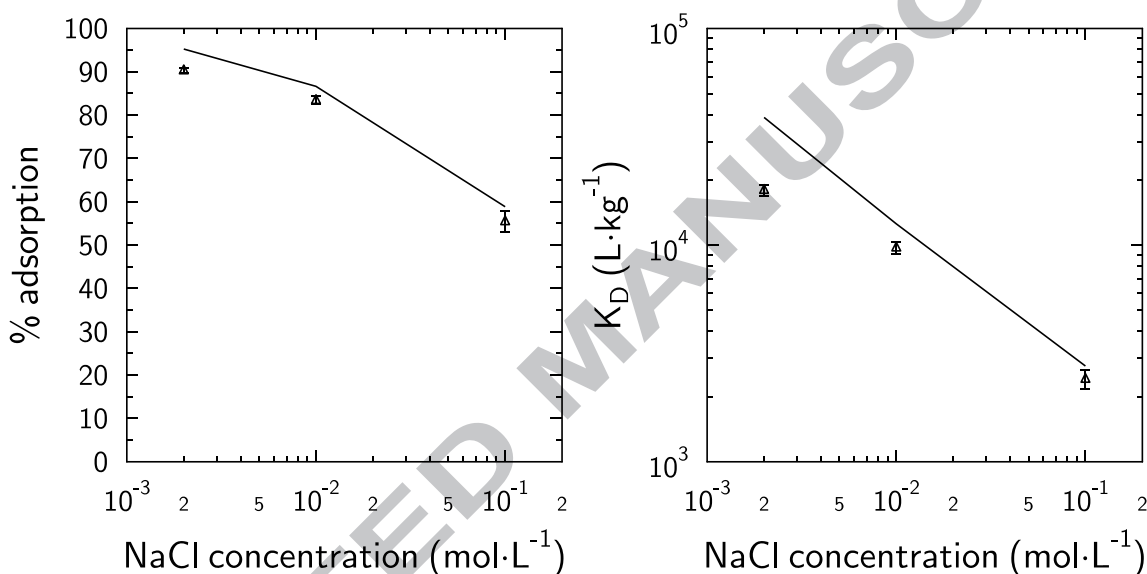


Figure 6. U(VI) adsorption as a function of ionic strength under laboratory air conditions (symbols: data; line: model predictions). The model prediction was calculated for each data point taking into account individually measured DIC concentrations and pH values (5.6, 5.4, 5.2 at 0.002, 0.01 and 0.1 M NaCl, respectively). The solid concentration was 0.52 g·L⁻¹; the total U(VI) concentration was $9.5 \cdot 10^{-7}$ M.

At greater DIC concentrations (due to elevated pCO_2), U(VI) adsorption data were also correctly predicted by the model without changing fitting parameters or adding new surface complexes. The model underpredicted the measured values in percent U(VI) adsorbed by 15% or less (Figure 7). However, it was not possible to enhance the quality of the fit by including a uranyl-

carbonato surface complex without deteriorating the data fits obtained in laboratory air or CO₂-“free” conditions.

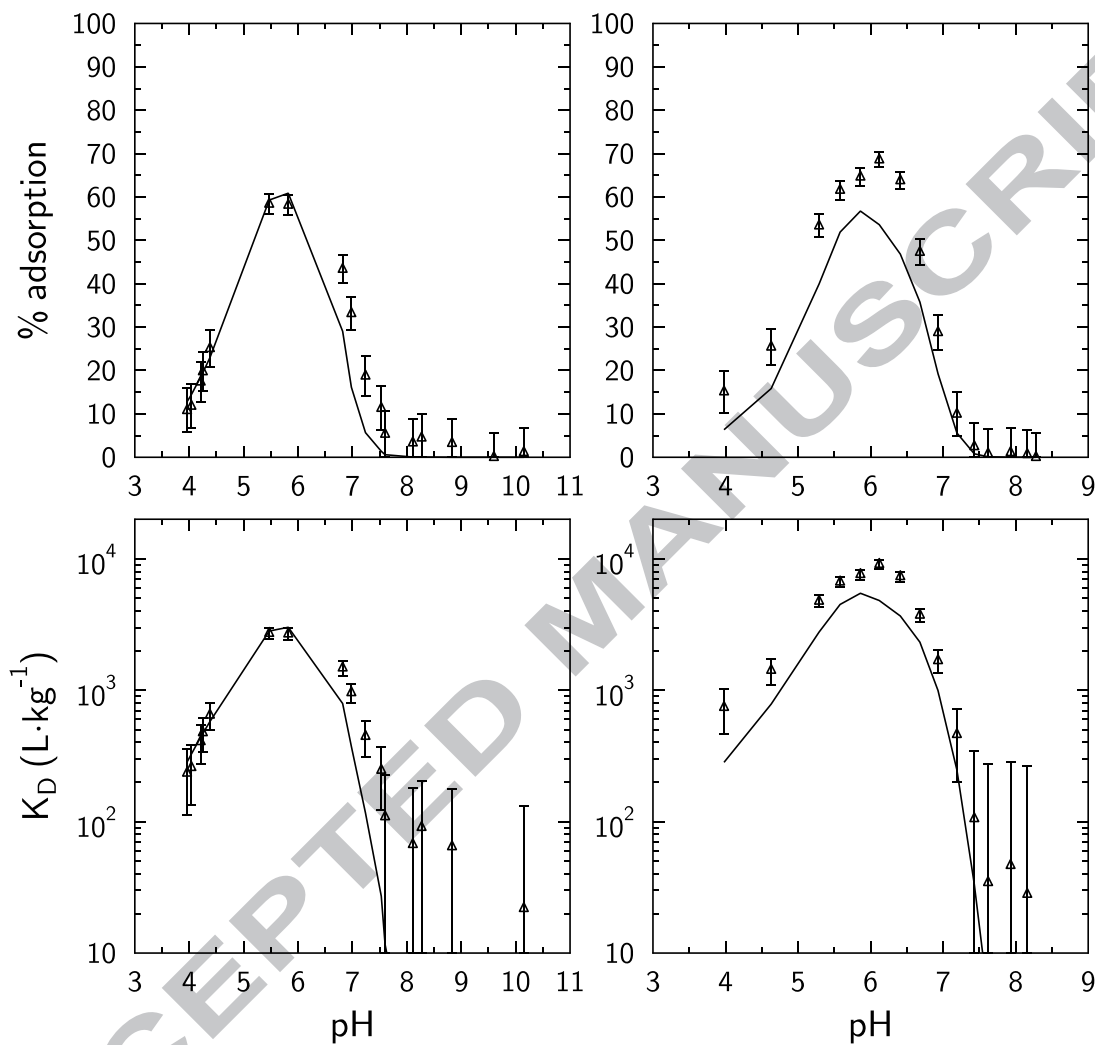


Figure 7. U(VI) adsorption in the presence of elevated pCO₂ (symbols: data; line: model predictions). The model was calculated for each data point taking into account individually measured DIC concentrations. Solid concentrations were 0.52 g·L⁻¹ (left) or 0.24 g·L⁻¹ (right). Total concentrations of U(VI) were 8.1·10⁻⁷ M (left) and 9.8·10⁻⁷ M (right).

4.5. Model predictions of literature data

A wide range of literature data is available for U(VI) adsorption on montmorillonite (McKinley et al., 1995; Pabalan and Turner, 1996; Turner et al., 1996; Hyun et al., 2001; Bradbury and Baeyens, 2005; Marques Fernandes et al., 2015; Troyer et al., 2016). Thus, it was possible to test the predictive capabilities of the model over a wider range of conditions than those tested in the experiments described above. However, the limitations of this benchmarking approach are at least two-fold. First, the origin and preparation of the clay material (fine fraction separation and further chemical purification) can influence adsorption results because of variations in reactive surface area and surface chemistry. Second, DIC concentrations were not reported in previous studies, while the results presented here demonstrate the importance of this parameter.

The following modeling and data presentation strategies were applied in order to avoid any misinterpretations regarding the quality of the model predictions. Data from the literature were first compared with a blind modeling prediction without any adjustment of model parameters given in Table 2 (reference model). In the case of experiments carried out under atmospheric conditions, a $\log_{10}(\text{pCO}_2)$ value of -3.45 was assumed for these reference calculations. In case of CO_2 -“free” conditions, a $\log_{10}(\text{pCO}_2)$ value of -99 was applied. In a second step, various hypotheses were tested to achieve a better fit of the data, if necessary. In particular, as our reference model did not include cation exchange reactions, it was necessary to include these reactions to reproduce U(VI) adsorption data obtained at low ionic strength and low pH ($\text{pH} < 4$) conditions.

4.5.1. Data of Troyer et al. (2016).

The data of Troyer et al. (2016) were acquired in the presence of atmospheric pCO_2 on a clay material similar to the one used in this study ($< 2 \mu\text{m}$ fraction of SWy-2 montmorillonite), but in the presence of a 0.01M NaCl electrolyte, thus promoting cation exchange reactions compared to our conditions. We tested the model on the authors' three adsorption isotherms obtained at pH 4, 6 and 8. Data obtained at pH 6 could be adequately reproduced without changing any parameter from the reference model (Figure 8). Data obtained at pH 4 could be reproduced only by adding a cation exchange reaction to the reference model (Table 3). Data at pH 8 were not satisfactorily reproduced in the first calculations. However, a slight change in the pH value (7.8 instead of 8)

or $p\text{CO}_2$ value ($10^{-3.7}$ atm instead of $10^{-3.45}$ atm) made it possible to fit the data very well, again showing the great sensitivity of the system to pH/ $p\text{CO}_2$ over this range of conditions.

Some data at high U(VI) surface coverage could not be predicted by the model, even after changing some of the parameters. The origin of this problem can be understood by comparing the measured U(VI) surface coverage with the maximum available surface site density. If we consider a site density of $2.06 \text{ sites}\cdot\text{nm}^{-2}$ (Bourg et al., 2007; Tournassat et al., 2016a) and a specific surface area of $14 \text{ m}^2\cdot\text{g}^{-1}$, the maximum adsorption capacity for U(VI) complexes should be $\sim 0.05 \text{ mol}\cdot\text{kg}^{-1}$. If we further assume that no U multinuclear complexes form at the surface, this value decreases to $\sim 0.025 \text{ mol}\cdot\text{kg}^{-1}$ (perfect ordering). This value is similar to the maximum adsorbed concentration value measured in Troyer et al. (2016) at pH 6, but far lower than the maximum value measured at pH 8. Hence, the much higher measured than simulated extent of U(VI) adsorption cannot be explained by the formation of isolated mononuclear bidentate U(VI) surface complexes alone. These data must include additional uptake processes that are not described in the model developed here, and are beyond the scope of this study, e.g. polymerization on the surface, or precipitation. The latter cannot be fully ruled out at elevated U(VI) concentrations, since a supersaturation of schoepite was predicted at 1.3 and 62 μM U(VI) at pH 6 and pH 8 respectively, based on the U(VI) aqueous speciation model of Troyer et al. (2016).

Table 3. Cation exchange reaction parameters added to the reference model in order to reproduce literature data obtained at low ionic strength and low pH^a.

| | | |
|---|---------------------|--|
| Surface reactions on montmorillonite basal surfaces | $\text{Log}_{10} K$ | |
| $X^- + \text{Na}^+ = \text{XNa}$ | 0 | |
| Cation exchange reactions with U(VI) species (as a function of literature data) | $\text{Log}_{10} K$ | CEC ($\text{mol}\cdot\text{kg}^{-1}$) ^b |
| Troyer et al. (2016), Hyun et al. (2001) | | |
| $2 \text{XNa} + \text{UO}_2^{2+} = \text{X}_2 \text{UO}_2 + 2 \text{Na}^+$ | 0.95 | 0.9 |
| Pabalan et al. (1996) | | |
| $2 \text{XNa} + \text{UO}_2^{2+} = \text{X}_2 \text{UO}_2 + 2 \text{Na}^+$ | 0.75 | 1.2 |

| McKinley et al. (1995) | | |
|--|-----|------|
| $2 \text{XNa} + \text{UO}_2^{2+} = \text{X}_2 \text{UO}_2 + 2 \text{Na}^+$ | 1.2 | 0.8 |
| Turner et al. (1996) | | |
| $2 \text{XNa} + \text{UO}_2^{2+} = \text{X}_2 \text{UO}_2 + 2 \text{Na}^+$ | 0.7 | 0.41 |

^a Cation exchange reactions were modeled with a classic diffuse layer model that was already calibrated for Na^+ and Ca^{2+} by Tinnacher et al. (2016). The total specific surface area for cation exchange reactions was set to the crystallographic surface area for montmorillonite, i.e. $\sim 750 \text{ m}^2 \cdot \text{g}^{-1}$ (Tournassat and Appelo, 2011; Tournassat et al., 2011, 2015b; Tournassat and Steefel, 2015).

^b Values measured in the reference papers.

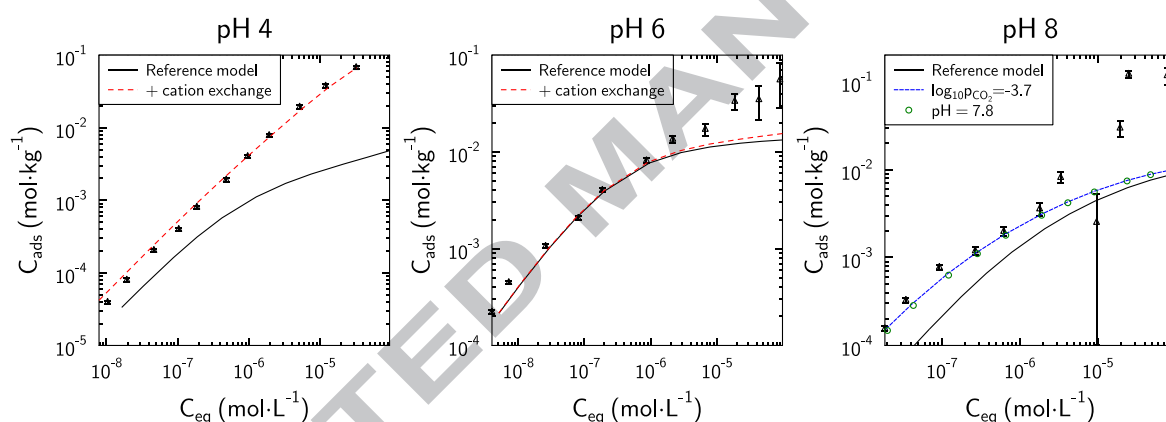


Figure 8. Comparison of model predictions with the U(VI) adsorption data on montmorillonite of Troyer et al. (2016).

4.5.2. Data of Hyun et al. (2001).

The data of Hyun et al. (2001) were also acquired in the presence of atmospheric pCO_2 on a clay material similar to the one used in this study (fine fraction of SWy-2 montmorillonite). Uranium(VI) adsorption was characterized at two fixed total U(VI) concentrations (10^{-7} and $10^{-5} \text{ mol} \cdot \text{L}^{-1}$), with variable pH, and for two ionic strengths ($I=0.001$ and $I=0.1$), and at a relatively high solid concentration ($\sim 6\text{-}7 \text{ g} \cdot \text{L}^{-1}$). The reference model provided a good prediction of the data (Figure 9).

At low ionic strength, the addition of cation exchange reactions, with the same parameters as for the study of Troyer et al. (2016), had almost no influence on the results. At pH 4 and low ionic strength, the high level of adsorption is mainly due to the increase in the surface potential value at edge surfaces. At high pH, the disagreement between experimental data and model predictions could be attributed to the fact that carbonate concentrations were not constrained experimentally (Hyun et al., 2001). Pabalan and Turner (1996) reported that, under some conditions, an equilibration period of ten days with the atmosphere was necessary to reach equilibrium between DIC and atmospheric CO_2 . Insufficient time of equilibration with the atmosphere in the experiments of Hyun et al. (2001) could have led to pCO_2 values that were lower than the atmospheric value considered in the calculations: fitted value were $\log_{10} \text{pCO}_2 = -4.4$ at pH 9 and -5.05 at pH 9.55 (blue line in Figure 9).

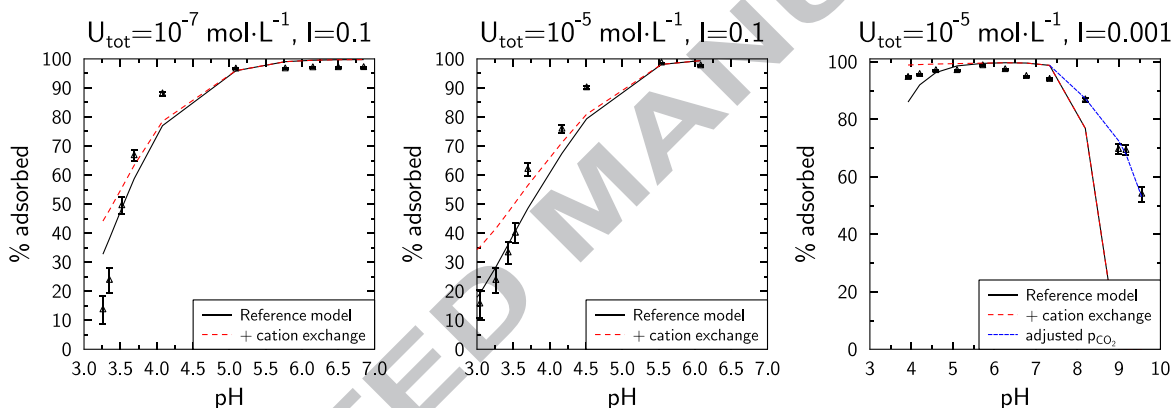


Figure 9. Comparison of model predictions with the U(VI) adsorption data on montmorillonite of Hyun et al. (2001).

4.5.3. Data of Pabalan and Turner (1996).

The data of Pabalan and Turner (1996) were obtained in the presence of atmospheric pCO_2 on a clay material, SAZ-1, that was different from SWy-2. Experimental conditions were otherwise quite similar to those used in the present study. In particular, close equilibrium with atmospheric pCO_2 was ensured by the addition of bicarbonate to the solutions. Again, the predictions of the model were in very good agreement with the experimental data without any further adjustments (Figure 10), despite the different nature of the clay.

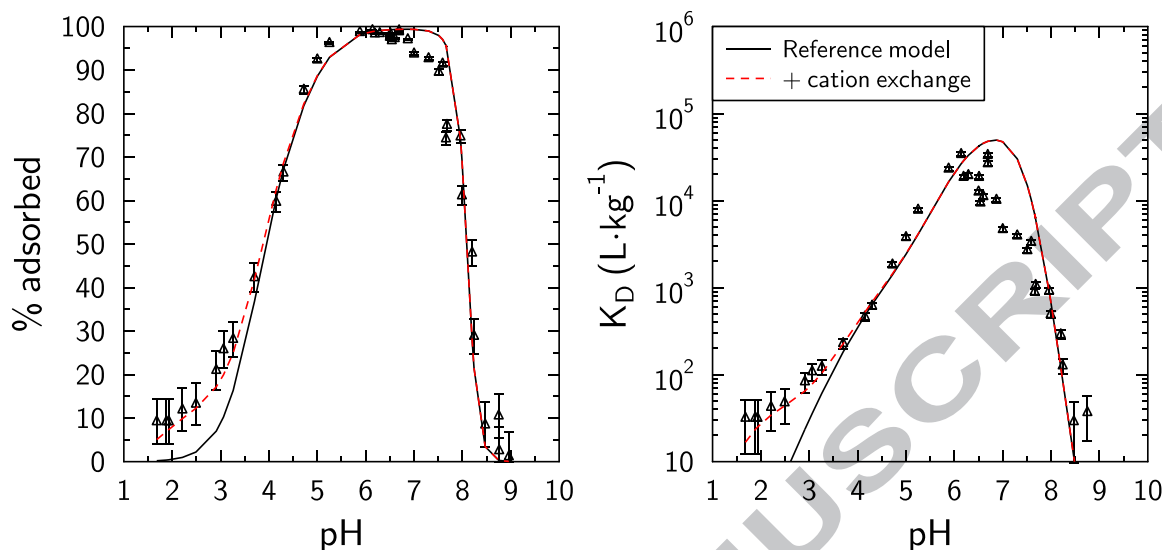


Figure 10. Comparison of model predictions with U(VI) adsorption data of Pabalan and Turner (1996). Cation exchange parameters are given in Table 3. Solid concentration = $3.2 \text{ g}\cdot\text{L}^{-1}$; total U(VI) concentration = $2\cdot 10^{-7} \text{ mol}\cdot\text{L}^{-1}$. The results are presented in percentage adsorbed (left) and in $\log_{10} K_D$ values (right) for a better evaluation of model fits at low (left) and high (right) U(VI) adsorption.

4.5.4. Data of McKinley *et al.* (1995).

McKinley *et al.* (1995) reported U(VI) adsorption data on the $<2 \text{ }\mu\text{m}$ fraction of Swy-1 montmorillonite as a function of pH and ionic strength. At first sight, these data were not satisfactorily reproduced by the reference model (Figure 11). The addition of cation exchange reactions improved predictions at low pH, but U(VI) adsorption at $\text{pH} > 5.5$ was still overestimated. However, these discrepancies can be satisfactorily explained by taking into account that the edge specific surface area of the Swy-1 sample from McKinley *et al.* (1995) was lower than the area of the Swy-2 sample, i.e. $12.6 \text{ m}^2\cdot\text{g}^{-1}$ instead of $14 \text{ m}^2\cdot\text{g}^{-1}$. Both values are within the range of montmorillonite edge surface area values reported in the literature, which vary from $5 \text{ m}^2\cdot\text{g}^{-1}$ to $25 \text{ m}^2\cdot\text{g}^{-1}$ (Tournassat *et al.*, 2015a, 2016a).

4.5.5. Data of Turner et al. (1996).

Turner et al. (1996) reported U(VI) adsorption data on the $<2\ \mu\text{m}$ fraction of a smectite isolate from a sedimentary rock fraction (Kenoma smectite). Kenoma smectite is a beidellite, meaning that most of its structural charge originates from tetrahedral isomorphous substitutions, instead of octahedral substitutions for montmorillonite. Despite this difference, U(VI) adsorption data could be fitted equally well using the same approach as for the data of McKinley et al. (1995). Only U(VI) adsorption data obtained at very low ionic strength ($I=0.001$) were overestimated (Figure 12). Since the solid/liquid separation was achieved by centrifugation, it may be possible that finer particles were not completely removed from solution at this ionic strength, causing a lower apparent extent of U(VI) adsorption. (At low ionic strength, separation of solids from solution based on density differences is more difficult, due to the increased intensity of electrostatic repulsive interactions between montmorillonite layers (Van Olphen, 1992)).

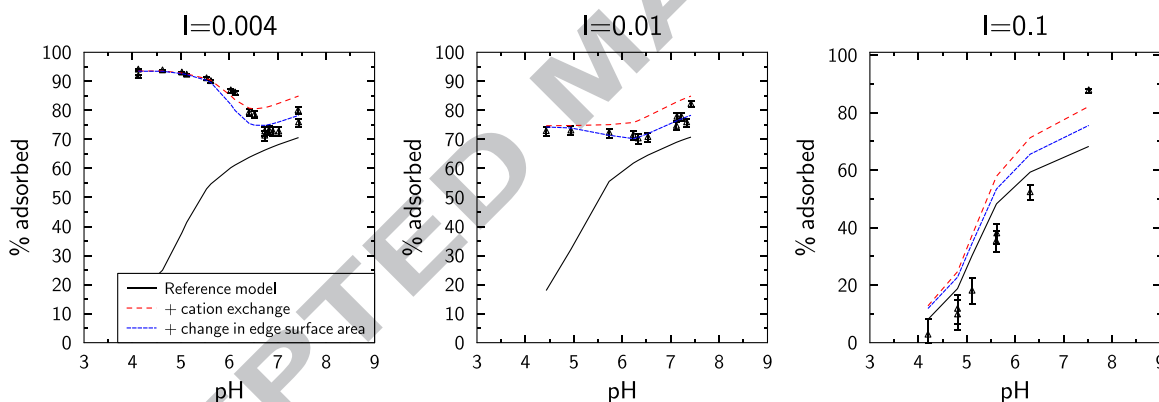


Figure 11. Comparison of model predictions with U(VI) adsorption data of McKinley et al. (1995). For the blue curve, the total edge specific surface area was set to $12.6\ \text{m}^2\cdot\text{g}^{-1}$ instead of the reference model value of $14\ \text{m}^2\cdot\text{g}^{-1}$. Cation exchange parameters are given in Table 3.

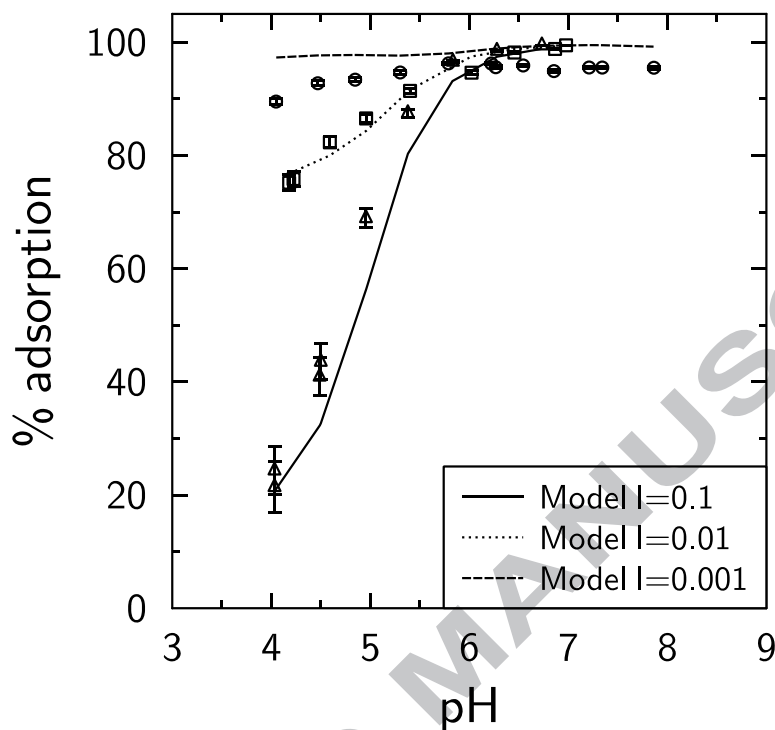


Figure 12. Comparison of model predictions (lines) with U(VI) adsorption data of Turner et al. (1996) (symbols). Cation exchange parameters are given in Table 3.

4.5.6. Data of Marques Fernandes et al. (2012).

Marques Fernandes et al. (2012) conducted U(VI) adsorption experiments on the $<0.5 \mu\text{m}$ fraction of a SWy-1 montmorillonite over a wide range of pH and total U(VI) concentrations while varying pCO_2 . Experimental data at $\text{pH} > 7$, in the presence and absence of atmospheric pCO_2 (actual DIC concentrations were not measured), were predicted satisfactorily by the reference model without further modifications (Figure 13). Experimental data obtained at lower pH, however, had higher adsorption than predicted by the reference model. The position of the pH adsorption edge could only be reproduced by increasing the edge surface area by a factor 8. This is obviously not a justifiable assumption, even if we consider that the authors used a finer clay fraction ($<0.5 \mu\text{m}$) than in most other reported studies ($< 2 \mu\text{m}$). With the large edge surface

area, U(VI) adsorption was also greatly overestimated at $\text{pH} > 7$ (Figure 13). The SWy-1 montmorillonite material of Marques Fernandes et al. (2012) thus exhibits U(VI) adsorption properties that are significantly different from the SWy-1 material studied by McKinley et al. (1995) and all other montmorillonite materials studied in the literature, given the otherwise good agreement between experimental data and the model predictions presented here for a large number of other studies. Based on the quality of fit, Marques Fernandes et al. (2012) attributed the very high adsorption affinity of SWy-1 montmorillonite to “strong sites”, with a specific site density of $\sim 2 \text{ mmol} \cdot \text{kg}^{-1}$. However, if present, the influence of such strong sites should have been apparent in the many other studies discussed above, where the U(VI) to solid concentration ratio was lower than the putative “strong site” density. Hence, it appears that, for most other solid materials previously studied, these strong sites either do not exist or are present at a far lower site density than the reported value of $\sim 2 \text{ mmol} \cdot \text{kg}^{-1}$ (Marques Fernandes et al. (2012)). Differences in material preparation procedures could potentially explain this difference in reactivity; e.g., Marques Fernandes et al. (2012) acidified their clay sample to pH 3.5 to remove acid-soluble impurities, while pH 5 was used in this and other previous studies.

Marques Fernandes et al. (2012) also conducted U(VI) adsorption experiments in the presence of added NaHCO_3 in order to probe the adsorption of U(VI)-carbonate complexes at the surface. These data could be predicted with our model after an adjustment of the equilibrium DIC concentrations (Figure 14). Our calculations led to the conclusion that the equilibrium DIC value was 30 % to 40 % lower than the initially guessed values. Since measured DIC values are not available from the above reference, it is not possible to give a definitive conclusion with regards to the adequacy of the model prediction with the data. However, the discrepancy between *guessed* and *fitted* DIC values is similar to the one that we recorded in our own experiments between *guessed* and *measured* values (see materials and methods section and Fig. 2). Hence, we believe that Marques et al. (2012) may have experienced similar, experimental problems.

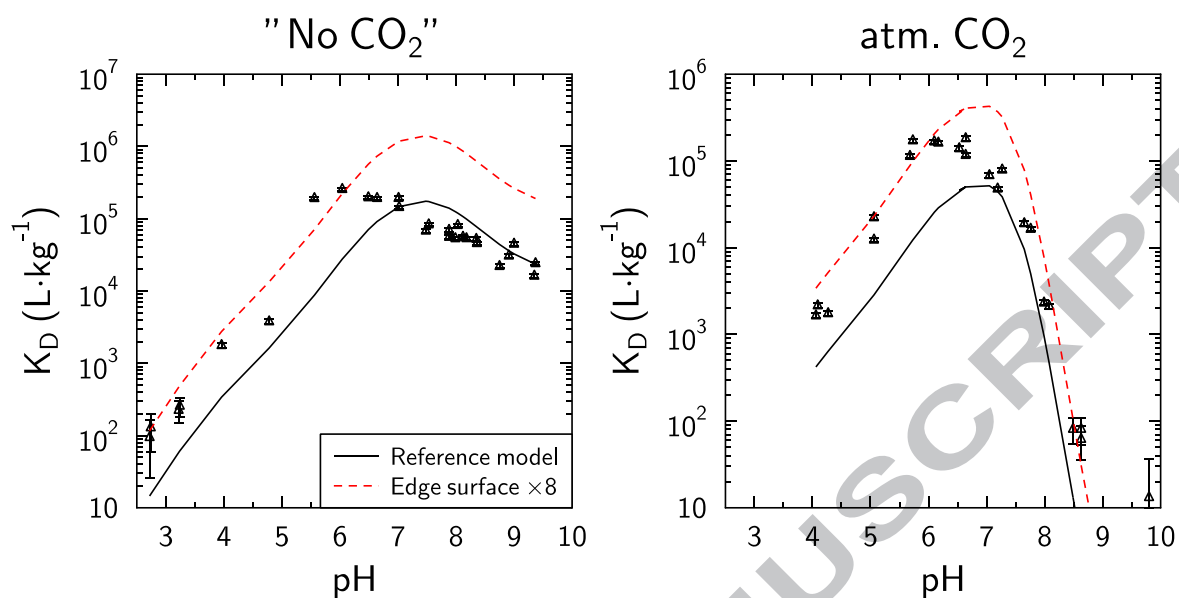


Figure 13. Comparison of model predictions (lines) with experimental U(VI) adsorption data on montmorillonite of Marques Fernandes et al. (2012) (symbols).

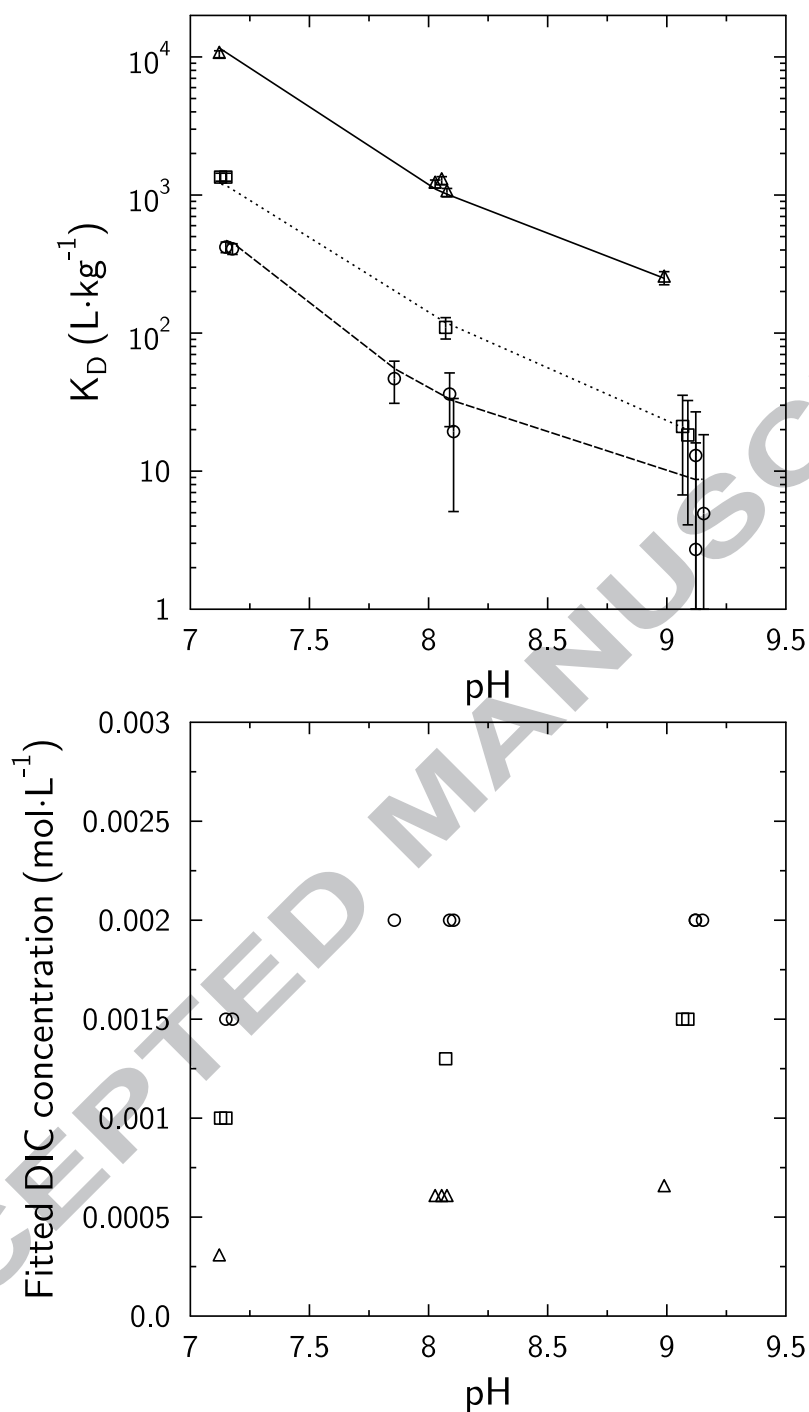


Figure 14. Top: comparison of model predictions (lines) with experimental U(VI) adsorption data on montmorillonite of Marques Fernandes et al. (2012) in the presence of added NaHCO_3 guessed concentration of 1 $\text{mmol} \cdot \text{L}^{-1}$ (triangles), 3 $\text{mmol} \cdot \text{L}^{-1}$ (squares), and 5 $\text{mmol} \cdot \text{L}^{-1}$ (circles).

The actual values of DIC were adjusted in order to fit the data. Fitted DIC values are plotted in the bottom figure.

4.6. -SUMMARY OF MODELING RESULTS

The reference U(VI) adsorption model presented here is based on a state-of-the-art description of the reactivity of montmorillonite clay edges that specifically takes into account the spillover effect of the basal surface potential on the edge surface potential (Bourg et al., 2007; Tournassat et al., 2013, 2015a, 2016a). This model accurately predicts adsorption of U(VI) on montmorillonite surfaces over a wide range of experimental conditions, with only one specific adsorption site, three different U(VI) complexes at the surface, and one cation exchange reaction. Within the limits of data accuracy, there was no need to include the formation of uranyl-carbonato surface complexes in the model to simulate the experimental data. Including such a species would only be justified if: (1) the discrepancies between experimental data and model predictions (without including these surface complexes) were larger than the combined uncertainties associated with experimental errors and formation constants for aqueous U(VI)-carbonate complexes, and (2) if actual measurement data are available for all solution parameters, including DIC concentrations (or alternatively, alkalinity). Without these data, the uncertainties of assumed $p\text{CO}_2$ values are too large to draw any conclusions regarding the presence of ternary U(VI)-carbonato surface complexes.

For illustration, the effect of varying $p\text{CO}_2$ conditions on U(VI) adsorption is shown in Figure 15. Based on these calculations with the reference model, at $\text{pH} > 9$ a “true” absence of CO_2 can be interpreted only if it can be demonstrated that actual $p\text{CO}_2$ values are lower than 10^{-6} atm. This partial pressure corresponds to 1 ppm CO_2 in the surrounding atmosphere, i.e. experimental conditions that could be met only with great difficulty in the laboratory, even in a specially equipped glove box. It can be concluded that an “absence of CO_2 ” at $\text{pH} > 9$ (ideally corresponding to $p\text{CO}_2 = 10^{-9.9}$ atm in Figure 15), is, in fact, obtained because of slow gas exchange rates between degassed solutions and the surrounding atmosphere, and not a true equilibrium with the partial pressure of CO_2 in that atmosphere. Under these conditions, it is thus necessary to measure DIC concentrations to assess the exact concentrations in solutions exposed to low levels of $p\text{CO}_2$. To our knowledge, this type of measurement has never been performed in

previously reported U(VI) adsorption studies on montmorillonite. Most likely, this has sometimes led to false assumptions that previous experiments were conducted at $p\text{CO}_2$ levels that did not impact U(VI) adsorption.

For example Schlegel and Descostes (2009) reported U(VI) adsorption results in the “absence of CO_2 ” that clearly show evidence of $p\text{CO}_2$ at higher values than 10^{-5} bars (compare their Figure 1 with Figure 15 of this paper). Even a precise interpretation of data obtained at atmospheric $p\text{CO}_2$ may be problematic. The value of atmospheric $p\text{CO}_2$ can fluctuate as a function of geographic location, season, and above all the presence of humans in an enclosed lab setting because of respiration and poor ventilation. In addition, a slight change in pH after pre-equilibration of a solution (e.g., due to reagent addition) can impact the final $p\text{CO}_2$ value in a reaction vessel if the time-frame of the pH re-adjustment is too short to allow for full gas-solution re-equilibration. A $p\text{CO}_2$ of $10^{-3.2}$ instead of $10^{-3.45}$ atm has a significant effect on the prediction of U(VI) adsorption at $\text{pH} > 7$. Hence, even with a ‘forced’ pre-equilibration of background electrolyte solutions using NaHCO_3 additions for intended pH values, CO_2 exchange with the surrounding atmosphere and other experimental artefacts add a significant uncertainty to the modeling results, unless actual measured DIC concentrations are used during the model fitting process. This effect is well illustrated with the modeling of U(VI) adsorption data by Troyer et al. (2016) at $\text{pH} \sim 8$ (Figure 12).

While DIC concentrations are critical parameters in the evaluation of U(VI) adsorption, the combined presence of Ca and carbonate further increases the level of complexity and uncertainty in the model calculations. This is due to the formation of aqueous calcium-uranyl-carbonate complexes (Meleshyn et al., 2009), with unknown adsorption impacts (Fox et al., 2006). According to the reference model, the effect of the formation of this complex on U(VI) adsorption could be significant for Ca^{2+} concentrations larger than $2 \text{ mmol} \cdot \text{L}^{-1}$, which is in agreement with our experimental results (Figure 16).

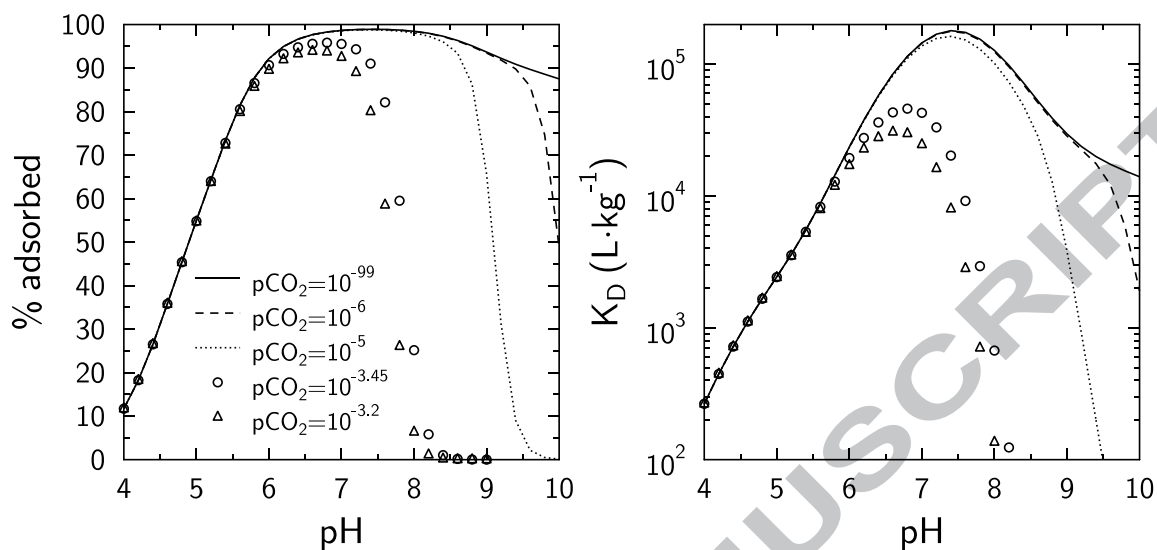


Figure 15. Predicted effect of $p\text{CO}_2$ on U(VI) adsorption onto montmorillonite using the reference model with a solid concentration of $0.5 \text{ g}\cdot\text{L}^{-1}$, a 0.1M NaCl background electrolyte and a total U(VI) concentration of 10^{-7} M .

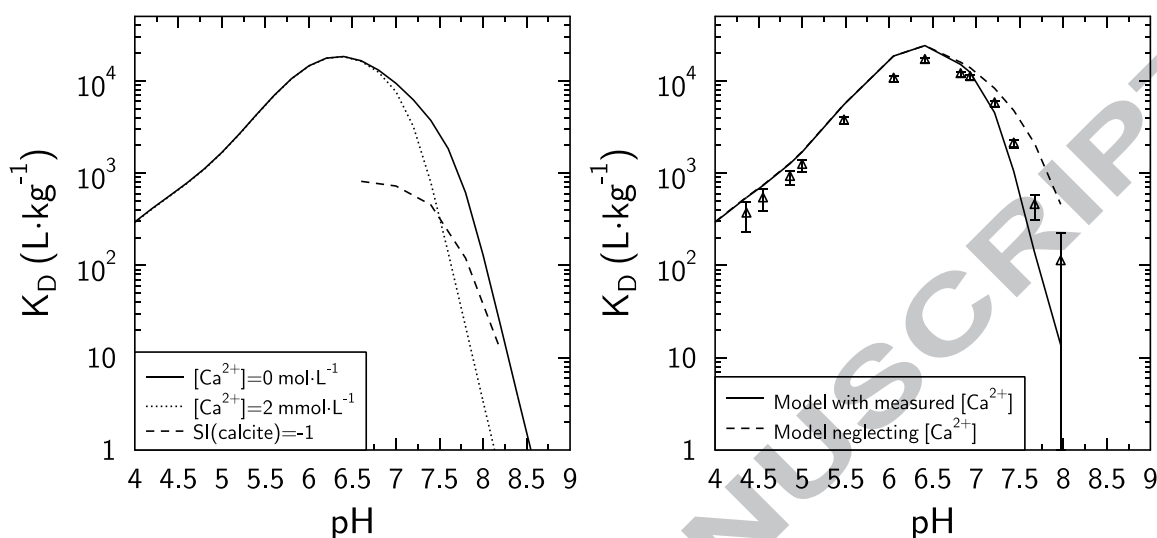


Figure 16. Left: Predicted effect of Ca^{2+} concentration on U(VI) adsorption using the reference model with a solid concentration of $0.5 \text{ g} \cdot \text{L}^{-1}$, a 0.1 M NaCl background electrolyte, a total U(VI) concentration of 10^{-6} M , and a $\text{pCO}_2 = 10^{-3.2} \text{ atm}$. Solubility index (SI) for calcite is plotted for comparison. Right: Comparison of our experimental data with model results with and without taking into consideration the impact of Ca^{2+} on U(VI) solution speciation.

5. CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS

Overall, we can summarize the major findings and implications of this study in the following:

1. We developed a new surface complexation model (SCM) that specifically accounts for the ‘spillover’ of the electrostatic surface potential of basal cation exchange sites on the surface potential of neighboring edge sites. This model allows us to simulate U(VI) adsorption onto Na-montmorillonite over a wide range of chemical solution conditions with a lower number of fitting parameters than previous SCM concepts, and without including a second site type or the formation of ternary U(VI)-carbonato surface complexes. This SCM allows us to simulate U(VI) sorption onto montmorillonite as a

function of chemical solution conditions, while minimizing the number of fitting parameters in subsequent uranium(VI) diffusion models.

2. Modeling results suggest that an accurate description of the unique characteristics of electrostatic surface potentials on montmorillonite edge sites is highly important, in order to accurately predict U(VI) sorption and transport behavior at larger field scales. Similar modeling approaches may also be useful for other charge-unbalanced, layered mineral phases.
3. Our modeling results further emphasize the strong influence of dissolved carbonate ligands on U(VI) sorption, which is driven by the competition between U(VI)-carbonate complexation reactions in solution and U(VI) surface complexation reactions on montmorillonite edge sites. As a consequence, predictive U(VI) transport models need to capture potential changes in dissolved inorganic carbon (DIC) concentrations over time and space, e.g. in case of variable contents in carbonate minerals along transport pathways and/or fluctuating pH conditions. For instance, calcite impurities in bentonite, the proposed buffer material at future nuclear waste repositories, may affect U(VI) sorption by providing a source of dissolved carbonate concentrations.
4. Lastly, a measurement of DIC concentrations appears to be crucial for accurate simulations of U(VI) aqueous speciation during the development and calibration of SCMs. Assumptions of a full exclusion of inorganic carbon from sample solutions in CO₂-“free” adsorption experiments, or a complete solution equilibration with atmospheric/elevated CO₂ levels in the local atmosphere, may often not be justified. This is due to the generally challenging nature of CO₂-“free” adsorption experiments, and the potentially slow CO₂ gas exchange between sample solutions and the local atmosphere under atmospheric/elevated CO₂ conditions. Hence, we recommend that DIC analysis or alkalinity titrations are included as routine measurements in future U(VI) adsorption studies. Furthermore, future experimental designs should also take into account the experimental challenges experienced in this study, with regards to achieving constant pCO₂ conditions across a series of sample solutions in a given adsorption experiment.

6. Acknowledgements

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Electronic Annex for

Modeling uranium(VI) adsorption onto montmorillonite under varying carbonate concentrations: A surface complexation model accounting for the spillover effect on surface potential

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1. Uranium(VI) Aqueous Speciation as a Function of Partial Pressures of CO₂ and Calcium Concentrations

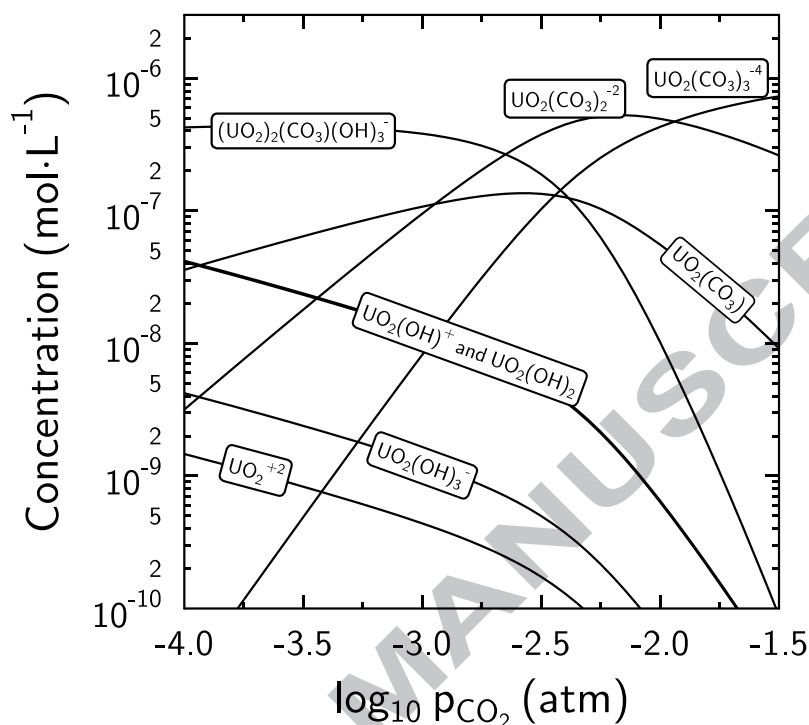


Figure EA-1: Uranium(VI) speciation as a function of the partial pressure of CO₂ in a 1 μ M U(VI) solution in 0.1 M NaCl at pH 7 in the absence of Ca. Calculations were made with PHREEQC (Parkhurst and Appelo, 1999, 2013) and the THERMOCHEMIE database (Giffaut et al., 2014).

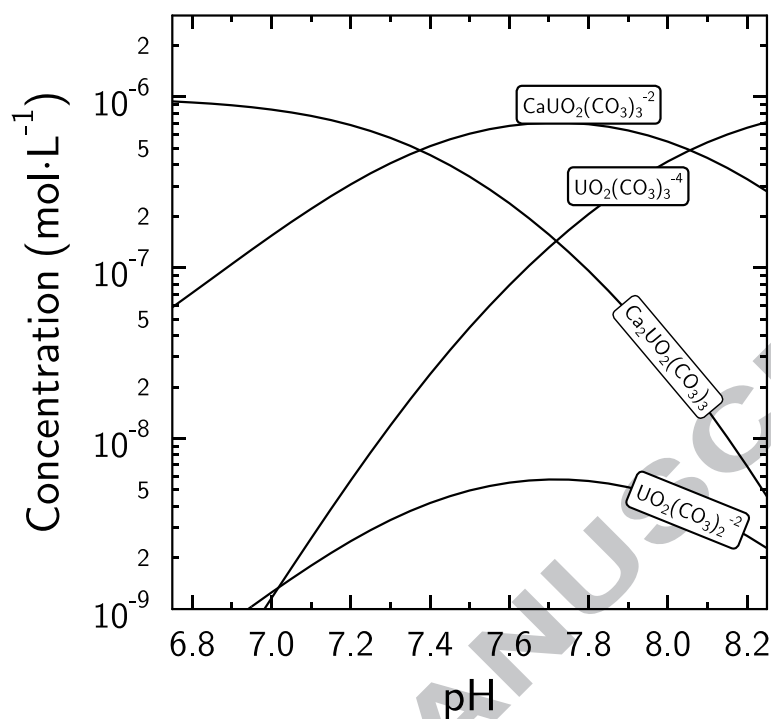


Figure EA-2: Uranium(VI) speciation as a function of pH in a 1 μM U(VI) solution in 0.1 M NaCl in equilibrium with a partial pressure of CO_2 at 1% and in equilibrium with calcite. Calculations were made with PHREEQC (Parkhurst and Appelo, 1999, 2013) and the THERMOCHEMIE database (Giffaut et al., 2014).

2. Background Concentrations of Uranium-238 and Calcium

Uranium. Most electrolyte blanks had U-238 background concentrations below the ICP-MS detection limits ($<0.005 \mu\text{g/L}$, $<2.1\text{E-}11 \text{ M U-238}$). The highest background concentration was measured at $6.2\text{E-}10 \text{ M U-238}$, which represented 0.04% of the total U(VI) concentration ($1.52\text{E-}6 \text{ M}$) in that particular experiment. Hence, dissolved concentrations of U(VI) were not corrected for U(VI) background concentrations.

Calcium. Figure EA-3 illustrates total Ca concentrations versus the concentrations released from the pre-treated Na-montmorillonite. The latter were calculated based on average Ca concentrations in electrolyte blanks and U(VI) standards (containing no mineral phase).

Without taking into account experiment 4, where calcium was specifically added to solutions, the average calcium contributions from background electrolyte solutions ranged from $7.4\text{E-}7$ to $7.2\text{E-}6 \text{ M Ca}$, which represents between 5.6% to 79.8% of the total Ca in solution. The addition of sodium bicarbonate buffer may slightly add to Ca background levels, but cannot fully explain the observed increase in Ca concentrations at higher pH. (At a 99.998% degree of purity for NaHCO_3 and assuming that all impurities in the bicarbonate buffer are due to Ca, the buffer addition at pH 10 would increase Ca background levels by around $3.0\text{E-}6 \text{ M Ca}$.) Instead, the pH trend may indicate an enhanced Ca release from the solid in the presence of carbonate ligands in solution. This hypothesis is further supported by lower Ca concentrations found in solutions in contact with atmospheric CO_2/CO_2 -“free” gas phases compared to solutions in contact with elevated CO_2 levels.

Furthermore, comparable low concentrations of Ca are released from montmorillonite during all experiments without any specific calcium additions. In contrast, a small uptake of Ca was observed in experiment 4, where a concentration of 2.1 mM Ca was added. In experiments without specific calcium additions, total Ca concentrations ($6.4 - 27 \mu\text{M}$) were not high enough to affect U(VI) solution speciation in terms of the formation of ternary aqueous U(VI)-Ca-carbonate complexes.

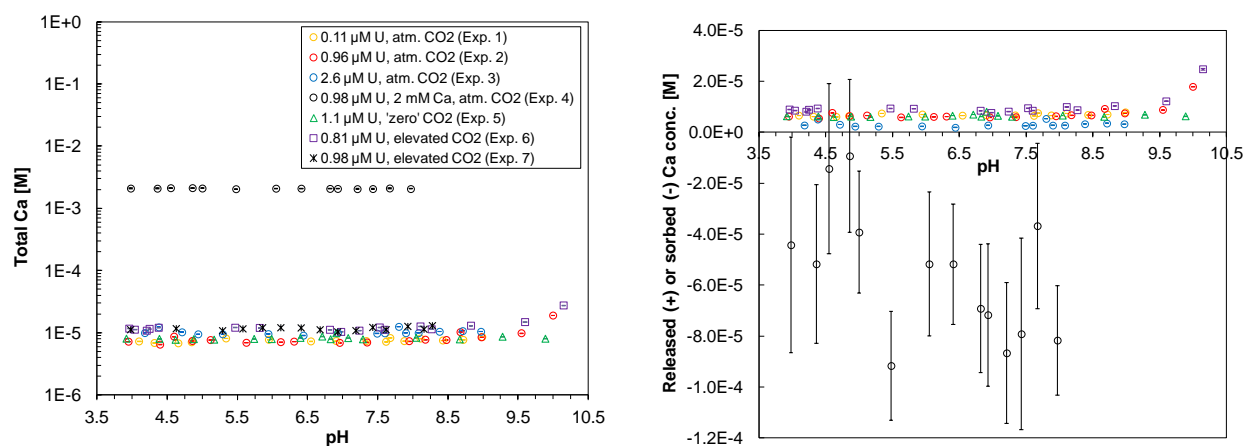


Figure EA-3. Total (left) and released (+)/adsorbed (-) (right) concentrations of calcium determined in U(VI) adsorption experiments with Na-montmorillonite under various chemical solution conditions. Data symbols are identical for both figures. Calcium was specifically added only in experiment 4. Error bars represent analytical uncertainties with invisible error bars being smaller than data points.

3. Batch U(VI) Adsorption Kinetic Experiment

Experimental Setup

Uranium(VI) adsorption behavior was characterized as a function of time based on the repeated sampling of the same clay suspension at specified time-points. The experiment was set up at room temperature (22.5 – 23.5 °C), with a nominal total U(VI) concentration of 10^{-6} M and a Na-montmorillonite concentration of 0.5 g/L. Solutions were in contact with atmospheric CO₂ (~0.04%, 400 ppm) at a total ionic strength of 0.1 M NaCl and a target pH value of pH-5, without any pH buffering. The standard concentration, representing 100% of U(VI) in solution in the absence of a mineral phase, was calculated based on direct ICP-MS analysis of duplicate 5- μ L aliquots of the U(VI) stock solution.

The experiment consisted of two main steps: (1) the pre-equilibration of a U(VI) solution and a separate Na-montmorillonite suspension at pH-5 and 0.1 M NaCl; and (2) the time-dependent adsorption of U(VI) onto the clay, which was characterized by repeated sampling of the montmorillonite suspension. On the first day, a 43.8-mL U(VI)-electrolyte solution and clay-electrolyte suspension were prepared by combining Milli-Q water with 1 M NaCl, and an aliquot of either the U(VI) stock solution or Na-montmorillonite stock suspension. After adjusting the pH to pH 5 with small volumes of HCl and NaOH (1, 0.1, 0.01, 0.001 M), the vials were set up on a shaking table for pre-equilibration overnight.

On the next day, a second pH check/adjustment was performed for both vials individually. Then, the kinetic experiment was started by pouring the clay suspension into the Nalgene bottle containing the U(VI) solution at the same pH and ionic strength. After a brief mixing by hand, four 1-mL volume fractions were transferred into four 2-mL centrifugation vials. (Suspension volumes of 1 mL in 2-mL centrifugation vials allowed us to minimize the height of liquid levels, sample centrifugation times, and hence, the minimum time-frames required in between sampling events.) The remaining sample suspensions were set up for continuous adsorption equilibration under shaking. Sampled suspensions were centrifuged in order to remove >50 nm clay particles, based on calculations using Stokes law (Beckman Coulter Allegra 64R, F3602 rotor, 11 minutes at 26,000 g / 16,335 rpm). After centrifugation, two 0.75-mL supernatant fractions were combined twice to give two 1.5-mL sample solutions for ICP-MS analysis.

The same sampling/centrifugation procedure was followed for the rest of the kinetic experiment, but only one 1.5-mL ICP-MS sample was created per sampling event. In addition, on the first and last day of the experiment a similar procedure was applied to collect supernatant solutions for dissolved inorganic carbon (DIC) analysis on a Shimadzu TOC-V. Last, pH values of sample suspensions were recorded every couple of days in order to monitor for potential changes in pH over time.

Results

Uranium(VI) shows a fast initial uptake, followed by slower apparent adsorption kinetics (Figure EA-3), which resulted in a slight increase in U(VI) adsorption distribution coefficients (K_D values) from 1709 L/kg (2.0 days) to 2479 L/kg (13.2 days) over time. Dissolved inorganic carbon (DIC) concentrations remained fairly constant throughout the experiment with values of 0.34 ± 0.02 and 0.28 ± 0.02 mg/L DIC on the first and last sampling days. In contrast, pH appears to consistently increase over time (Figure EA-4), from pH 5.00 to pH 5.19 and pH 5.25 after 1.0, 7.4, and 13.2 days into the experiment.

In order to evaluate if the slight increase in U(VI) K_D values in the kinetic experiment is driven by slow adsorption processes or the shift to higher pH conditions, we draw a comparison between batch kinetic data and adsorption results determined in a batch adsorption experiment after 48.5-hours reaction time under the same chemical conditions (see manuscript for experimental details). First, at a pH value between 5.00 and 5.07, the U(VI) K_D value determined in the kinetic experiment after 2.0 days (1709 L/kg) compares well with the adsorption distribution coefficient from the 48.5-hour adsorption experiment (1,892 L/kg, pH 5.12, 0.262 ± 0.001 mg/L DIC). Hence, the slightly different experimental setups had no apparent effect on U(VI) adsorption results. Second, at the longest reaction time in the kinetic experiment (13.2 days), we computed a U(VI) K_D value of 2479 L/kg at pH 5.25. A directly comparable data point at the same pH value is not available from the adsorption experiment with a 48.5-hour reaction time. However, a graphical interpolation between neighboring data points (data not reported) results in estimated 48.5-hour U(VI) K_d values between 2,523 and 2,784 L/kg.

Based on these results, the observed increase in U(VI) K_d values in the kinetic experiment is most likely due to changing pH conditions, and not driven by secondary slow

U(VI) adsorption processes under the given set of experimental conditions. Hence, under these conditions, distribution coefficients determined at adsorption equilibration times of 48.5 hours are most likely at, or close to, values determined under steady-state conditions.

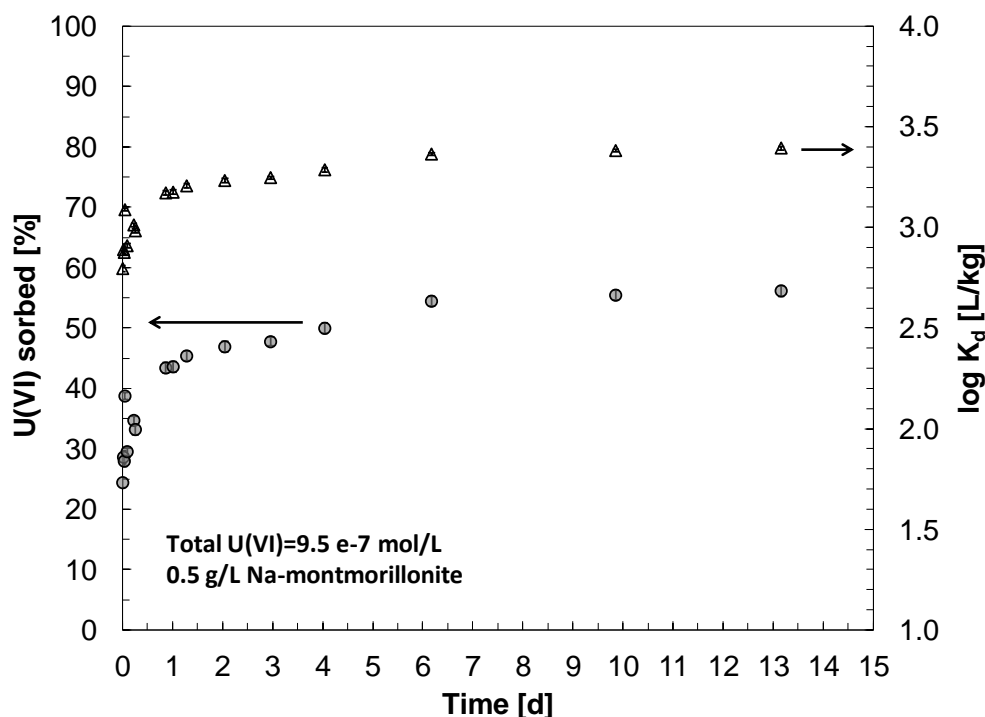


Figure EA-4. Adsorption of 9.5×10^{-7} M U(VI) as a function of time, at a target pH of 5, $I=0.1$ M NaCl, in a 0.5 g/L Na-montmorillonite suspension equilibrated with atmospheric CO₂. Error bars represent analytical uncertainties, which are smaller than data points.

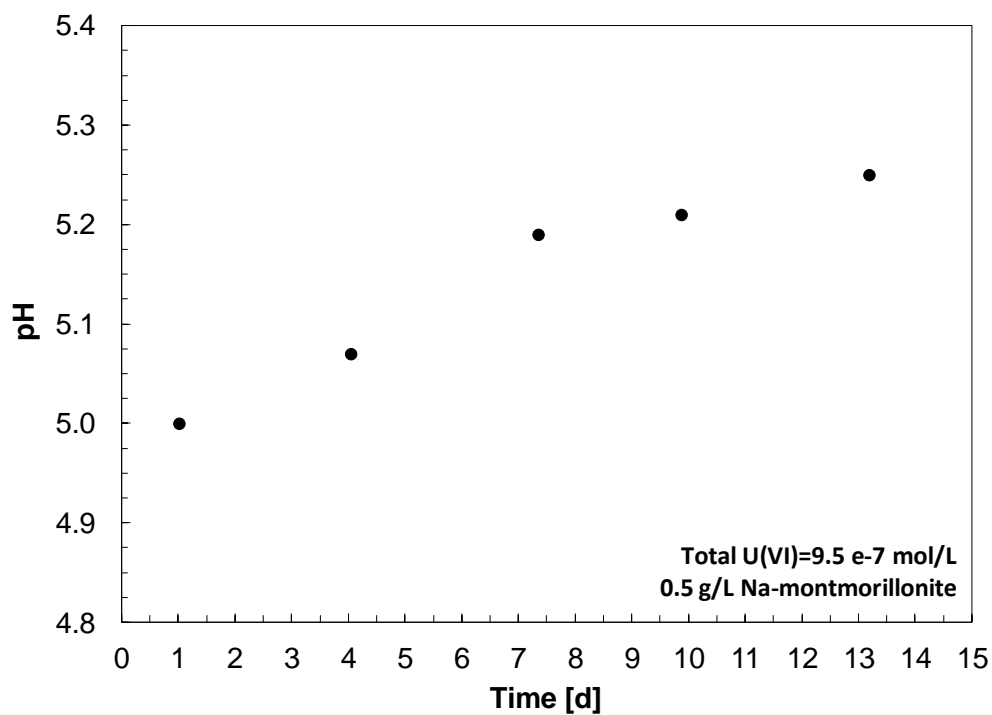


Figure EA-5. Changes in pH as a function of time during the U(VI) batch kinetic experiment at a target pH of 5, $I=0.1$ M NaCl, in a 0.5 g/L Na-montmorillonite suspension equilibrated with atmospheric CO_2 .

4. Experimental Procedure for Quantification of Analytical Detection Limits and Background Values for Dissolved Inorganic Carbon

The manufacturer of the Shimadzu TOC-V_{CSH} instrument reports a detection limit of 4 $\mu\text{g}\cdot\text{L}^{-1}$ carbon. However, actual method detection limits are often dependent on the specific purity of water and reagents used to prepare calibration standards. Hence, following recommendations by the U.S. EPA (U.S. EPA, 1995), the Method Detection Limit (MDL) and Minimum Level (ML) were determined for the specific setup of our DIC analysis on two separate days. Both limits were based on a nonconsecutive analysis of seven Milli-Q water (MQW) blanks after establishing a MQW blank-corrected DIC calibration curve with the same MQW as solution matrix (standard concentrations of 0, 0.025, 0.05, 0.1, 0.5, 1 and 5 $\text{mg}\cdot\text{L}^{-1}$ DIC, corresponding to 0, 2.1E-6, 4.2E-6, 8.3E-6, 4.2E-5, 8.3E-5 and 4.2E-4 mol L^{-1} DIC). The MDL represents the minimum DIC concentration that can be identified, measured and reported with a 99 % confidence that the concentration is greater than zero (U.S. EPA, 1995). It is calculated from the standard deviation of DIC concentrations in seven replicate MQW blanks multiplied by the Student t-value for the 99 % confidence level with six degrees of freedom (3.14). The ML is defined as the smallest measured concentration of a constituent that may be reliably reported using a given analytical method. Its value corresponds to the limit of quantitation (LOQ) established by the American Chemical Society, and is computed by multiplying the MDL by a factor of 3.18.

Potential DIC contributions from various sources in the CO_2 -“free” batch adsorption experiment, performed in the 93.3% N_2 /5.7% H_2 glove box environment, were quantified. In particular, it was important to understand if measured DIC concentrations had been present in solution during U(VI) adsorption equilibration, or if they represent a DIC contamination that was introduced into samples at a later point in time. For this particular experimental setup, potential sources of DIC contamination include: (1) DIC background concentrations in MQW (before and after purging with nitrogen gas) used for later sample preparation in the glove box, (2) handling of open sample vials in the glove box, if CO_2 was not fully excluded from the glove box atmosphere (maximum handling time for open vials estimated at 3-4 h), (3) introduction of CO_2 into closed sample vials during centrifugation under atmospheric CO_2 outside the glove box, and (4) diffusion of atmospheric CO_2 into refrigerated, closed sample vials during a six-day storage period prior to DIC analysis.

In order to determine potential sources of DIC contamination in the CO₂-“free” batch adsorption experiment, approximately one liter of heated MQW was sparged with N₂(g) using a glass sparger and a 20 µm tube-fitting filter for approximately 20 h. Inside a glove box filled with 5% H₂/95% N₂ gas, samples were prepared to provide DIC background values for the N₂-purged MQW (in triplicates), plus a series of samples with known, added concentrations of NaHCO₃ (nominal concentrations of 0.031, 0.063, 0.125, 0.250, 0.500 and 1.000 mg·L⁻¹ DIC, corresponding to 2.6E-6, 5.2E-6, 1.0E-5, 2.1E-5, 4.2E-5 and 8.3E-5 mol L⁻¹ DIC). Exact volumes of added 0.001 M NaHCO₃ solution and N₂-purged MQW were determined by weight. The same procedure was also applied to volume fractions of the same N₂-purged MQW after: (1) centrifuging solutions in the same manner as during the CO₂-“free” batch adsorption experiments, (2) storage of N₂-purged MQW solutions in open 50 ml polycarbonate vials in the glove box for 22.6 h (about 5-times the time-frame estimated for the actual CO₂-“free” adsorption experiment), and (3) storage in closed glass vials in the fridge for approximately seven days.

5. Calculated Partial Pressures of CO₂ in U(VI) Adsorption Experiments

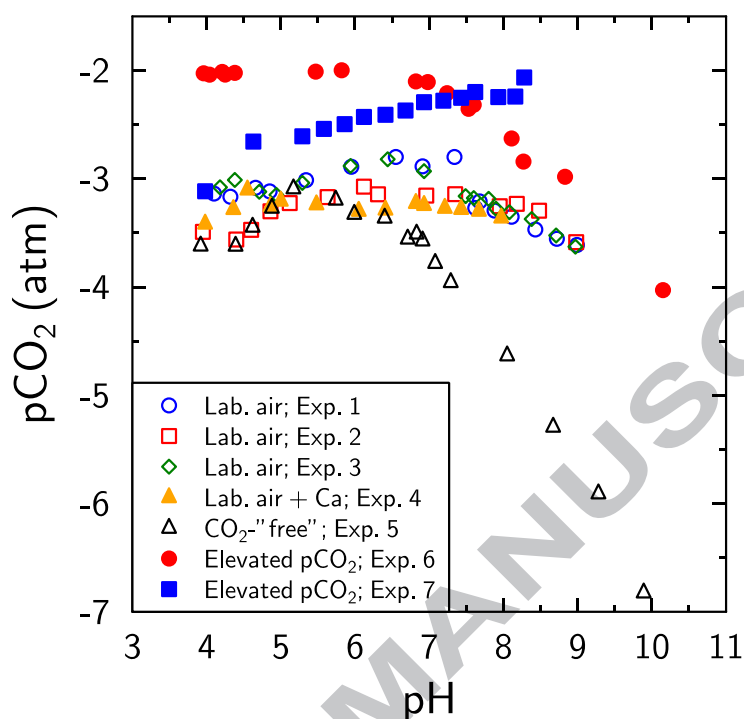


Figure EA-6. pCO₂ partial pressures inside each experimental centrifuge tube, calculated from the measured pH values and DIC concentrations in supernatant samples. Calculations were made with PHREEQC (Parkhurst and Appelo, 1999, 2013) and the THERMOCHEMIE database (Giffaut et al., 2014).

6. Summary of Batch U(VI) Adsorption Data

Experiment 1: 1.11E-7 M U(VI) total, atmospheric CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|------|----------------------|----------|----------|----------------------------|----------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.5161 | 4.10 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 7.23E-06 | 5.50E-06 | 1.02E-07 | 2.49E-05 | -3.14 |
| 2 | 0.5161 | 4.32 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 6.83E-06 | 5.31E-06 | 8.97E-08 | 2.34E-05 | -3.17 |
| 3 | 0.5161 | 4.66 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 6.74E-06 | 5.25E-06 | 7.13E-08 | 2.87E-05 | -3.08 |
| 4 | 0.5161 | 4.85 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 7.02E-06 | 5.26E-06 | 5.43E-08 | 2.70E-05 | -3.12 |
| 5 | 0.5161 | 5.34 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 8.07E-06 | 5.23E-06 | 2.43E-08 | 3.72E-05 | -3.01 |
| 6 | 0.5161 | 5.95 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 7.69E-06 | 5.21E-06 | 8.91E-09 | 6.70E-05 | -2.89 |
| 7 | 0.5161 | 6.55 | 1.01E-01 | 1.00E-01 | 1.11E-07 | 7.24E-06 | 5.21E-06 | 1.25E-08 | 1.68E-04 | -2.80 |
| 8 | 0.5085 | 6.91 | 9.97E-02 | 9.85E-02 | 1.11E-07 | 7.33E-06 | 5.07E-06 | 1.94E-08 | 2.58E-04 | -2.89 |
| 9 | 0.5133 | 7.34 | 1.01E-01 | 9.95E-02 | 1.11E-07 | 7.33E-06 | 5.10E-06 | 5.93E-08 | 7.59E-04 | -2.80 |
| 10 | 0.5161 | 7.62 | 1.01E-01 | 9.98E-02 | 1.11E-07 | 7.14E-06 | 5.17E-06 | 4.24E-08 | 4.74E-04 | -3.27 |
| 11 | 0.5166 | 7.68 | 1.01E-01 | 9.98E-02 | 1.11E-07 | 8.20E-06 | 5.28E-06 | 5.70E-08 | 6.23E-04 | -3.21 |
| 12 | 0.5161 | 7.88 | 1.01E-01 | 9.95E-02 | 1.11E-07 | 7.32E-06 | 5.13E-06 | 7.94E-08 | 8.07E-04 | -3.29 |
| 13 | 0.5164 | 8.11 | 1.01E-01 | 9.91E-02 | 1.11E-07 | 8.04E-06 | 5.18E-06 | 1.05E-07 | 1.20E-03 | -3.35 |
| 14 | 0.5161 | 8.43 | 1.01E-01 | 9.84E-02 | 1.11E-07 | 7.49E-06 | 5.02E-06 | 1.18E-07 | 1.94E-03 | -3.47 |
| 15 | 0.5180 | 8.72 | 1.02E-01 | 9.78E-02 | 1.11E-07 | 7.65E-06 | 4.89E-06 | 1.23E-07 | 3.22E-03 | -3.55 |
| 16 | 0.5319 | 8.99 | 1.05E-01 | 9.76E-02 | 1.11E-07 | 8.52E-06 | 4.90E-06 | 1.26E-07 | 5.62E-03 | -3.61 |

In this and all following, related tables, Na and Cl concentrations take into account additions of NaCl, NaOH and HCl to sample solutions.

Experiment 2: 9.6E-7 M U(VI) total, atmospheric CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|-------|----------------------|----------|----------|----------------------------|----------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.5166 | 3.95 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 7.16E-06 | 7.44E-06 | 8.75E-07 | 1.10E-05 | -3.49 |
| 2 | 0.5166 | 4.40 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 6.42E-06 | 7.17E-06 | 7.85E-07 | 9.45E-06 | -3.56 |
| 3 | 0.5166 | 4.60 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 8.63E-06 | 7.57E-06 | 7.48E-07 | 1.17E-05 | -3.47 |
| 4 | 0.5166 | 4.86 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 7.35E-06 | 7.05E-06 | 6.62E-07 | 1.77E-05 | -3.30 |
| 5 | 0.5166 | 5.12 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 7.60E-06 | 7.04E-06 | 4.81E-07 | 2.18E-05 | -3.22 |
| 6 | 0.5166 | 5.63 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 6.88E-06 | 6.88E-06 | 2.37E-07 | 2.88E-05 | -3.17 |
| 7 | 0.5166 | 6.12 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 7.04E-06 | 6.86E-06 | 9.85E-08 | 5.12E-05 | -3.07 |
| 8 | 0.5166 | 6.31 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 7.18E-06 | 6.70E-06 | 7.60E-08 | 5.41E-05 | -3.14 |
| 9 | 0.5166 | 6.96 | 1.00E-01 | 1.00E-01 | 9.56E-07 | 6.86E-06 | 8.83E-06 | 1.70E-07 | 1.53E-04 | -3.16 |
| 10 | 0.5166 | 7.35 | 1.00E-01 | 9.98E-02 | 9.56E-07 | 6.94E-06 | 8.12E-06 | 3.25E-07 | 3.52E-04 | -3.14 |
| 11 | 0.5166 | 7.95 | 1.00E-01 | 9.95E-02 | 9.56E-07 | 7.31E-06 | 8.79E-06 | 7.99E-07 | 1.04E-03 | -3.25 |
| 12 | 0.5166 | 8.18 | 1.00E-01 | 9.91E-02 | 9.56E-07 | 7.71E-06 | 6.61E-06 | 9.31E-07 | 1.86E-03 | -3.23 |
| 13 | 0.5166 | 8.48 | 1.00E-01 | 9.84E-02 | 9.56E-07 | 7.62E-06 | 6.52E-06 | 9.52E-07 | 3.26E-03 | -3.30 |
| 14 | 0.5166 | 8.68 | 1.14E-01 | 9.71E-02 | 9.56E-07 | 1.02E-05 | 1.17E-05 | 9.62E-07 | 1.62E-02 | -3.59 |
| 15 | 0.5166 | 8.98 | 1.00E-01 | 9.47E-02 | 9.56E-07 | 8.43E-06 | 6.23E-06 | 9.55E-07 | 5.78E-03 | -3.49 |
| 16 | 0.5166 | 9.55 | 1.05E-01 | 8.16E-02 | 9.56E-07 | 9.80E-06 | 5.65E-06 | 9.65E-07 | 1.85E-02 | -3.56 |
| 17 | 0.5166 | 10.00 | 1.36E-01 | 2.48E-02 | 9.56E-07 | 1.89E-05 | 8.09E-06 | 9.77E-07 | 7.22E-02 | -3.47 |

Experiment 3: 2.55E-6 M U(VI) total, atmospheric CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|------|----------------------|----------|----------|----------------------------|----------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.5158 | 4.18 | 1.01E-01 | 1.00E-01 | 2.55E-06 | 9.94E-06 | 6.33E-06 | 2.51E-06 | 2.85E-05 | -3.08 |
| 2 | 0.5158 | 4.38 | 1.01E-01 | 1.00E-01 | 2.55E-06 | 1.23E-05 | 6.43E-06 | 2.43E-06 | 3.35E-05 | -3.01 |
| 3 | 0.5158 | 4.71 | 1.01E-01 | 1.00E-01 | 2.55E-06 | 1.02E-05 | 6.11E-06 | 2.24E-06 | 2.65E-05 | -3.12 |
| 4 | 0.5158 | 4.94 | 1.01E-01 | 1.00E-01 | 2.55E-06 | 9.50E-06 | 5.72E-06 | 1.93E-06 | 2.53E-05 | -3.15 |
| 5 | 0.5158 | 5.29 | 1.01E-01 | 1.00E-01 | 2.55E-06 | 9.49E-06 | 5.80E-06 | 1.33E-06 | 3.47E-05 | -3.04 |
| 6 | 0.5158 | 5.94 | 1.01E-01 | 9.99E-02 | 2.55E-06 | 9.57E-06 | 5.69E-06 | 6.29E-07 | 6.78E-05 | -2.88 |
| 7 | 0.5158 | 6.44 | 1.01E-01 | 9.99E-02 | 2.55E-06 | 9.05E-06 | 5.57E-06 | 6.29E-07 | 1.36E-04 | -2.82 |
| 8 | 0.5158 | 6.93 | 1.01E-01 | 9.99E-02 | 2.55E-06 | 9.93E-06 | 5.62E-06 | 7.37E-07 | 2.43E-04 | -2.93 |
| 9 | 0.5158 | 7.49 | 1.01E-01 | 9.98E-02 | 2.55E-06 | 9.74E-06 | 5.67E-06 | 1.23E-06 | 4.59E-04 | -3.16 |
| 10 | 0.5159 | 7.60 | 1.01E-01 | 9.97E-02 | 2.55E-06 | 9.86E-06 | 5.61E-06 | 1.47E-06 | 5.62E-04 | -3.18 |
| 11 | 0.5159 | 7.80 | 1.02E-01 | 1.00E-01 | 2.55E-06 | 1.25E-05 | 5.75E-06 | 2.07E-06 | 8.69E-04 | -3.18 |
| 12 | 0.5162 | 7.90 | 1.02E-01 | 9.96E-02 | 2.55E-06 | 9.89E-06 | 5.59E-06 | 2.14E-06 | 8.82E-04 | -3.28 |
| 13 | 0.5162 | 8.08 | 1.02E-01 | 9.91E-02 | 2.55E-06 | 9.90E-06 | 5.57E-06 | 2.37E-06 | 1.24E-03 | -3.31 |
| 14 | 0.5162 | 8.38 | 1.02E-01 | 9.84E-02 | 2.55E-06 | 1.04E-05 | 5.46E-06 | 2.86E-06 | 2.16E-03 | -3.37 |
| 15 | 0.5282 | 8.71 | 1.05E-01 | 9.97E-02 | 2.55E-06 | 1.07E-05 | 5.38E-06 | 2.78E-06 | 3.39E-03 | -3.52 |
| 16 | 0.5311 | 8.97 | 1.05E-01 | 9.75E-02 | 2.55E-06 | 1.04E-05 | 5.23E-06 | 2.77E-06 | 5.15E-03 | -3.63 |

Experiment 4: 1.52E-6 M U(VI) total, atmospheric CO₂, 2.1 mM Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|------|----------------------|----------|----------|----------------------------|----------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.516625 | 3.98 | 9.74E-02 | 1.02E-01 | 1.52E-06 | 2.10E-03 | 1.20E-05 | 8.91E-07 | 1.31E-05 | -3.42 |
| 2 | 0.516625 | 4.36 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.09E-03 | 1.26E-05 | 8.23E-07 | 1.80E-05 | -3.28 |
| 3 | 0.516625 | 4.55 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.13E-03 | 1.16E-05 | 7.60E-07 | 2.75E-05 | -3.10 |
| 4 | 0.516625 | 4.86 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.13E-03 | 1.28E-05 | 6.60E-07 | 1.97E-05 | -3.25 |
| 5 | 0.516625 | 5.00 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.10E-03 | 1.12E-05 | 5.92E-07 | 2.25E-05 | -3.20 |
| 6 | 0.516625 | 5.48 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.05E-03 | 1.16E-05 | 3.07E-07 | 2.32E-05 | -3.24 |
| 7 | 0.516625 | 6.05 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.09E-03 | 1.12E-05 | 1.21E-07 | 2.87E-05 | -3.30 |
| 8 | 0.516625 | 6.41 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.09E-03 | 1.10E-05 | 8.07E-08 | 4.48E-05 | -3.29 |
| 9 | 0.516625 | 6.82 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.07E-03 | 1.70E-05 | 1.23E-07 | 1.01E-04 | -3.22 |
| 10 | 0.516625 | 6.93 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.07E-03 | 1.13E-05 | 1.33E-07 | 1.19E-04 | -3.24 |
| 11 | 0.516625 | 7.21 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.05E-03 | 1.13E-05 | 2.38E-07 | 1.98E-04 | -3.27 |
| 12 | 0.516625 | 7.43 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.06E-03 | 1.39E-05 | 4.66E-07 | 3.10E-04 | -3.28 |
| 13 | 0.516625 | 7.67 | 9.70E-02 | 1.01E-01 | 1.52E-06 | 2.11E-03 | 1.14E-05 | 7.90E-07 | 5.08E-04 | -3.30 |
| 14 | 0.516625 | 7.97 | 9.73E-02 | 1.01E-01 | 1.52E-06 | 2.06E-03 | 1.12E-05 | 9.28E-07 | 8.69E-04 | -3.36 |

Experiment 5: 1.12E-6 M U(VI) total, 'zero' CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ |
|------------|------------|------|----------------------|----------|----------|----------------------------|----------|----------|----------|-------------------------------|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [atm] (log ₁₀) |
| 1 | 0.5166 | 3.92 | 1.00E-01 | 1.01E-01 | 1.12E-06 | 8.01E-06 | 7.50E-06 | 9.24E-07 | 8.20E-06 | -3.62 |
| 2 | 0.5166 | 4.39 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.96E-06 | 7.72E-06 | 8.48E-07 | 8.26E-06 | -3.62 |
| 3 | 0.5166 | 4.62 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.69E-06 | 9.86E-06 | 7.42E-07 | 1.25E-05 | -3.44 |
| 4 | 0.5166 | 4.88 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.87E-06 | 6.72E-06 | 6.74E-07 | 1.91E-05 | -3.27 |
| 5 | 0.5166 | 5.17 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.72E-06 | 6.70E-06 | 4.97E-07 | 3.00E-05 | -3.09 |
| 6 | 0.5166 | 5.74 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.93E-06 | 7.14E-06 | 1.88E-07 | 2.88E-05 | -3.19 |
| 7 | 0.5166 | 5.99 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.89E-06 | 7.08E-06 | 1.16E-07 | 2.54E-05 | -3.33 |
| 8 | 0.5166 | 6.40 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.24E-06 | 7.01E-06 | 7.22E-08 | 3.70E-05 | -3.36 |
| 9 | 0.5166 | 6.71 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.66E-06 | 7.62E-06 | 7.61E-08 | 3.85E-05 | -3.55 |
| 10 | 0.5166 | 6.83 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.86E-06 | 8.80E-06 | 7.97E-08 | 5.31E-05 | -3.51 |
| 11 | 0.5166 | 6.91 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 9.80E-06 | 9.06E-06 | 7.48E-08 | 5.33E-05 | -3.57 |
| 12 | 0.5166 | 7.08 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.18E-06 | 9.13E-06 | 8.14E-08 | 4.62E-05 | -3.78 |
| 13 | 0.5166 | 7.29 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.82E-06 | 1.21E-05 | 9.76E-08 | 4.76E-05 | -3.96 |
| 14 | 0.5166 | 8.05 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.27E-06 | 8.97E-06 | 1.04E-07 | 5.46E-05 | -4.63 |
| 15 | 0.5166 | 8.67 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 7.80E-06 | 7.32E-06 | 1.09E-07 | 5.21E-05 | -5.29 |
| 16 | 0.5166 | 9.28 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.61E-06 | 7.65E-06 | 1.37E-07 | 6.21E-05 | -5.91 |
| 17 | 0.5166 | 9.89 | 1.00E-01 | 1.00E-01 | 1.12E-06 | 8.00E-06 | 4.21E-06 | 1.49E-07 | 5.26E-05 | -6.82 |

Experiment 6: 8.1E-7 M U(VI) total, '2%' CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|-------|----------------------|----------|----------|----------------------------|----------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.5166 | 3.96 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.16E-05 | 7.66E-06 | 7.13E-07 | 3.21E-04 | -2.03 |
| 2 | 0.5166 | 4.04 | 1.00E-01 | 1.01E-01 | 8.05E-07 | 1.12E-05 | 7.50E-06 | 7.07E-07 | 3.12E-04 | -2.04 |
| 3 | 0.5166 | 4.21 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.08E-05 | 7.44E-06 | 6.60E-07 | 3.32E-04 | -2.01 |
| 4 | 0.5166 | 4.25 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.15E-05 | 7.44E-06 | 6.41E-07 | 3.14E-04 | -2.04 |
| 5 | 0.5166 | 4.38 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.20E-05 | 7.34E-06 | 5.95E-07 | 3.27E-04 | -2.02 |
| 6 | 0.5166 | 5.47 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.20E-05 | 7.24E-06 | 3.25E-07 | 3.89E-04 | -2.01 |
| 7 | 0.5166 | 5.82 | 1.00E-01 | 1.00E-01 | 8.05E-07 | 1.19E-05 | 7.41E-06 | 3.24E-07 | 4.75E-04 | -2.00 |
| 8 | 0.5166 | 6.82 | 1.00E-01 | 9.94E-02 | 8.05E-07 | 1.11E-05 | 7.39E-06 | 4.50E-07 | 1.33E-03 | -2.10 |
| 9 | 0.5166 | 6.98 | 1.00E-01 | 9.93E-02 | 8.05E-07 | 1.03E-05 | 7.04E-06 | 5.34E-07 | 1.78E-03 | -2.11 |
| 10 | 0.5166 | 7.24 | 1.00E-01 | 9.92E-02 | 8.05E-07 | 1.08E-05 | 7.07E-06 | 6.49E-07 | 2.39E-03 | -2.21 |
| 11 | 0.5166 | 7.53 | 1.01E-01 | 9.89E-02 | 8.05E-07 | 1.21E-05 | 7.14E-06 | 7.11E-07 | 3.21E-03 | -2.35 |
| 12 | 0.5166 | 7.60 | 1.01E-01 | 9.85E-02 | 8.05E-07 | 1.11E-05 | 7.05E-06 | 7.60E-07 | 4.08E-03 | -2.32 |
| 13 | 0.5166 | 8.11 | 1.01E-01 | 9.78E-02 | 8.05E-07 | 1.26E-05 | 7.07E-06 | 7.76E-07 | 6.37E-03 | -2.63 |
| 14 | 0.5166 | 8.27 | 1.01E-01 | 9.65E-02 | 8.05E-07 | 1.13E-05 | 6.95E-06 | 7.67E-07 | 5.65E-03 | -2.84 |
| 15 | 0.5166 | 8.83 | 1.01E-01 | 9.41E-02 | 8.05E-07 | 1.30E-05 | 6.71E-06 | 7.79E-07 | 1.61E-02 | -2.98 |
| 16 | 0.5166 | 9.60 | 1.05E-01 | 8.10E-02 | 8.05E-07 | 1.48E-05 | 6.39E-06 | 8.07E-07 | 2.96E-02 | -4.03 |
| 17 | 0.5166 | 10.15 | 1.25E-01 | 2.41E-02 | 8.05E-07 | 2.74E-05 | 8.99E-06 | 7.96E-07 | 1.27E-01 | -2.03 |

Experiment 7: 9.8E-7 M U(VI) total, '2%' CO₂, no Ca added

| Sample no. | Clay conc. | pH | Total concentrations | | | Supernatant concentrations | | | | Calc. pCO ₂ [atm] (log ₁₀) |
|------------|------------|------|----------------------|----------|----------|----------------------------|---------|----------|----------|---|
| | | | Na | Cl | U | Ca | Mg | U | DIC | |
| [] | [g/L] | [] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | [mol/L] | |
| 1 | 0.2400 | 3.98 | 1.00E-01 | 1.00E-01 | 9.86E-07 | | | 8.37E-07 | 2.61E-05 | -3.12 |
| 2 | 0.2400 | 4.63 | 1.00E-01 | 1.00E-01 | 9.86E-07 | | | 7.35E-07 | 7.67E-05 | -2.66 |
| 3 | 0.2400 | 5.29 | 1.00E-01 | 1.00E-01 | 9.86E-07 | | | 4.60E-07 | 9.34E-05 | -2.61 |
| 4 | 0.2400 | 5.58 | 1.00E-01 | 1.00E-01 | 9.86E-07 | | | 3.79E-07 | 1.20E-04 | -2.54 |
| 5 | 0.2400 | 5.86 | 1.00E-01 | 1.01E-01 | 9.86E-07 | | | 3.49E-07 | 1.55E-04 | -2.50 |
| 6 | 0.2400 | 6.12 | 1.00E-01 | 1.00E-01 | 9.87E-07 | | | 3.10E-07 | 2.26E-04 | -2.43 |
| 7 | 0.2400 | 6.41 | 1.00E-01 | 1.00E-01 | 9.86E-07 | | | 3.57E-07 | 3.35E-04 | -2.41 |
| 8 | 0.2400 | 6.68 | 1.00E-01 | 9.95E-02 | 9.86E-07 | | | 5.20E-07 | 5.58E-04 | -2.37 |
| 9 | 0.2400 | 6.93 | 1.00E-01 | 9.89E-02 | 9.86E-07 | | | 7.03E-07 | 1.05E-03 | -2.29 |
| 10 | 0.2400 | 7.19 | 1.00E-01 | 9.80E-02 | 9.86E-07 | | | 8.88E-07 | 1.83E-03 | -2.28 |
| 11 | 0.2400 | 7.43 | 1.00E-01 | 9.63E-02 | 9.87E-07 | | | 9.62E-07 | 3.25E-03 | -2.25 |
| 12 | 0.2400 | 7.62 | 1.00E-01 | 9.35E-02 | 9.87E-07 | | | 9.78E-07 | 5.57E-03 | -2.20 |
| 13 | 0.2400 | 7.93 | 1.00E-01 | 8.81E-02 | 9.86E-07 | | | 9.76E-07 | 1.01E-02 | -2.24 |
| 14 | 0.2400 | 8.16 | 1.00E-01 | 7.88E-02 | 9.86E-07 | | | 9.80E-07 | 1.73E-02 | -2.24 |
| 15 | 0.2400 | 8.28 | 1.00E-01 | 6.20E-02 | 9.87E-07 | | | 9.96E-07 | 3.44E-02 | -2.06 |

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