Environ Earth Sci (2011) 63:925–934
DOI 10.1007/s12665-010-0761-6

ORIGINAL ARTICLE

Sorption of uranium(VI) at the clay mineral–water interface

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Received: 11 November 2009 / Accepted: 26 September 2010 / Published online: 11 October 2010

Abstract Batch experiments were conducted to study the sorption of uranium on selected clay minerals (KGa-1b and KGa-2 reference kaolinite, SWy-2 and STx-1b reference montmorillonite, and IBECO natural bentonite) as a function of pH (4–9) and 0.001, 0.01, and 0.025 M NaCl in equilibrium with the CO_2 partial pressure of the atmosphere. Uranium concentrations were kept below 100 μg L^{-1} to avoid precipitation of amorphous Uranium-hydroxides. Solely PTFE containers and materials were used, because experiments showed significant sorption at higher pH on glass ware. All batch experiments were performed over a period of 24 h, since kinetic experiments proved that the common 10 or 15 min are in many cases by far not sufficient to reach equilibrium. Kaolinite showed much greater uranium sorption than the other clay minerals due to the more aluminol sites available. Sorption on the poorly crystallized KGa-2 was higher than on the well-crystallized KGa-1b. Uranium sorption on STx-1b and IBECO exhibited parabolic behavior with a sorption maximum around pH 6.5. Sorption of uranium on montmorillonites showed a distinct dependency on sodium concentrations because of the effective competition between uranyl and sodium ions, whereas less significant differences in sorption were found for kaolinite. The presence of anatase as impurity in kaolinite enhanced the binding of uranyl-carbonate complexes with surface sites. The kinetic of uranium sorption behavior was primarily dependent on the clay minerals and pH. A multisite surface complexation model without assuming exchange is based on the binding of the most dominant uranium species to aluminol and silanol edge sites of montmorillonite, respectively to aluminol and titanol surface sites of kaolinite. For eight surface species, the log_k was determined from the experimental data using the parameter estimation code PEST together with PHREEQC.

Keywords Montmorillonite · Kaolinite · Uranium(VI) · Sorption · Surface complexation model

Introduction

Uranium is of increasing environmental concern due to a grown awareness of its risk to soil and water. Elevated concentration of uranium can be related to uranium milling and mining sites (Morrison and Cahn 1991), nuclear fuel and nuclear weapons production sites (Riley et al. 1992), combustion of coal and oil, in particular, when no proper combustions gas cleaning systems are installed, and the application of phosphate fertilizers (Barisic et al. 1992; Zielinski et al. 2006). A provisional drinking water MCL for uranium of 15 μg L^{-1} has been established by the World Health Organization (WHO 2004). However, it is discussed worldwide that 10 or 5 μg L^{-1} would be more reasonable (BFR 2005; Hickox and Denton 2001; Kurttio et al. 2002; Raymond-Whish et al. 2007). Geochemical processes occurring naturally, including dissolution/precipitation, redox reactions, and sorption/desorption reactions at the water–rock interface, control the mobility and transport of uranium in the subsurface system, such as aquifer sediments, soils, and groundwater.

Sorption is an important removal mechanism that controls uranium concentration in groundwater (Prikryl et al. 2001). However, the dependence of sorption on aqueous

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solution properties (e.g., pH, E_h, total uranium concentration, ionic strength, and presence of complexing ligands) and characteristics of sorbing materials (e.g., mineral compositions, surface area, density of sorptive surface sites, solid/solution ratio) makes the prediction of uranium retardation difficult (Prikryl et al. 2001). The sorption of uranium in natural water, on geological material typically increases with increasing pH up to the neutral region, while in system equilibrated with air, a significant decrease of sorption above pH 7 due to a stable uranyl-carbonate complexation is observed (Payne 1999).

Among common sorbing materials are clay minerals, which have a very high retention capacity due to (1) their large surface area as well as their osmotic swelling capacity and consequently their plasticity and impermeability and (2) the property of these minerals to simultaneously create a permanent negative charge within the structure and a variable charge at the particle edge. The negative surface charge is created due to the extensive isomorphous substitution of cations in the lattice by cations of lower charge (e.g., the substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} for Al^{3+} in the octahedral sheet). Positive charge may occur due to the edge defects (e.g., protonation of broken Al–OH bonds exposed at particle edges). On the other hand, kaolin minerals do not have extensive isomorphous substitution of metals in tetrahedral and octahedral sheets. Thus, edge defects are more important sources of positive charge than isomorphic substitution (Lin and Puls 2000). Hence, clay minerals can sorb cations and/or anions that neutralize the structure charge. Some of the most important clays are montmorillonite and kaolinite, both because of their prevalence in soil and ground water environments and because they have been recognized as fundamental for retarding the migration of many contaminates in soils, sediments, and rocks (Bachmaf et al. 2008; Borovec 1981; Catalano and Brown 2005; Hyun et al. 2001; Olguin et al. 1997; Payne et al. 2004). They are as well considered as a barrier material for radionuclide retention in nuclear waste repositories (Lajudie et al. 1995; Neall et al. 1995).

Sorption of uranium by clay minerals has been extensively documented in the literature. However, most of the previous sorption investigations have been performed at relatively high uranium concentration ($>100\ \mu g\ L^{-1}$). Using the geochemical code PHREEQC (Parkhurst and Appelo 1999) with the updated Nuclear Energy Agency thermodynamic database (NEA 2007) (Grenthe et al. 2007), positive saturation indices were found for certain uranium minerals (e.g. Schoepite) when the total uranium concentration was higher than $100\ \mu g\ L^{-1}$, in particular, at pH above 5. Furthermore, X-ray characterizations for kaolinite treated with higher concentration of uranium showed evidence of uranium mineral precipitation on the surface of clays. Thus, it is likely that amorphous phases have been precipitated in studies using uranium concentrations above $100\ \mu g\ L^{-1}$. The practical relevance for conducting experiments at uranium concentration below $100\ \mu g\ L^{-1}$is that uranium occurs naturally in low concentrations (a few parts per million) in soil, rock as well as in surface and groundwaters (Bernhard 2005; Langmuir 1997).

The purpose of this investigation was to examine the sorption of uranium with five different types of clay minerals as a function of pH and varying NaCl concentrations. Monodentate and bidentate uranyl binding (as UO_2^{2+} cation and various monomeric or polymeric hydrolyzed species) to permanent charged surface sites as well as to edge hydroxyl groups of clay minerals were considered to be important in sorption modeling approaches (Pabalan et al. 1996; Prikryl et al. 1994). Specific surface area, clay composition, and surface site density were evaluated in these models, and the corresponding equilibrium constants for various modes of binding were calculated.

Different models have been employed to elucidate uranyl sorption onto clay minerals. Ion exchange modeling used by (Fletcher and Sposito 1989) was an early approach. A more recent and sophisticated approach is surface complexation modeling (Kowal-Fouchard et al. 2004; McKinley et al. 1995; Pabalan et al. 1996; Turner et al. 1996; Zachara and Mckinley 1993). Although previous researchers assumed that the uranyl sorption by clay minerals at acidic to neutral pH values is dominated by ion exchange reactions, recent works e.g., (Arda et al. 2006; Chisholm-Brause et al. 2004) have shown that the reactivity of metal-oxides like edge sites in clay minerals is responsible for uranium sorption over a wide range of pH and electrolyte concentration. A modified multisite surface complexation model developed by (Zachara and Mckinley 1993) for montmorillonite, and that developed by (Payne et al. 2004) for kaolinite was used to explain the mechanisms controlling the uranium sorption.

Materials and methodology

Clay minerals characterization

Selected reference clay minerals, well-crystallized kaolinite (KGa-1b), poorly crystallized kaolinite (KGa-2), Ca-montmorillonite (STx-1b), and Na-montmorillonite (SWy-2) were supplied from the Clay Minerals Society (CMS) Source Clays Repository (University of Purdue, West Lafayette). Morocco natural bentonite (IBECO) was obtained from the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover (Germany). Powder X-ray diffraction (XRD) analyses were used to characterize the mineralogical composition of the phyllosilicate clay minerals according to (Chipera and Bish 2001; Ufer et al. 2004). The results show that KGa-1b and KGa-2 contain predominantly titanium as a trace of anatase (Pruett and Webb 1993). Standard STx-1b and SWy-2 montmorillonite and natural bentonite are mainly composed of smectites (67, 75, and 80%, respectively) and small amounts of impurity phases, such as quartz, feldspar, kaolinite, plagioclase, orthoclase, and opal. The chemical compositions of the five materials are summarized in Table 1, which shows the presence of approximately 1.7% TiO_2 in each of the Georgia kaolinite samples. Specific surface areas and cation exchange capacities of the clay sorbents are provided from the previous studies and given in Table 1. Those authors determined the specific surface area by multi-point Brunauer- Emmett-Teller (BET) N_2 sorption with a Quantisorb Jr. surface area analyzer (Quantachrome Corporation, Syosset, NY). The procedures performed to measure the cation exchange capacity are explained by (Borden and Giese 2001). The intention of this research was to use the source clay materials without any pretreatment to preserve their natural mineralogy.

Uranium solutions and analytical procedures

Uranium stock solutions of 100 μg L^{-1} (4.2×10^{-7} M) were prepared by dissolving uranyl nitrate hexahydrated $UO_2\ (NO_3)_2.6H_2O$ (Chemapol, Germany) in Milli-Q ultrapure water (18 MΩ/cm). All experiments were carried out in a matrix of sodium chloride (Merck, Darmstadt-Germany) at constant values of 0.001, 0.01, and 0.025 M, respectively. The pH of each test solution was adjusted to the required value with diluted NaOH or HCl solutions (Merck, Germany) using a combined glass electrode (WTW GmbH, Germany). The determination of total uranium was carried out by differential pulse adsorptive cathodic stripping voltammetry using a hanging mercury drop electrode (HMDE) as working electrode (797 Va Computrace, Methrohm, Switzerland). The technique is based upon adsorptive accumulation of the metal ion complexed with the ligand chloranilic acid at the electrode surface and then scanning the potential on the working electrode in the negative direction. The detection limit of the voltammetry was determined to be 0.05 μg L^{-1}. All experiments and all analytical determinations were performed in duplicates. The maximum experimental error was ±3%.

Experimental procedure

All sorption batch experiments were carried out by reacting 1.5 g of the respective clay mineral with 900 mL of the 100 μg L^{-1} uranium(VI) solution with 0.001, 0.010, and 0.025 M NaCl in 1 L PTFE vessels under ambient atmosphere (Pco_2 $10^{-3.5}$ hPa). The pH was monitored in all experiments and adjust when necessary with 0.1 M NaOH or 0.1 M HCl (Merck, Germany) using an automated titrator (794 Basic Titrino, program version 5.794.0010, Methrohm, Switzerland) in "pH-stat" mode. For pre-equilibration, the suspension was continuously stirred using a magnetic stirrer (IAK®, Germany). For kinetic experiments, samples were taken and centrifuged after 0.5, 1, 3, 6, 12, and 24 h. For the majority of the batch experiments, samples were taken after 24 h and the solution was then separated from the solid by centrifugation (20 min, 8,000 rpm, MLW Medizintechnik). The supernatants of all individual samples were filtered (0.2 μm cellulose acetate

Table 1 Properties of clay minerals (chemical composition in %, cation exchange capacity, and specific surface area)

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI (110–550°C)	LOI (550–1,000°C)	CEC (meq/100 g)[d]	SSA (m^2/g)
KGa-1b[a]	45.2	39.1	0.21	1.64	0.05	0.02	0.04	0.02	–	–	13.8	3.0	13.1[f]
KGa-2[b]	43.49	38.14	1.15	1.91	0.04	0.03	0.06	0.02	0.32	13.3	1.73	3.7	21.7[f]
STx-1b[b]	70.03	17.86	1.20	0.26	3.79	1.73	0.31	0.07	0.01	0.99	3.64	89	83.79[g]
SWy-2[b]	61.46	22.05	4.37	0.09	2.94	1.18	1.47	0.02	–	0.61	5.15	85	22.7[f]
IBECO[c]	53.2	21.2	2.0	0.2	2.1	1.3	1.95	0.95	0.041	–	16.63	112[e]	35[h]

LOI Loss of ignition, *CEC* cation exchange capacity, *SSA* specific surface area

[a] From (Pruett and Webb 1993)

[b] From (Mermut and Cano 2001)

[c] From (Bachmaf et al. 2008)

[d] From (Borden and Giese 2001)

[e] From (Meier and Kahr 1999)

[f] From (Dogan et al. 2006)

[g] From (Van Olphen and Fripiat 1997)

[h] From (Kowal-Fouchard et al. 2004)

filters, Membrex, Germany) and immediately analyzed by voltammetry for uranium and by ion chromatography (850 Professional IC, Methrohm, Switzerland) for Na^+, Ca^{2+}, and Mg^{2+}. Total Fe and Si^{4+} were determined by photometry (Hach, USA). For XRD characterizations, the residual solids were dried in an oven at temperature below 45°C for 1 month and crushed with a mortar and pestle to pass a 40 μm sieve. The percentage of sorbed uranium was calculated from the difference between the initial and final uranium concentration using the following Eq. (1):

$$\text{Sorption (\%)} = \left(\frac{C_i - C_f}{C_i}\right) \times 100, \qquad (1)$$

where C_i and C_f are the uranium concentrations in the initial and final solutions, respectively.

Blank experiments carried out without a mineral sorbing phase indicated substantial uptake of uranium on glass container walls, particularly in the pH range from 4 to 9 and at low uranium concentration. Therefore, all tools used in the experiments (e.g., vessels, centrifugation tubes, magnetic stirrer) were made of PTFE, which exhibited no reaction with uranium solution (<1% uptake on container walls for all pH). Supplementary experiments were conducted to estimate the influence of filtration on results. The supernatants were analyzed for uranium prior and after filtration and it was shown that cellulose acetate filters have no effect on the results.

Results and discussion

Uranium aqueous speciation

Uranium aqueous speciation were computed for the solution with a total uranium of 100 μg L^{-1} in a background electrolyte of 0.01 M NaCl equilibrated with atmosphere (i.e., partial pressure of $10^{-3.5}$ hPa for P_{CO_2}). The distribution of aqueous uranyl species was calculated with the geochemical code PHREEQC-2 (Parkhurst and Appelo 1999) with Nuclear Energy Agency (NEA 2007) thermodynamic database. Uranium speciation are presented in Fig. 1. Free uranyl ion UO_2^{2+} is the dominant species in the acidic pH range up to 5. With increasing pH, uranyl ion becomes more hydrolyzed and forms hydrolyzed uranyl species such as UO_2OH^+. In the equilibrium with atmospheric levels of CO_2, the most predominant aqueous uranium species under neutral and alkaline conditions are uranyl-carbonate-complexes ($(UO_2)_2CO_3(OH)_3^-$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$).

Kinetic rates of sorption

The aim of kinetic experiments was to examine the time required for uranium sorption equilibration. The results for sorption of uranium on clay minerals at constant pH of 4, 6, and 8 are shown in Fig. 2. The results for other pH were similar and are not shown here. Only the results for KGa-2 are presented, because the other kaolinite showed a very similar behavior. The general observation in Fig. 2 indicated that under neutral conditions both smectites and kaolinites exhibited a classic biphasic sorption of uranium which is characterized by an initial rapid uptake over the first 30 min followed by a slower increase in the uranium sorption over the reminder of the experiments. In contrast, under acidic and alkaline conditions, smectites demonstrated an initially fast uranium uptake followed by a slower decrease in the uranium sorption. The much faster sorption for SWy-2 than other smectites is due to the high content of iron, which can rapidly interact with uranium forming inner-sphere complexes. The second slower step of sorption is due to interparticle and intraparticles diffusions in pores. At pH 6 and 8, the sorption curve of KGa-2 reaches a maximum after 30 min. Then, it appears stable over 24 h, whereas 5 h were required to reach the sorption equilibrium at pH 4. This tendency suggests the gradual saturation of the surface sites at increasing experimental time: at neutral conditions, uranium is more effectively bound and thus correspondingly retained more rapidly. Comparison between kinetic sorption data for all smectites observed at pH 8 reveals that sharp decrease in uranium sorption occurred after 30 min from the beginning of the sorption experiments. This can be explained by the formation of uranyl-carbonate complexes, which are weakly binding to the surface of smectites. Yet, this phenomenon was not seen for uranium sorption on kaolinites, which can be attributed to the presence of anatase as impurity phase. The results clearly show that data taken from routinely done titration experiments with only 10 or 15 min

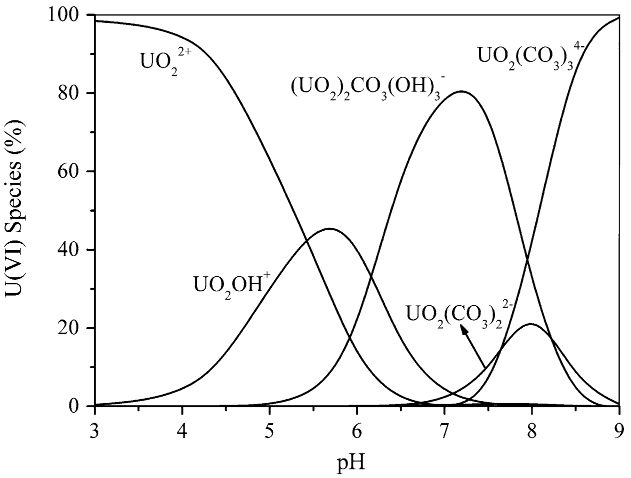

Fig. 1 Uranium speciation in 0.01 M NaCl, ΣU = 100 μg L^{-1}, $P_{CO_2} = 10^{-3.5}$ hPa, 25°C, calculated with the geochemical code PHREEQC using NEA_2007 database

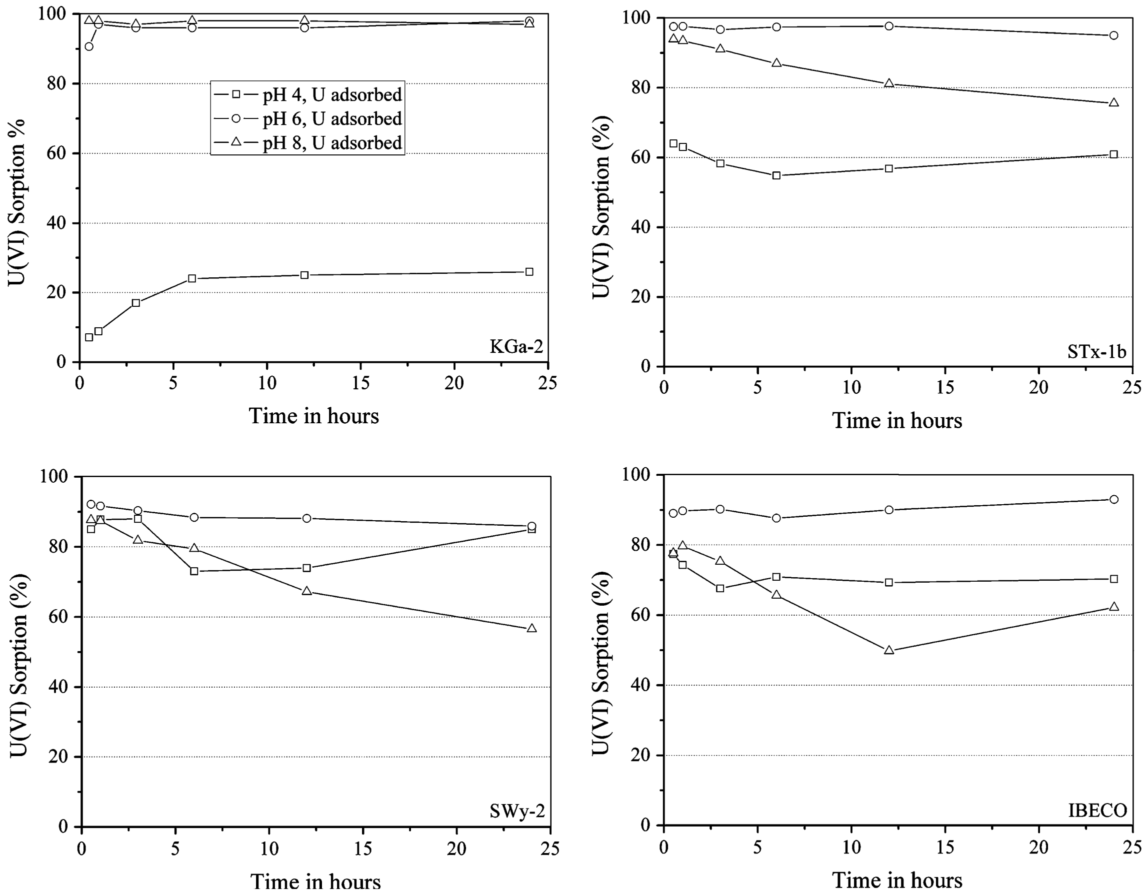

Fig. 2 Kinetic sorption of uranium onto kaolinite (KGa-2), montmorillonite (SWy-2), montmorillonite (STx-1b), and natural bentonite (IBECO). Sorption experimental conditions: $\Sigma U_0 = 100\ \mu g\ L^{-1}$, $I = 0.01$ M, suspension density = $1.66\ g\ L^{-1}$, $Pco_2 = 10^{-3.5}$ *bar*, 25°C, reaction time = 24 h

equilibrium time might be biased. However, even 24 h was observed as under estimating time for equilibrium in all cases as well.

Effect of pH and Na^+ concentration on U(VI) sorption

The effect of pH and the Na^+ concentration on the uranium sorption behavior onto the selected clay minerals is illustrated in Fig. 3. General similarities between the two kaolinites (KGa-1b and KGa-2) include lower uranium sorption at pH 4 and much greater uranium uptake than other three clay minerals in the pH range 5–9. Minor ionic strength dependency was exhibited for kaolinites at pH above 6. Conversely, the sorption of uranyl by smectites (IBECO bentonite, Na-montmorillonite, and Ca-montmorillonite) varied with pH and ionic strength. Sorption was most dependent on the ionic strength at low pH. The high sorption capability of SWy-2 observed at pH 4 is resulted from the high Na^+ content in its structure. This can suppress the competition between uranyl ions and Na^+ electrolyte and allow uranium species to bind to the surface sites of SWy-2. By comparison, competitive effect of sodium with uranium species can minimize the sorption of uranium onto STx-1b and IBECO bentonite at pH 4. This assumption is supported by (Suter et al. 2008), who demonstrated that sodium can form an inner sphere complex on the surface of smectites. However, for the pH range from 5 to 9, differences between uranium sorption on all clay minerals due to the variations in ionic strength were typically less than 15%. These observations did agree well with those reported by (Hayes et al. 1988) and (McBride 1997). They found that ions that form outer-sphere surface complexes exhibit reducing sorption with increasing solution ionic strength, while ions that form inner-sphere surface complexes demonstrate minor ionic strength dependence or show increasing sorption with increasing solution ionic strength. Relating to the ionic strength dependency, there are general similarities between our results and those reported by (Manning and Goldberg 1997) who found an increase of As(III) sorption on KGa-1b and SWy-1 with

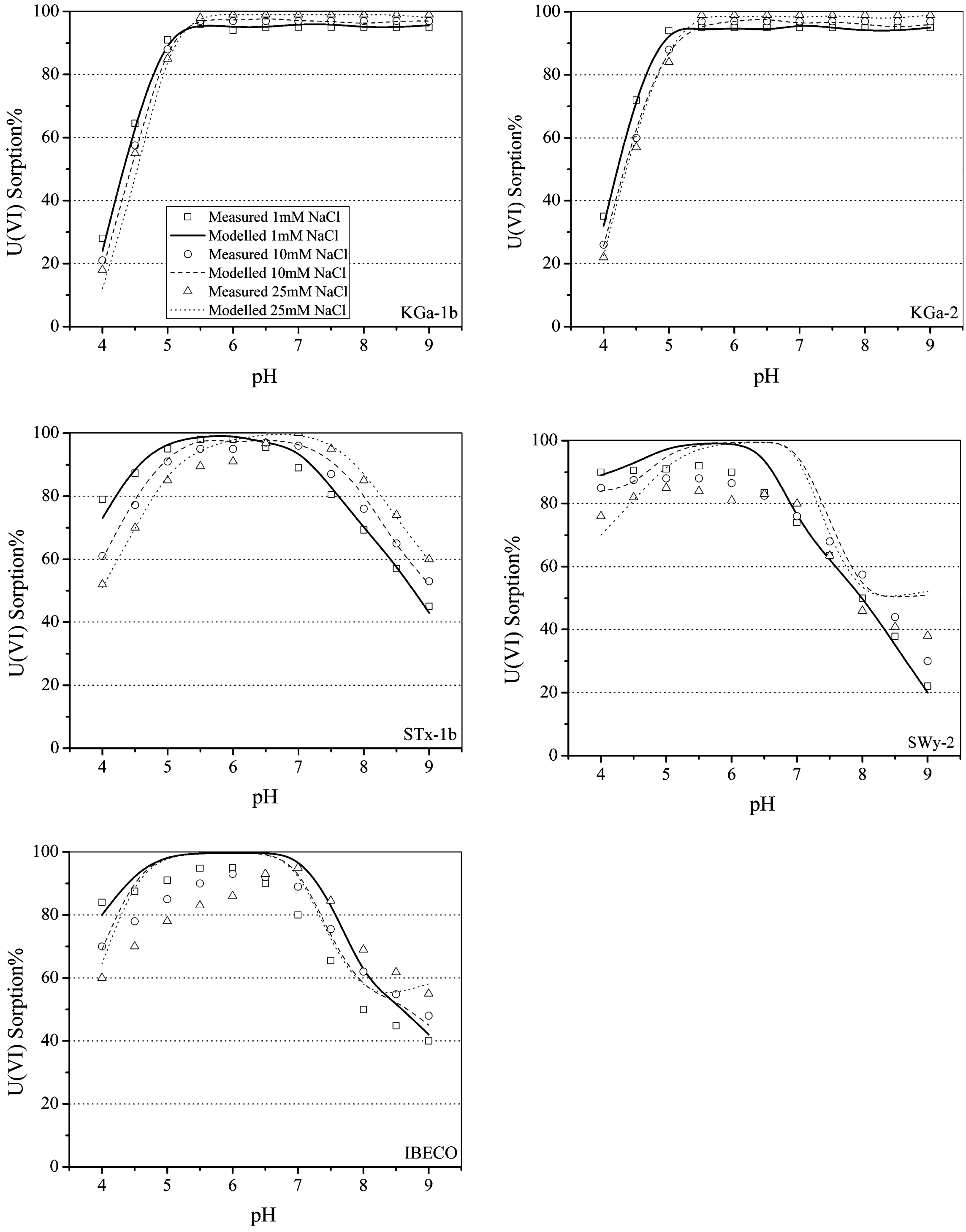

Fig. 3 Comparison of uraniumsorption data on kaolinite (KGa-1b), kaolinite (KGa-2), montmorillonite (STx-1b), montmorillonite (SWy-2), and natural bentonite (IBECO) and the surface complexation model (SCM). Experimental conditions: $\Sigma U = 100\ \mu g\ L^{-1}$, suspension density = $1.66\ g\ L^{-1}$, $Pco_2 = 10^{-3.5}$ hPa, 25°C, $I = 0.001$, 0.01, and 0.025 M, reaction time = 24 h. *Solid lines*, *dash lines* and *dot lines* represent modeled data for 1, 10 and 25 mL NaCl, respectively. *Open square*, *open circles* and *open triangle* represent measured data for 1, 10, and 25 mL NaCl, respectively

decreasing sodium chloride concentration at low pH, and increasing arsenic sorption with increasing sodium concentration at high pH.

Indeed, kaolinic minerals such as KGa-1b and KGa-2 have Si/Al ratios of 1, whereas smectites, such as IBECO bentonite, SWy-2 and STx-1b have Si/Al ratios of 2. Based on the greater activity of aluminol sites toward uranium than silanol sites (Borovec 1981; Kohler et al. 1992), which are major surface components of phyllosilicates, it would be expected that kaolinites, that contain exposed sheets of Al octahedral, would result in greater uranium uptake by kaolinic minerals than smectites.

With pH between 6.0 and 9.0, aqueous uranium species are present as uranyl carbonate, and uranyl carbonate hydroxide (Fig. 1). In addition, maximum sorption of carbonate was attained at pH 5.5 (Zachara et al. 1987). Hence, the distinct reduced uranium sorption on smectites at higher pH is related either to the low affinity of uranium carbonate complexes to the surface sites of clay minerals or to competition between carbonate ions and uranium species. On contrary, no decrease in uranium sorption on kaolinite (KGa-1b and KGa-2) was observed when uranyl-carbonate complexes are predominant in the solution. This behavior could suggest that uranyl-carbonate species have high affinity toward anatase present as impurity phase in kaolinites.

Surface complexation modeling

A multisite layer surface complexation model was developed by Zachara and Mckinley (1993) to describe uranium sorption data by smectites. Their model is composed of pH independent exchange (X^-) sites and hydroxylated edge sites for SiOH and AlOH. They assumed that at low pH and low Na^+ concentration, adsorption by fixed-charge site is predominant. At high pH and high Na^+ concentration, the binding to the AlOH and SiOH edge sites caused the sorption. On contrary to Zachara and Mckinley, we suppose that sorption of uranium on the selected smectites preferentially occur to the edge sites of aluminol and silanol, even under acidic conditions. Our assumption is supported by the recent spectroscopy study of (Chisholm-Brause et al. 2004), who confirmed that reactivity of metal-oxide like edge sites in clay minerals are highly responsible for uranium sorption over a wide range of pH and electrolyte concentration. This assumption is also based on the relatively high Na^+ electrolyte concentration (0.01 and 0.025 M) in comparison to very low uranium concentration in the solution. This can prevent the exchange between uranyl ions and cations present in the basal plane of smectites. Furthermore, our suggestions are supported by the results of X-ray characterizations, which exhibited indistinguishable patterns for the clay minerals before and after uranium treatment. In addition, dissolution experiments performed clearly showed that similar amounts of Na^+, Ca^{2+}, and Mg^{2+} cations were released from each clay mineral at all pH values (data not shown). A comparison between pH for samples collected at the beginning and at the end of sorption experiments showed a slight variation (<0.5 unit) indicating only insignificant cation exchange reactions.

Earlier modeling attempts for uranium sorption onto kaolinite have involved various assumptions. The attempt of (Kohler et al. 1992) postulated that actinide binding on kaolinite only occupies the edge surface sites, which were modeled as aluminol sites. Their hypothesis was based on the results of parallel experiments with gibbsite containing only AlOH sites and quartz (only SiOH sites). This experiment yielded that sorption on quartz was much weaker. The work of (Borovec 1981) also demonstrated very little affinity of U for Si-oxide surfaces. The supposition of (Turner and Sassman 1996) exhibited that reactive kaolinite surface comprised stoichiometric proportion of silanol (SiOH) and aluminol (AlOH).

In our model, uranium sorption onto Georgia kaolinites is based on the sorption on both titanol (TiOH) and aluminol sites (AlOH). The approach was adapted from (Payne et al. 2004). Their assumptions were established upon the transmission electron microscopy equipped with energy dispersive X-ray spectroscopy (TEM/EDS) analyses and the main finding that uranium was preferentially bound to anatase present as impurity phase in kaolinite.

The equilibrium constants for acid–base surface reactions of aluminol (Eqs. 1 and 2 in Table 2) are taken from (Zachara and Mckinley, 1993), while the constants for acid–base surface reactions of silanol (Eqs. 6 and 7 in Table 2) were derived from (Mckinley et al. 1993). The non-linear least squares parameter estimation program PEST 11.8 (Doherty 2006) in conjunction with PHREEQC (Parkhurst and Appelo 1999) was used to determine the equilibrium constants for the other surface reactions given in Table 2. PEST has the advantage over FITEQL (Westall 1985), that activity coefficients can be calculated according to either extended Wateq Debye-Hückel or a SIT (specific ion interaction theory) and provides users with statistical information on the uncertainty of the estimate. Sodium sorption was also incorporated into the model (Eqs. 4, 11, 16, and 22 in Table 2) since sodium was proven to sorb onto clay minerals (Suter et al. 2008) and was used by several authors (Turner et al. 1996; Zachara and Mckinley 1993) to model uranium sorption under a broad range of ionic strength. Results of the batch experiments and the multisite surface complexation model are plotted in Fig. 3.

The agreement between the modeled-calculated and experimentally measured values was quantified by the root mean square error (RMSE)

$$\mathrm{RMSE} = \left[\frac{1}{n_\mathrm{d} - n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{d}} (\%\mathrm{Re}m - \%\mathrm{Re}\hat{m})^2\right]^{1/2}$$

where n_d is the number of data points, n_p is the number of adjustable parameters, i is an index, $\%\mathrm{Re}m$ is the

Table 2 Surface reactions and parameters used in the model calculations. If not indicated by Zachara and Mckinley (1993) or Mckinley et al. (1993) data were calculated with PEST and PHREEQC

	Surface reactions on smectites	Log k		
		SWy-2	STx-1	IBECO
(1)	$\mathrm{Edg\_alOH + H^+ = Edg\_alOH_2^+}$	12.30[a]	12.30[a]	12.30[a]
(2)	$\mathrm{Edg\_alOH = Edg\_alO^- + H^+}$	−13.16[a]	−13.16[a]	−13.16[a]
(3)	$\mathrm{Edg\_alOH + UO_2^{2+} = Edg\_alOUO_2^+ + H^+}$	7.51	6.77	8.58
(4)	$\mathrm{Edg\_alOH + Na^+ = Edg\_alONa + H^+}$	15.0	−12.75	−15.0
(5)	$\mathrm{Edg\_alOH + 2UO_2^{2+} + CO_3^{2-} + 3H_2O = Edg\_alO(UO_2)_2CO_3(OH)_3^{2-} + 4H^+}$	0.99	1.0	1.0
(6)	$\mathrm{Edg\_siOH + H^+ = Edg\_siOH_2^+}$	−0.95[b]	−0.95[b]	−0.95[b]
(7)	$\mathrm{Edg\_siOH = Edg\_siO^- + H^+}$	−6.95[b]	−6.95[b]	−6.95[b]
(8)	$\mathrm{Edg\_siOH + UO_2^{2+} = Edg\_siOUO_2^+ + H^+}$	4.06	3.0	2.52
(9)	$\mathrm{Edg\_siOH + UO_2OH^+ = Edg\_siOUO_2OH + H^+}$	1.0	0.94	1.0
(10)	$\mathrm{Edg\_siOH + UO_2(OH)_3^- = Edg\_siOHUO_2(OH)_3^-}$	6.90	0.1	0.04
(11)	$\mathrm{Edg\_siOH + Na^+ = Edg\_siONa + H^+}$	−2.71	−4.45	−3.04
(12)	$\mathrm{Edg\_siOH + UO_2^{2+} + 3CO_3^{2-} = Edg\_siOUO_2(CO_3)_3^{5-} + H^+}$	6.65	5.19	2.76

	Surface reactions on kaolinite	KGa-1b	KGa-2
(13)	$\mathrm{S\_alOH + H^+ = S\_alOH_2^+}$	13.33	8.83
(14)	$\mathrm{S\_alOH = S\_alO^- + H^+}$	−4.72	−9.75
(15)	$\mathrm{S\_alOH + UO_2^{2+} + H_2O = S\_alOUO_2OH + 2H^+}$	6.0	1.29
(16)	$\mathrm{S\_alOH + Na^+ = S\_alONa + H^+}$	−4.58	−15.0
(17)	$\mathrm{S\_tiOH + H^+ = S\_tiOH_2^+}$	6.89	4.96
(18)	$\mathrm{S\_tiOH = S\_tiO^- + H^+}$	−1.07	−9.81
(19)	$\mathrm{S\_tiOH + UO_2^{2+} = S\_tiOUO_2^+ + H^+}$	4.66	2.98
(20)	$\mathrm{S\_tiOH + UO_2OH^+ = S\_tiOUO_2OH + H^+}$	6.3	2.91
(21)	$\mathrm{S\_tiOH + UO_2(OH)_3^- = S\_tiOHUO_2(OH)_3^-}$	1.23	10
(22)	$\mathrm{S\_tiOH + Na^+ = S\_tiONa + H^+}$	1.0	−7.84
(23)	$\mathrm{S\_tiOH + UO_2^{2+} + 3CO_3^{2-} = S\_tiOUO_2(CO_3)_3^{5-} + H^+}$	9.57	10
(24)	$\mathrm{S\_tiOH + 2UO_2^{2+} + CO_3^{2-} + 3H_2O = S\_tiO(UO_2)_2CO_3(OH)_3^{2-} + 4H^+}$	0.25	0.9

Surface site density in mol of site × 10^{-6}	KGa-1b	KGa-2	SWy-2	STx-1b	IBECO
SiOH			99.85	99.9	99.9
AlOH	0.719	0.7	92.12	92.135	92.14
TiOH	0.65	0.641			

Edg_alOH aluminol surface at edge sites, *Edg_siOH* silanol surface at edge sites, *S_alOH* aluminol site surface, *S_tiOH* titanol site surface

[a] From (Zachara and Mckinley 1993)

[b] From (Mckinley et al. 1993)

percentage of uranium measured removal, $\%\mathrm{Re}\hat{m}$ is the percentage of uranium predicted removal. The RMSE is an estimate of the standard deviation between the predicted and the measured values expressed in dimensionless form as a fraction on the initial

The modeled data presented in Fig. 3 indicate that the model predicts the major trends of sorption of uranium with respect to pH and NaCl concentrations for the five clay minerals, and in particular for Georgia kaolinite and STx-1b montmorillonite. On the contrary an over predication of sorption can be stated on SWy-2 and IBECO for a pH range 5–7. The overestimation is probably due to the presence of impurities phases such as quartz, feldspar, plagioclase, and orthoclase, which have been not taken into account in our approach so far. The root mean square error (RMSE) obtained was 2.8, 2.3, 3.4, 12.1, and 12.1 for KGa-1b, KGa-2, STx-1b, SWy-2, and IBECO, respectively.

All fitted constants are automatically corrected to zero ionic strength with respect to either ion dissociation theory (e.g. Davies or Wateq-Debye-Hückel equation) or SIT.

Conclusions

Experimental and modeled data derived in this study indicate that sorption experiments must be performed at low uranium concentration to avoid precipitation of amorphous uranium-hydroxides. Furthermore, PTFE containers are found to be appropriate materials comparing with glass ware which appeared significant uranium sorption at higher pH.

Kinetic experiments clearly showed that the common 10 or 15 min are in many cases by far not sufficient to reach sorption equilibrium, therefore, a period of 24 h was selected as contact time to conduct the sorption experiments.

Although smectite has higher cation exchange capacity than kaolinite, both kaolinite minerals showed much greater uranium sorption than smectites in the pH range (5–9). This can be considering as an obvious evidence that surface complexation was the dominant mechanism for uranium sorption under our experimental conditions. The high uranium sorption capability for kaolinite is because it contains more exposed aluminol surface site, which have greater activity toward uranium than silanol sites.

Uptake of uranium on montmorillonites demonstrated a distinct dependency on sodium concentrations because of the effective competition between uranyl and sodium ions, whereas less significant differences in sorption were found for kaolinite. The presence of anatase as impurity in kaolinite enhanced the binding of uranyl-carbonate complexes with surface sites.

A sufficient matching between the experimental results and the modeled data was obtained using a multisite surface complexation model without assuming exchange. This model is based on the binding of the most dominant uranium species to aluminol and silanol edge sites of montmorillonite, respectively, to aluminol and titanol surface sites of kaolinite. The parameter estimation code PEST together with PHREEQC is an extremely powerful tool to estimate the equilibrium constants estimated in this work. The good agreement between measured and predicted data implies that conceptual models based on SCM approach, such as one the developed here, could be useful in extrapolating radionuclide sorption behavior over a range of geochemical conditions based on the model parameters derived from a limited set of laboratory data.

Acknowledgments We would like to thank Dr. R Kleeberg from institute of Mineralogy for his kind assistance with XRD analyses. The scientific and technical assistance from Dr. Sascha Kummer, Hajo Peter, Sreejesh. M.C, Stephan Kaufhold, Wondem Gezahegne, Michael Sekul, and Tino Beyer are gratefully acknowledged.

References

Arda D, Hizal J, Apak R (2006) Surface complexation modelling of uranyl adsorption onto kaolinite based clay minerals using FITEQL 3.2. Radiochim Acta 94(12):835–844

Bachmaf S, Planer-Friedrich B, Merkel BJ (2008) Effect of sulfate, carbonate, and phosphate on the uranium(VI) sorption behavior onto bentonite. Radiochim Acta 96(6):359–366

Barisic D, Lulic S, Miletic P (1992) Radium and uranium in phosphate fertilizers and their impact on the radioactivity of waters. Water Res 26(5):607–611

Bernhard G (2005) Speciation of uranium in environmental relevant compartments. Landbauforschung Volkenrode 55:139–148

BFR (2005) Uran in Mineralwasser: Bei Erwachsenen geringe Mengen tolerierbar, Wasser für Säuglingsnahrung sollte uranfrei sein. Bundesinstitut für Risikobewertung, Stellungnahme Nr. 024/2005, pp 1–6

Borden D, Giese RF (2001) Baseline studies of the clay minerals society source clays: cation exchange capacity measurements by the ammonia-electrode method. Clays Clay Miner 49(5): 444–445

Borovec Z (1981) The adsorption of uranyl species by fine clay. Chem Geol 32(1–2):45–58

Catalano JG, Brown GE (2005) Uranyl adsorption onto montmorillonite: evaluation of binding sites and carbonate complexation. Geochim Cosmochim Acta 69(12):2995–3005

Chipera SJ, Bish DL (2001) Baseline studies of the clay minerals society source clays: powder X-ray diffraction analyses. Clays Clay Miner 49(5):398–409

Chisholm-Brause CJ, Berg JM, Little KM, Matzner RA, Morris DE (2004) Uranyl sorption by smectites: spectroscopic assessment of thermodynamic modeling. J Colloid Interface Sci 277(2):366–382

Dogan AU, Dogan M, Onal M, Sarikaya Y, Aburub A, Wurster DE (2006) Baseline studies of the clay minerals society source clays: Specific surface area by the Brunauer Emmett Teller (BET) method. Clays Clay Miner 54(1):62–66

Doherty J (2006) Model-independent parameter estimation, user manual, 5th edn. Watermark Numerical Computing, Brisbane, pp 1–336

Fletcher P, Sposito G (1989) The chemical modeling of clay electrolyte interactions for montmorillonite. Clay Miner 24(2):375–391

Grenthe I, Fuger J, Konings R, Lemire RJ, Muller AB, Wanner J (2007) The chemical thermodynamincs of uranium Elsevier, New York

Hayes KF, Papelis C, Leckie JO (1988) Modeling ionic-strength effects on anion adsorption at hydrous oxide solution interfaces. J Colloid Interface Sci 125(2):717–726

Hickox WH and Denton JE (2001) Public health goal for uranium in drinking water. Office of Environmental Health Hazard Assessment California Environmental Protection Agency:30

Hyun SP, Cho YH, Hahn PS, Kim SJ (2001) Sorption mechanism of U(VI) on a reference montmorillonite: binding to the internal and external surfaces. J Radioanal Nucl Chem 250(1):55–62

Kohler M, Wieland E, Leckie JO (1992) Metal-ligand-surface interactions during sorption of uranyl and neptunyl on oxides and silicates. In: Kharaka YK, Maest AS (eds) Water–rock interaction (VII). Balkema, Rotterdam, pp 51–54

Kowal-Fouchard A, Drot R, Simoni E, Ehrhardt JJ (2004) Use of spectroscopic techniques for uranium (VI)/montmorillonite interaction modeling. Environ Sci Technol 38(5):1399–1407

Kurttio P, Auvinen A, Salonen L, Saha H, Pekkanen J, Makelainen I, Vaisanen SB, Penttila IM, Komulainen H (2002) Renal effects of uranium in drinking water. Environ Health Perspect 110(4): 337–342

Lajudie A, Raynal J, Petit JC and Toulhoat P (1995) Clay-based materials for engineered barriers—a review. Scientific Basis for Nuclear Waste Management Xviii, Pts 1 and 2 Vol 353. pp 221–230, 1433

Langmuir D (1997) Actinides and their daughter and fission products. In: Aqueous environmental geochemistry. Prentice-Hall, Inc., Upper Saddle River, NJ, pp 487–547

Lin Z, Puls RW (2000) Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. Environ Geol 39(7):753–759

Manning BA, Goldberg S (1997) Adsorption and stability of arsenic(III) at the clay mineral-water interface. Environ Sci Technol 31(7):2005–2011

McBride MB (1997) A critique of diffuse double layer models applied to colloid and surface chemistry. Clays Clay Miner 45(4):598–608

Mckinley JP, Zachara JM and Smith SC (1993) An experimental and modeling investigation of Uo2(2+) interaction with smectite clays. vol 205. Abstracts of Papers of the American Chemical Society, USA, pp 118–129

McKinley JP, Zachara JM, Smith SC, Turner GD (1995) The influence of uranyl hydrolysis and multiple site-binding reactions on adsorption of U(VI) to montmorillonite. Clays Clay Miner 43(5):586–598

Meier LP, Kahr G (1999) Determination of the cation exchange capacity (CEC) of clay minerals using the complexes of copper(II) ion with triethylenetetramine and tetraethylenepentamine. Clays Clay Miner 47(3):386–388

Mermut AR, Cano AF (2001) Baseline studies of the clay minerals society source clays: chemical analyses of major elements. Clays Clay Miner 49(5):381–386

Morrison SJ, Cahn LS (1991) Mineralogical residence of alpha-emitting contamination and implications for mobilization from uranium mill tailings. J Contam Hydrol 8(1):1–21

Neall FB, Baertschi P, Mckinley IG, Smith PA, Sumerling T and Umeki H (1995) Comparison of the Concepts and Assumptions in 5 Recent Hlw/Spent Fuel Performance Assessments. Scientific Basis for Nuclear Waste Management Xviii, Pts 1 and 2, vol 353. pp 503–510, 1433

Olguin MT, SolacheRios M, Acosta D, Bosch P, Bulbulian S (1997) UO22+ sorption on bentonite. J Radioanal Nucl Chem 218(1):65–69

Pabalan RT, Bertetti FP, Prikryl JD and Turner DR (1996) Uranium(VI) sorption onto selected mineral surfaces: key geochemical parameters, vol 211. Abstracts of Papers of the American Chemical Society, USA, pp 55–67

Parkhurst DL and Appelo CAJ (1999) User's Guide to PHREEQC (version 2) A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculation USGS, Water Resources Investigation Report, pp 99–4259

Payne TE (1999) Uranium (VI) interactions with mineral surfaces: controlling factors and surface complexation modeling. PhD thesis, New South Wales University, Australia

Payne TE, Davis JA, Lumpkin GR, Chisari R, Waite TD (2004) Surface complexation model of uranyl sorption on Georgia kaolinite. Appl Clay Sci 26(1–4):151–162

Prikryl JD, Pabalan RT, Turner DR and Leslie BW (1994) Uranium sorption on alpha-alumina: effects of pH and surface-area/solution-volume ratio. Chemistry and migration behaviour of actinides and fission products in the geosphere, pp 295–300, 841

Prikryl JD, Jain A, Turner DR, Pabalan RT (2001) Uranium(VI) sorption behavior on silicate mineral mixtures. J Contam Hydrol 47(2–4):241–253

Pruett RJ, Webb HL (1993) Sampling and analysis of Kga-1B well-crystallized kaolin source clay. Clays Clay Miner 41(4):514–519

Raymond-Whish S, Mayer LP, O'Neal T, Martinez A, Sellers MA, Christian PJ, Marion SL, Begay C, Propper CR, Hoyer PB, Dyer CA (2007) Drinking water with uranium below the US EPA water standard causes estrogen receptor-dependent responses in female mice. Environ Health Perspect 115(12):1711–1716

Riley RG, Zachara JM and Wobber FJ (1992) Chemical contaminants on DOE lands and selection of contaminant mixtures for subsurface science research DOE/ER-0547T US Department of Energy

Suter JL, Boek ES, Sprik M (2008) Adsorption of a sodium ion on a smectite clay from constrained ab initio molecular dynamics simulations. J Phys Chem C 112(48):18832–18839

Turner DR, Sassman SA (1996) Approaches to sorption modeling for high-level waste performance assessment. J Contam Hydrol 21(1–4):311–332

Turner GD, Zachara JM, McKinley JP, Smith SC (1996) Surface-charge properties and UO22+ adsorption of a subsurface smectite. Geochim Cosmochim Acta 60(18):3399–3414

Ufer K, Roth G, Kleeberg R, Stanjek H, Dohrmann R, Bergmann J (2004) Description of X-ray powder pattern of turbostratically disordered layer structures with a Rietveld compatible approach. Zeitschrift Fur Kristallographie 219(9):519–527

Van Olphen H, Fripiat JJ (1997) Data handbook for clay materials and other non-metallic minerals. Pergamon Press, New York

Westall JC (1985) A program for the determination of chemical equilibrium constants from experimental data, user's guide, version 20 Chem Dept. Oregon State University, Corvallis

WHO (2004) Guidelines for drinking-water quality, 3rd edn. World Health Organization, Geneva

Zachara JM, Mckinley JP (1993) Influence of hydrolysis on the sorption of metal-cations by smectites—importance of edge coordination reactions. Aquat Sci 55(4):250–261

Zachara JM, Girvin DC, Schmidt RL, Resch CT (1987) Chromate adsorption on amorphous iron oxyhydroxide in the presence of major groundwater ions. Environ Sci Technol 21(6):589–594

Zielinski RA, Orem WH, Simmons KR, Bohlen PJ (2006) Fertilizer-derived uranium and sulfur in rangeland soil and runoff: a case study in central Florida. Water Air Soil Pollut 176(1–4):163–183