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REVIEW PAPER

Interactions of aqueous U(VI) with soil minerals in slightly alkaline natural systems

Nikolla P. Qafoku · Jonathan P. Icenhower

Abstract Uranium (U) is a common contaminant at numerous surface and subsurface sites in proximity to areas involved with weapons manufacturing and atomic energy related activities. This paper covers some important aspects of the aqueous hexavalent uranium [U(VI)] interactions with soil minerals that are present in contaminated soils and sediments. The retention of U via interactions with soil minerals has significant consequences for the prediction of its short- and long-term behavior in soils and geological systems. Studies of the nature and type of these interactions have provided the necessary evidence for assessing the geochemical behavior of U in natural systems under different physical, biogeochemical, hydrological, and reducing or oxidizing conditions. Over the last 20 years, aqueous U(VI): soil mineral interactions have been studied by geochemists, soil chemists, clay and soil mineralogists, and the progress in some areas is remarkable. Although a mechanistic description and understanding of the complex interactions involving U and soil minerals in natural systems is currently difficult, results from carefully designed and executed field and laboratory experiments with these materials have improved our understanding of the heterogeneous system's behavior and U contaminant mobility and transport. There are, however, areas that warrant further exploration and study. Numerous research publications were reviewed in this paper to present recent important findings to reveal the current level of the understanding of the U(VI) interactions with soil minerals, and to provide ideas for future needs and research directions.

Keywords Uranium · U(VI) · U(IV) · Adsorption · Desorption · Redox reactions · Soils · Sediments · Heterogeneous natural media · Soil minerals · Fe oxides · Phyllosilicates · Calcite

1 Introduction

1.1 The extent of U contamination

Mainly because of its essential role in the production of nuclear weapons, uranium (U) is a common contaminant at numerous sites throughout the world. For example, U is a common contaminant at sites in the United States of America (USA), where production of nuclear weapons and handling of U in various forms has occurred (Riley et al. 1992). Anthropologic sources of U contamination belong to three categories: (i) U from weapons production; (ii) U from nuclear energy activities; and (iii) U from scientific and other uses (Todorov and Ilieva 2006). Elevated

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concentrations of U are also found in some agricultural drainage waters generally associated with P fertilizers (Duff and Amrhein 1996) and, recently, it is observed that there is near-surface contamination of depleted U at several USA Army testing grounds and battle fields.

Elevated concentrations of this radionuclide heavy metal are present at a variety of locations around the world, seriously threatening human health. Evaluating societal risks posed by U contamination from waste management facilities, mining sites, and heavy industry requires knowledge about U transport in groundwater, typically the most significant pathway of exposure to humans (Bargar et al. 1999).

The movement of U through soil profiles may be retarded because of interactions with the soil minerals, which affect significantly U short- and long-term behavior in soils and geological systems. Studies conducted over the last few years have provided evidence for such interactions and U geochemical behavior in natural systems under different physical, biogeochemical, hydrological, and reducing or oxidizing conditions.

This review covers important aspects of the aqueous hexavalent U [U(VI)] interactions with the soil minerals in natural systems under slightly alkaline conditions. Our attention is restricted to U(VI) fate and mobility because in its reduced form U(IV) is far less mobile. We also focus on the mobility of U(VI) in slightly alkaline waters because, under typical geochemical conditions, the mobility of U(VI) is enhanced by the relatively high carbonate concentrations that characterize many alkaline systems. To this end, many research publications published in the last few years are reviewed in this paper with the objectives of: (i) summarizing important findings in the literature; (ii) revealing the current level of knowledge and understanding of the U(VI) interactions with soil minerals; and (iii) providing ideas for future needs and directions in this area of research.

Even though this is a review of publications covering different aspects of U interaction with soil minerals and is germane to many sites worldwide, the discussion focuses on recent findings from research conducted at different contaminated sites in the USA, where there is an abundance of information. In addition, important aspects of the U interaction with organic matter, biologically-mediated reactions and

reduction of U(VI) to U(IV) and the potential for re-oxidation back to U(VI), and modeling techniques used to fit experimental data and predict U behavior has been effectively described in earlier publications and are not within the scope of this review.

1.2 Soil mineralogy of some contaminated sites

Aqueous U(VI) may interact with many soil minerals that are typically present in contaminated surface and subsurface natural media. A key to predicting U(VI) remobilization and future risk associated with contaminated plume spreading is an understanding of aqueous U(VI): solid phase interactions as a control on the migration potential of sorbed U(VI) in retreating and advancing regions of the contaminated plumes. Mineralogical characteristics of some of the most contaminated and problematic sites in the USA, where a great deal of time and effort have been spent in recent years to understand complex U(VI) behavior in heterogeneous natural systems, are presented below.

1.2.1 Hanford 200 Area, Washington

Neutron bombardment of uranium targets yielded a number of activation products, in addition to fissile ^{239}Pu. Following extraction of plutonium and uranium, the unwanted activation products were stored in large underground tanks. The tanks, earlier ones represented by single-shell and later by double-shell varieties, were grouped together in "tank farms". The waste tank farms are distributed between the 200 West and East Areas at Hanford. The 200 Areas reside on the "200-Area plateau" where depth to groundwater ranges from 200 to 300 feet. Single-shell tanks that have leaked or are suspected to have leaked are present in both Areas; so far, the double-shell tanks show no evidence of release. The 200 Areas are underlain by a sequence of suprabasaltic sediments of Pleistocene and Pliocene age (Serne et al. 2001). These sediments include four primary units: (1) course-grained glacio-fluvial gravels and sands in the Hanford formation; (2) Cold Creek upper subunit; (3) the Cold Creek lower subunit; and (4) fluvial-lacustrine gravel/sand/silt lithofacies of the Ringold formation. The Hanford formation represents about 85% of the vadose zone. The Hanford formation has a mineralogy dominated by quartz and

plagioclase feldspar with minor amounts (<15%) of biotite, potassium feldspar, smectite, chlorite and amphibole (Serne et al. 2001). The clay fraction (<2 μm) is dominated by smectite, with appreciable abundances of plagioclase, biotite, quartz, K-feldspars, and chlorite also present. The occurrence of Fe(II)-bearing minerals like biotite, chlorite and magnetite in the sediments is very important because they serve as sources of inorganic reductants, i.e., Fe(II) that is released upon mineral dissolution, or they may be involved in heterogeneous redox reactions that take place at their surfaces (magnetite). Calcite is present in generally increasing amounts with depth reaching maximum in Cold Creek lower subunit (35% by weight), making this site unique in terms of studying natural calcite: aqueous U(VI) interactions. The morphology of calcite varies with depth (Qafoku et al. 2008b). Small calcite particles, within aggregates and thin coatings (~ 10–30 μm) that partially cover single soil particles, are present in the sediment collected as 69 feet below ground surface. Most of these calcium carbonate microstructures are fine mineral particulates aggregated around larger particles. Note, however, that even when carbonate coats are thin, the effect on U(VI) mobility is strong. Because carbonate coatings cover a number of phases that would otherwise affect U(VI) sorption, such as iron oxyhydroxides and aluminous phases, U(VI) sorption is sometime typically governed by its interaction with calcite (Dong et al. 2005). In contrast, the morphology of sediment from 110 feet consists of large calcite particles (>200 μm diameter) and thick Ca carbonate coatings (~ 100–150 μm) that cover mineral phases and/or cement particles together in aggregates. The thick Ca carbonate coatings have a very fine structure as confirmed by numerous micrographs taken in this sediment (Qafoku et al. 2008b).

1.2.2 Hanford 300 Area, Washington

A groundwater U(VI) plume is present beneath the North and South Process Ponds and other trenches where substantial amounts of contaminated liquids were discharged (Lindberg and Peterson 2004). Unlike the 200 Area sediments, the plume beneath the 300 Area process ponds and their underlying sediments are subject to a more dynamic and complex flow regime because of its proximity to the Columbia River and the attendant short-term

gradient changes in response to fluctuations in the Columbia River stage (Serne et al. 2002; Lindberg and Peterson 2004; Zachara et al. 2005). The plume at the 300 Area is located approximately 100 m from the Columbia River. It underlies a 7–10 m vadose zone that was contaminated by infiltrating waste fluids of surface processing ponds and other waste process trenches nearby. The most abundant soil minerals in these sediments are quartz, feldspars and amphibole (Serne et al. 2002). The clay fraction is dominantly composed of muscovite, chlorite (ferroan clinochlore), montmorillonite (interstratified smectite, smectite–clinochlore, or smectite–vermiculite), and vermiculite (Qafoku et al. 2008a). The sediments also contain chlorite which has a strong affinity for U(VI) (Baik et al. 2004b).

1.2.3 Naturita and Rifle sites, Colorado

The former U mill tailings site is located along the San Miguel River in southwestern Colorado (Davis and Curtis 2003; and the references therein). The sediments are composed of poorly sorted, weathered and abraded rocks of different types. Soil minerals are mostly quartz with lesser amounts of detrital feldspars (microcline, perthite, sanidine, anorthoclase, plagioclase), carbonates and magnetite. The clay fraction is made up of intricate mixed layer illite/smectite clays, with chlorite as a minor phase. All soil grains have Fe-rich and Al–Si-rich coatings. Fe-rich and highly heterogeneous phases are also present as small scattered particles immersed in the clay coatings. They are composed mainly of mixed domains of hematite, goethite, and amorphous Fe oxyhydroxides. The carbonate mineral content is about 2.5% by weight (mainly calcite with trace amount of aragonite). Calcite is generally not present as cement but as individual crystals or clusters of disseminated crystals, typically between 2 and 10 μm in size.

The U Mill Tailings site in Rifle has plumes contaminated with U (Anderson et al. 2003; Yabusaki et al. 2007). X-ray diffraction analyses indicated that quartz is the dominant phase in the <2 mm fraction (Kukkadapu RK and Qafoku NP, personal communication). The clay-size fraction is dominated by phyllosilicates, such as muscovite, clinochlore, montmorillonite and kaolinite, but small amounts of albite, amphibole, magnetite, hematite and calcite are

also present. The <2-mm size fraction was also characterized by Mössbauer spectroscopy (a Fe specific technique), which clearly indicates the presence of hematite and well-crystalline magnetite, Al-substituted goethite (predominately Fe-oxide), and phyllosilicates.

1.2.4 The complexity of the soil mineral/aqueous U(VI) system

The mineralogical characteristics of these sites clearly show the wide variety of soil minerals in one specific soil system. Multiple U(VI) sorbents, e.g., Fe oxides, phyllosilicates, calcite, are present in all these natural systems in varying amounts. The behavior of natural assemblages of soil minerals, such as soils and sediments, is different from the behavior of single soil minerals; and it is even different from the behavior of an artificial mixture of pure soil minerals. In addition, the minerals in natural systems occur rarely as pure ideal phases. Usually they occur as solid solutions, mixed domains of minerals of one or more groups, as coating materials that are all derived from the breakdown of existing rocks or primary minerals, or are the end-products of specific weathering pathways and other soil forming processes that occur at a specific area.

Aqueous U(VI):solid phase interactions that occur in natural heterogeneous systems are not simple, one-step reactions but complex reactions and processes possibly coupled to parallel or sequential reactions. Adsorption and desorption reactions are often coupled with dissolution, precipitation and redox reactions. For this reason, the study of these systems necessitates collaborative efforts involving researchers from different scientific areas, such as geochemists, soil chemists, soil physicists, soil microbiologists, civil and environmental engineers, hydrologists, computer modelers, physicists, chemists, microbiologists, etc. In addition, a combination of useful techniques (such as extractions) combined with state-of-the-art techniques, such as spectroscopy, microscopy, electron and X-ray microprobes, X-ray micro-diffraction, etc., should be used to initially characterize the sediments and subsequently study different aspects of the aqueous U(VI): soil mineral interactions in natural heterogeneous systems, such as soils and sediments.

1.3 Aqueous U(VI) speciation

In groundwater, U is commonly found as U(VI), which is generally considered a mobile or semi-mobile contaminant at circumneutral (Read et al. 1993) to mildly alkaline pH conditions that typically results in subsurface migration (Serne et al. 2002). Carbonate forms stable neutral (Kalmykov and Choppin 2000; Bernhard et al. 2001) or anionic (Grenthe et al. 1992; Clark et al. 1995) aqueous complexes with U(VI) in these environments and increases the overall mobility of U (Tripathi 1983; Hsi and Langmuir 1985; Duff and Amrhein 1996; Rovira et al. 2000; Wang et al. 2004). In addition, U(VI) may sorb to micro- or nano-size soil mineral particles suspended in pore water. These U(VI) loaded small particles (colloids) may move with groundwater since under circumneutral or slightly alkaline conditions colloidal stability is favored over flocculation or coagulation, although, in some contaminated plumes, the relatively high ionic strength and prevalence of polyvalent cations may offset the stabilizing effect of pH.

Information about the formation constants for uranyl (UO_2^{2+}) aqueous species is included in the following reference (Davis and Curtis 2003) and the references therein. The most stable aqueous species are the binary species UO_2CO_3, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_3(CO_3)_6^{6-}$ and the ternary species $Ca_2UO_2(CO_3)_3$ and $CaUO_2(CO_3)_3^{2-}$. Assessment of the binding energies of the binary species indicate that the $UO_2(CO_3)_2^{2-}$ anion is more stable than the $UO_2(CO_3)_3^{4-}$ anion due to the accumulation of excess charge in the latter (de Jong et al. 2005).

The formation constants of ternary uranyl carbonate complexes such as $MUO_2(CO3)_3^{2-}$ and $M_2UO_2(CO_3)_3^{0}$ (where M denotes Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) were determined with an anion exchange method (Dong and Brooks 2006). The results indicated that the complexes of $MUO_2(CO_3)_3^{2-}$ and $M_2UO_2(CO_3)_3$ were simultaneously formed for Ca^{2+} and Ba^{2+}, while Mg^{2+} and Sr^{2+} formed only the $MUO_2(CO_3)_3^{2-}$ complex under the tested experimental conditions (i.e., metal concentrations (0.1–5 mmol/l) at pH 8.1 and a constant ionic strength (0.1 mol/l $NaNO_3$) under equilibrium with atmospheric CO_2; Dong and Brooks 2006). Based on the formation constants obtained in this study, speciation calculations indicated that at low Ca^{2+} concentrations

(e.g., <2.2 mmol/l), $CaUO_2(CO_3)_3^{2-}$ is more important than $Ca_2UO_2(CO_3)_3$ and that the fraction of $Ca_2UO_2(CO_3)_3$ increased with increasing Ca concentration (Dong and Brooks 2006).

The numbers of Na and Ca atoms bound to the uranyl triscarbonate species depended on the Ca concentration, as predicted by speciation calculations, in a set of solutions containing 50 μM U(VI) and 30 mM Na bicarbonate with various Ca concentrations (0–5 mM) at nearly neutral pH values (Kelly et al. 2007). Results from XAFS measurements confirmed the presence of the Na-UO_2-CO_3 complex in this system, and that the number of Ca and/or Na atoms coordinated to a uranyl carbonate complex determined the net charge of the aqueous complex (Kelly et al. 2007). The identity of the species may significantly affect the extent of U(VI) adsorption.

Based on the data available in the literature and that generated from experiments with Hanford sediments, a surface complexation model was developed to describe and predict U(VI) adsorption and desorption in the equilibrium sites of calcite-poor and -rich sediments where the aqueous U(VI) and solid phase interactions were fast and demonstrated no time-dependency (Qafoku et al. 2008b). The model was very sensitive to aqueous phase pH and carbonate concentration, but showed moderate sensitivity towards Ca, even though other researchers have found that sorption of U(VI) to calcium carbonate decreased with increasing aqueous Ca concentration (Savenko 2001).

In a batch experiment conducted to test the effect of mass-to-volume (M/V) ratio on U(VI) speciation and adsorption, the distribution of U(VI) aqueous species calculated with the computer code MINTEQA2 (Allison et al. 1991, 1998) varied with the M/V ratio of 10 and 1000 g l^{-1} (for example, the percentage of $UO_2(CO_3)_3^{4-}$ was 16.2% and 5.5% at M/V ratios of 10 and 1000 g l^{-1}, respectively, and other species such as $(UO_2)_2(CO_3)(OH)_3^{-}$ were also present in the aqueous phase of the latter treatment; Qafoku et al. 2008a).

In Hanford sediments relatively enriched in calcite (up to 32% calcite by weight), exposed to different electrolyte solutions with varying carbonate and Ca contents, the U(VI) aqueous speciation changed significantly with pH and carbonate concentration (Qafoku et al. 2008b). The ternary species $Ca_2UO_2(CO_3)_3$ and the binary species $UO_2(CO_3)_3^{4-}$ were respectively the dominant aqueous species at lower and higher pH and dissolved inorganic carbon concentrations. U(VI) aqueous speciation changed with the M/V ratio, and $Ca_2UO_2(CO_3)_3$ was the dominant species; interestingly, $UO_2(CO_3)_3^{4-}$ and $UO_2(CO_3)_2^{2-}$ increased in concentration with decreasing M/V ratio (Qafoku et al. 2008b). Si was also released from this sediment (concentration varied from ∼550 to 40 μmol l^{-1} at M/V ratios of 1:2 and 1:100, respectively), but this did not affect U(VI) or other element aqueous speciation and the saturation indices of relevant solid phases. In all these experiments, the aqueous phase was undersaturated with respect to all U(VI) phases included in the updated database of MINTEQA2 with current information available in the literature.

Some ideas and trends for future studies are:

(i) Investigation of the formation and stability of U(VI)-Na-carbonate species in the presence of other competing elements (such as K, Mg, Ba, Sr) in the aqueous phase;

(ii) Elucidation of the role of uranyl metal carbonate species on U(VI) sorption to different pure soil minerals and sediments. Recent findings demonstrated that U uptake by synthetic imogolite decreased with increasing $NaNO_3$ concentration in the range from 0.02 to 0.5 M (Arai et al. 2006);

(iii) To decouple and separately measure the effects of aqueous Ca and carbonate ions on U(VI) sorption extent and rate;

(iv) Quantification of how and when the aqueous species are transformed to adsorption (solid phase) species during U(VI) adsorption, and identification of the driving forces behind this transformation. Speciation of adsorbed U(VI) may be constrained by the coordination environment at the surface and solid phase U(VI) speciation could be significantly less complex than aqueous speciation (Waite et al. 1994). Results from other studies have demonstrated the uncertainty in assuming that the composition and predominance of adsorbed species can be inferred from aqueous species (Bargar et al. 1999).

2 Interaction of aqueous U(VI) with soil minerals

2.1 U(VI) sorption to soil minerals

Experiments have evaluated the U sorption to a vast array of soil mineral and organic surfaces, as well as other sorbents, such as quartz (Prikryl et al. 2001; Greathouse et al. 2002; Froideval et al. 2003; Fox et al. 2006), mackinawite (Moyes et al. 2000; Livens et al. 2004), granite (Baik et al. 2004a), hematite surfaces colonized by sulfate-reducing bacteria (Neal et al. 2004), gibbsite (Baumann et al. 2005), negatively charged cell walls of *Bacillus subtilis* (Gorman-Lewis et al. 2005), synthetic imogolite (Arai et al. 2006), amorphous silica (Sylwester et al. 2000), silica gel (Reich et al. 1998), gamma alumina (Sylwester et al. 2000), nanocrystalline titanium dioxide (Wazne et al. 2006), zero valent iron (Noubactep et al. 2005), biogenic manganese oxide (Webb et al. 2006), bone charcoal and bone meal apatite (Fuller et al. 2003), hydroxyapatite (Fuller et al. 2002), clinoptilolite (Prikryl et al. 2001), natural sediments (Kohler et al. 1996; Rosentreter et al. 1998; Waite et al. 2000; Davis 2001; Bostick et al. 2002; Davis and Curtis 2003; Curtis et al. 2004, 2006; Davis et al. 2004, 2006; Kohler et al. 2004; Qafoku et al. 2005, 2008a, 2008b; Payne and Airey 2006; Um et al. 2007a), and nanoporous zirconium-phosphate (Um et al. 2007b).

There has been some recent research work suggesting that natural organic matter may play a role in both aqueous complexation of U and adsorption onto soil surfaces (Dong et al. 2006). The result from this study demonstrated that the migration of depleted uranium may be limited by a combination of processes that include rapid sorption of U(VI) species to natural organic matter, followed by slow, intrinsic bioreduction to U(IV).

In neutral to slightly alkaline systems, stable aqueous anionic or neutral aqueous U(VI)-carbonato species (Grenthe et al. 1992; Clark et al. 1995; Kalmykov and Choppin 2000; Bernhard et al. 2001) may sorb to different degrees on various soil minerals (Duff and Amrhein 1996; Pabalan et al. 1998; Payne et al. 1998; Bargar et al. 1999; Catalano and Brown 2005; Greathouse and Cygan 2005). Fe-oxide U(VI)-carbonato complexes are likely to be important transport-limiting species in oxic aquifers throughout a wide range of pH values (Bargar et al. 2000). The retardation extent of U(VI) under mildly alkaline

conditions is therefore controlled by competition between aqueous and surface complexation. Therefore, the questions of concern are:

(i) Under what conditions would the vertical and horizontal migration of aqueous U(VI) be minimized via adsorption?
(ii) What conditions favor the immobilization of aqueous U(VI);
(iii) Under what conditions will the U(VI) remobilize?

Although a mechanistic understanding of U(VI) sorption in natural heterogeneous systems such as soils and sediments is difficult to uniquely constrain, information collected from carefully designed and executed laboratory and field experiments conducted with a variety of materials is useful for understanding system's behavior and contaminant mobility and transport. The major variables that affect the extent of U(VI) sorption to pure soil minerals or soil mineral assemblages (such as soils and sediments) exposed to neutral or slightly basic solutions, are summarized below:

(i) Aqueous U(VI) concentration (Waite et al. 1994; Kohler et al. 1996; Pabalan et al. 1998);
(ii) pH and ionic strength of the contacting solution (Waite et al. 1994; Kohler et al. 1996; Pabalan et al. 1998; Payne et al. 1998; Rosentreter et al. 1998; Catalano and Brown 2005);
(iii) Aqueous carbonate concentration (Duff and Amrhein 1996; Curtis et al. 2006; Noubactep et al. 2006);
(iv) Aqueous Ca, Mg, Ba, Sr and Na concentrations (Dong and Brooks 2006; Kelly et al. 2007);
(v) Organic and inorganic ligand concentrations (such as oxalate, humic acid, phosphate, carbonate, nitrate, …) (Duff and Amrhein 1996; Payne et al. 1998; Duff et al. 2002; Noubactep 2005; Arai et al. 2006; Cheng et al. 2006; Krepelova et al. 2006);
(vi) Partial pressure of carbon dioxide (Waite et al. 1994; Duff and Amrhein 1996; Pabalan et al. 1998; Payne et al. 1998; Catalano and Brown 2005);
(vii) Solid-to-solution ratio (Pabalan et al. 1998; Phillippi et al. 2007).

Within the context of aqueous U(VI) interaction with soil minerals when they occur in heterogeneous

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assemblages such as soils and sediments, one of the most intriguing and unanswered question which remain unanswered is: Do some soil minerals exhibit a greater affinity for U(VI) than others? Are some minerals able to sorb U(VI) at a different extent and/ or with a different rate than others? What are the reasons for this behavior?

U(VI) sorption was studied in quartz, clinoptilolite, montmorillonite and α-alumina, which are sorbents possessing distinct mineralogical and surface characteristics (Pabalan et al. 1998). After comparing their results with those of the literature, the authors concluded that the similarity in the pH dependence of U(VI) sorption on quartz, α-alumina, clinoptilolite, montmorillonite, amorphous silica, kaolinite, and hydrous titanium oxide suggested that U(VI) sorption was not sensitive to the surface charge characteristics of the sorbent as compared to the effect of changing the number of available sorption sites (Pabalan et al. 1998). They found that the magnitudes of U(VI) sorption at a specific pH, initial U concentration and CO_2 partial pressure were essentially the same for the different minerals if normalized to an "effective" surface area. Changing M/V had little effect on U(VI) distribution coefficient (K_d), except at very low values (Pabalan et al. 1998).

Other authors have reinforced the idea that the extent of U(VI) sorption depends more on reactive surface area than on the surface properties of sorbents. For example, in a study conducted with 25 sediment samples, significant correlations between U(VI) sorption and surface area were found (Rosentreter et al. 1998). These authors claimed that mineralogy and grain size had essentially no influence on the sorptive capacity of these sediments (Rosentreter et al. 1998).

In summary, this topic is important and additional research is needed to determine if surface area is, in fact, the key parameter controlling the extent of U(VI) sorption in mixtures of different sorbents.

We will focus our review of published research work on three groups of soil minerals and U(VI) sorbents, i.e., Fe oxides, phyllosilicates and calcium carbonates (mainly calcite), which are ubiquitous in soils and sediments and, mainly for this reason, play an important role in determining U(VI) fate in contaminated natural systems under oxic or alternated oxic and anoxic conditions.

2.2 Fe oxides

Fe oxides are one of the end products of the weathering process, and occur in almost all soils and sediments as strongly pigmented clay-sized oxide, oxyhydroxide, and hydroxide minerals (Schwertmann and Taylor 1989; Kampf et al. 2000; Bigham et al. 2002; Cornell and Schwertmann 2003; Qafoku and Amonette 2003). Fe oxides form clay-sized particles as small as a few nanometers across (e.g., ferrihydrite) and have specific surfaces as high as several hundreds of $m^2 g^{-1}$ (Cornell and Schwertmann 1996). Even crystalline Fe oxides (e.g., hematite) may have a specific surface of greater than $100 m^2 g^{-1}$ (Schwertmann and Taylor 1989). They have a point of zero charge in the neutral or slightly basic pH range (Sposito 1984, 1989).

Numerous experimental observations and model calculations have demonstrated that Fe (hydr)oxides show great affinity for aqueous U(VI) under circumneutral and slightly alkaline conditions (Hsi and Langmuir 1985; Ho and Miller 1986; van Geen et al. 1994; Waite et al. 1994; Duff and Amrhein 1996; Reich et al. 1998; Bargar et al. 1999, 2000; Moyes et al. 2000; Villalobos et al. 2001; Dodge et al. 2002; Wazne et al. 2003; Cheng et al. 2006; Lefevre et al. 2006; Ulrich et al. 2006; Jang et al. 2007; Rovira et al. 2007). In a study of U sorption, uptake onto both goethite and lepidocrocite occurred by surface complexation and ceased when the surface sites were saturated (Moyes et al. 2000). XAS measurements indicated that bidentate inner-sphere surface complexes were formed on the iron hydroxides by coordination of two surface oxygens from an iron octahedron in the equatorial plane of the complex (Moyes et al. 2000).

Results from field studies also demonstrate that U(VI) is concentrated in Fe oxide nodules and veins that consist of goethite and hematite (Murakami et al. 2005), or in Fe oxide coatings on quartz grains (Read et al. 1993), and, thus, sediments behave as strong U(VI) sorbents when high-affinity soil minerals, such as Fe oxides, are present in high abundances. Researchers propose that strong U(VI) sorbents, such as Fe oxides, can significantly modify sorption behavior of natural systems even when they are present as minor phases (Payne et al. 1998).

2.2.1 Contacting aqueous solution

Carbonate concentration dramatically affects the adsorption of U onto Fe hydroxides and its mobility in the natural environment (Wazne et al. 2003). An increase in carbonate concentration causes a shift in the antisymmetric stretching vibration of the uranyl U–O bond toward lower wavenumbers, which indicates an increasing carbonate effect in the adsorbed uranyl carbonate complexes (Wazne et al. 2003).

Nevertheless, U(VI) carbonato complexes do sorb onto Fe oxide surfaces to a large extent. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) and extended X-ray absorption fine structure (EXAFS) spectroscopies were used to probe the identities, structures, and compositions of =FeO surface-U(VI)-carbonato complexes on hematite throughout the pH range of uranyl uptake under conditions relevant to aquifers (dilute U(VI) concentration, 0.1–47.2 μM, pH = 4.73–8.25, presence of CO_2; Bargar et al. 1999). U(VI)-carbonato complexes were found to be the predominant adsorbed U(VI) species at all pH values examined, a much wider pH range than previously postulated based on analogy to aqueous U(VI)-carbonato complexes, which are trace constituents at pH < 6 (Bargar et al. 1999).

In a follow up study by Bargar et al. (2000), EXAFS spectroscopy and electrophoretic measurements recorded under conditions relevant to surface waters and aquifers (pH 4.5–8.5), suggested the existence of anionic U(VI)-carbonato ternary complexes on hematite (Bargar et al. 2000). U(VI) was simultaneously coordinated to surface FeO_6 octahedra and carbonate (or bicarbonate) ligands in bidentate fashions, confirming that the ternary complexes have an inner-sphere metal bridging (hematite-U(VI)-carbonato) structure (Bargar et al. 2000). Greater than or equal to 50% of adsorbed U(VI) was comprised of monomeric hematite-U(VI)-carbonato ternary complexes, even at pH 4.5, while dimeric U(VI) species were observed at pH ≥ 6.5 (Bargar et al. 2000).

Other studies have corroborated these findings. Batch tests, zeta potential measurements, and Fourier transform infrared (FTIR) spectroscopic studies were utilized to characterize the nature of U(VI) adsorption on ferrihydrite (Wazne et al. 2003). Zeta potential and FTIR spectroscopic measurements indicated that U(VI) was adsorbed as a cationic species $(SO\text{-}UO_2^{2+})$ (where SO is an active surface site) in the absence of carbonate, and as anionic U(VI) complexes (uranyl carbonate complexes) in the presence of carbonate at neutral pH (Wazne et al. 2003).

Lastly, results from a recent study conducted with ferrihydrite indicated that in the presence of dissolved carbonate and near a pH value of 8.0, a distal carbonate O-atom at 4.3 Å supported the formation of ternary U(VI)-carbonato surface complexes (Ulrich et al. 2006). However, in slightly acidic conditions (pH 5–6) in equilibrium with atmospheric CO_2 the U(VI) sorption on ferrihydrite was dominated by the binary complex species $Fe(O)(2) = UO_2$, whereas ternary U(VI)-carbonato surface complexes were of minor relevance. These results confirm that U(VI) forms stable inner-sphere sorption complexes even in the presence of carbonate and at slightly alkaline pH (Ulrich et al. 2006). These authors also stated that the type of surface complexes may change from binary uranyl-ferrihydrite to ternary carbonato-uranyl-ferrihydrite complexes depending on the concentrations of U(VI) and carbonate. Definitely, detailed studies are required to determine whether these different binding mechanisms can influence the overall retention of U(VI) at the macroscopic level.

2.2.2 Speciation of sorbed U(VI)

Speciation of adsorbed U(VI) to Fe oxides has been a topic of discussion in the literature. The general belief is that sorbed surface species are of a different type than the aqueous complexes. Results from a study of U(VI) adsorption to ferrihydrite under alkaline conditions suggested the existence of a surface species and was modeled as a ternary surface complex with $UO_2CO_3^0$ binding to a bidentate surface site. This surface species was different than the predominant aqueous species such as multinuclear hydrolysis complexes of several U(VI)-carbonate complexes (Waite et al. 1994). As it was mentioned above (Sect. 2.3), other authors have emphasized the inadequacy of the common modeling assumption that the compositions and predominance of adsorbed species can be inferred from aqueous species (Bargar et al. 1999).

2.2.3 Surface mediated U(VI) precipitation and incorporation

Fe oxide surfaces may catalyze and mediate U(VI) precipitation reactions. The distinction between

sorption control and precipitation control of the dissolved U concentration was investigated in a recent study (Giammar and Hering 2001). In heterogeneous nucleation experiments, the dissolved U concentration was ultimately controlled by the solubility of a precipitated uranyl oxide hydrate, which was confirmed to be schoepite (Giammar and Hering 2001). Precipitation was kinetically hindered at low degrees of supersaturation (Giammar and Hering 2001). In one experiment, metastable sorption controlled dissolved U concentrations in excess of the solubility limit for more than 30 days (Giammar and Hering 2001).

U(VI) incorporation into Fe oxide structures is another topic not well explored in the literature. Because of the large ionic radius of UO_2^{2+} (~ 1.8 Å) relative to that of Fe^{3+} (0.65 Å), the UO_2^{2+} ion is unlikely to be incorporated in the place of Fe in Fe(Ill)-oxide structures (Duff et al. 2002). Solid-phase U(VI) can exist as the UO_2^{2+} species with two axial U–O double bonds and four or more equatorial U–O bonds or as the uranate species (such as gamma-UO_3) without axial U–O bonds (Duff et al. 2002). These authors found that U(VI) (with ionic radii of 0.72–0.8 Å, depending on the coordination environment) was incorporated in the Fe oxides as uranate (without axial O atoms) until a point of saturation is reached. When U concentrations reach saturation and overcome barriers to precipitation kinetics, U(VI) forms discrete crystalline uranyl phases that resemble the uranyl oxide hydrate schoepite (Duff et al. 2002). Molecular modeling studies reveal that U(VI) species could bond with O atoms from distorted Fe octahedra in the hematite structure with an environment that is consistent with the results of the XAFS, providing compelling evidence of U incorporation within the hematite structure (Duff et al. 2002).

2.3 Phyllosilicates

Phyllosilicates are common soil minerals that strongly influence both the chemical and physical properties of soils because of their small particle sizes, high surface areas, and unique exchange properties (Schulze 2002). A full understanding of their behavior in soil systems is central to understanding environmentally relevant reactions and processes.

Experimental observations as well as model and molecular dynamic calculations have demonstrated that phyllosilicates show great affinity for aqueous U(VI), which is adsorbed onto montmorillonite (Benes et al. 1998; Sylwester et al. 2000; Hyun et al. 2001; Kowal-Fouchard et al. 2004; Catalano and Brown 2005; Greathouse and Cygan 2005, 2006), muscovite (Moyes et al. 2000; Arnold et al. 2006), kaolinite (Payne et al. 2004; Krepelova et al. 2006, 2007), biotite (Ames et al. 1983), halloysite (Kilislioglu and Bilgin 2002) and beidellite (Greathouse and Cygan 2006).

2.3.1 Sorption affinity

Studies have been conducted to compare sorption affinities of Fe oxides and phyllosilicates. Studies conducted with pure samples of Fe oxides and phyllosilicates in single and/or mixed phase suspensions demonstrate that U(VI) uptake on kaolinite is much weaker than U(VI) uptake on ferrihydrite under similar experimental conditions, although U(VI) adsorption to both kaolinite and ferrihydrite is similarly dependent on experimental variables such as pH, total U(VI), and mass loading (Payne et al. 1998). These authors found that the sorption properties of a mixed system (kaolinite/ferrihydrite) are very similar to those of ferrihydrite, although ferrihydrite is the minor phase on a mass basis (about 2.2 wt.%; Payne et al. 1998).

2.3.2 Contacting aqueous solution

Many investigations have been conducted with the objective of studying U(VI) sorption to different phyllosilicates. The results presented in some of the most recent studies that emphasize the role of contacting solution composition and pH, will be summarized in the following paragraphs.

The uptake of uranyl by a specific type of kaolinite (KGA-1b) in air-equilibrated systems increased with pH and reached a maximum in the near-neutral pH range (Payne et al. 2004). Sorption extent decreased at higher pH due to the presence of aqueous uranyl carbonate complexes. Ti-rich impurities (predominantly anatase) were present in this kaolinite and TEM/EDS analyses performed in a post-treatment kaolinite showed that U was preferentially adsorbed by this impurity, which appears to play an important

role in retaining U at low uranyl concentrations. Uranyl sorption on the Georgia kaolinites was simulated with U sorption reactions on both titanol and aluminol sites, using a simple non-electrostatic surface complexation model (SCM). A ternary uranyl carbonate complex on the titanol site improved the fit to the experimental data in the higher pH range.

Investigators used molecular dynamics simulations to study the adsorption of aqueous uranyl species onto clay mineral surfaces in the presence of Na counterions and carbonato ligands (Greathouse and Cygan 2005). The model system consisted of the basal surface of a low-charge Na-montmorillonite clay in contact with aqueous uranyl carbonate solutions. Uranyl adsorption decreased as the aqueous uranyl carbonate concentration increased, while Na adsorption remained constant. The observed behavior is explained by physical and chemical effects. As the ionic strength of the aqueous solution increased, electrostatic factors prevented further uranyl adsorption once the surface charge had been neutralized. It is important to note that these authors found that the formation of aqueous uranyl carbonate complexes, including uranyl carbonato oligomers (an assemblage of a finite number of monomers), contributed to the decreased uranyl adsorption in montmorillonite.

Molecular dynamics simulations were also performed to provide a systematic study of aqueous uranyl adsorption onto the external surface of 2:1 dioctahedral smectitic clays in the presence of Na and carbonate (Greathouse and Cygan 2006). No adsorption occurred near the pyrophyllite surface, and there was little difference in uranyl adsorption onto the beidellite and montmorillonite, despite the difference in location of clay layer charge (Greathouse and Cygan 2006). At low uranyl concentrations, the pentaaquouranyl complex dominated in solution and readily adsorbed to the clay basal plane. At higher uranyl and carbonate concentrations, the mono carbonato complex formed in solution and uranyl adsorption decreased. Sodium adsorption onto beidellite had little effect on uranyl adsorption. Uranyl surface complexes consisted primarily of the pentaaquo cation (85%) and to a lesser extent the mono carbonato species (15%). Oligomeric uranyl complexes were observed at high ionic strength, particularly near the pyrophyllite and montmorillonite surfaces. Atomic density profiles of water oxygen

and hydrogen atoms are nearly identical near the beidellite and montmorillonite surfaces.

U(VI) sorption on kaolinite was a function of pH (pH = 3–10), CO_2 and the presence of humic acid (HA) in the contacting solution (Krepelova et al. 2006). Above pH 6 the U(VI) uptake remained unchanged. Because of the formation of negatively charged uranyl carbonate complexes, the decrease in the U(VI) sorption onto the negative surface of kaolinite was observed above pH 8 in the presence of CO_2. The formation of aqueous uranyl-humate complexes reduces the U(VI) sorption in the near neutral pH range. The ionic strength had a slight influence on the U(VI) sorption to kaolinite.

2.3.3 Speciation of sorbed U(VI)

Adsorption of uranyl onto Wyoming montmorillonite was investigated with extended X-ray absorption fine structure (EXAFS) spectroscopy (Catalano and Brown 2005). At near-neutral pH (~ 7) and high ionic strength (1 M), the equatorial oxygen shell of uranyl was split, indicating inner-sphere binding to edge sites. Analysis of the binding site on the edges of montmorillonite suggested that U(VI) sorbs preferentially to [Fe(O,OH)(6)] octahedral sites over [Al(O,OH)(6)] sites. When bound to edge sites, U(VI) occurred as uranyl-carbonato ternary surface complexes in systems equilibrated with atmospheric CO_2. These authors reported that polymeric surface complexes were not observed under any of the conditions studied.

Time-resolved laser-induced fluorescence spectroscopy (TRLFS) was used to study the U(VI) surface complexes on kaolinite in the presence or absence of humic acid (HA) (Krepelova et al. 2007). Aluminol binding sites were assumed to control the sorption of U(VI) onto kaolinite in this study. Two uranyl surface species were identified in the binary [U(VI)-kaolinite] and ternary systems [U(VI)-HA-kaolinite], respectively. In the binary system, both surface species can be attributed to adsorbed bidentate mononuclear surface complexes, which differ in the number of water molecules in their coordination environment. In the ternary system, U(VI) was directly bound to kaolinite, but it was sorbed as a uranyl-humate complex.

TRLFS and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)

were applied to investigate the speciation of ura-nyl(VI) adsorbed onto muscovite platelets and muscovite suspensions (Arnold et al. 2006). TRLFS provided evidence for the presence of two adsorbed U(VI) surface species on edge-surfaces of muscovite, with different coordination environments. The surface species with the shorter fluorescence lifetimes are interpreted as truly adsorbed bidentate surface com-plexes, in which the U(VI) binds to exposed aluminol groups of edge-surfaces. The surface species with the longer fluorescence lifetimes are interpreted to be an amorphous U(VI) condensate or nanosized clusters of polynuclear U(VI) surface species with a particle diameter of 1–2 nm (Arnold et al. 2006).

Laser-induced fluorescence spectroscopy (LIFS) and X-ray photoelectron spectroscopy (XPS) was performed on uranyl ion loaded montmorillonite in experiments where pH was varied from 2 to 8 (Kowal-Fouchard et al. 2004). The lifetime values and the U4f XPS spectra of U(VI) sorbed on montmorillonite demonstrated that this ion was sorbed on both exchange and edge sites. The interaction between uranyl ions and montmorillonite edge sites occurred via both AlOH and SiOH surface groups and involved three distinct surface complexes (Kowal-Fouchard et al. 2004).

2.3.4 Surface mediated U(VI) precipitation or incorporation

Surface mediated precipitation of U(VI) phases has been observed in experiments conducted with phyl-losilicates. For example, unlike the surface of Fe oxides, the muscovite surface did not become satu-rated and uptake of U(VI) increased linearly suggesting formation of a U phase on the surface (Moyes et al. 2000). U uptake on muscovite may occur through surface precipitation, the first layer of U atoms binding through equatorial coordination of two adjacent surface oxygen atoms from a silicate tetrahedron, with the axial oxygen atoms of the uranyl unit aligned across the hexagonal "cavities" (Moyes et al. 2000). HAADF-STEM revealed that nanoclusters of an amorphous U phase were attached to the edge-surfaces of muscovite powder during batch sorption experiments (Arnold et al. 2006). These U-nanoclusters were not observed on {001} cleavage planes of the muscovite.

2.3.5 The special case of clinochlore

We draw attention to one particular type of phyllos-ilicates: the chlorite group (Kohut and Warren 2002). Chlorite minerals are particularly reactive detrital phyllosilicates under the oxidizing conditions that exists in many soils and sediments. Chlorite is the weathering product of ferromagnesian minerals, and it typically not a primary phase. The excess negative charge in these minerals is balanced by a positively charged interlayer di- or tri-octahedral hydroxide sheet, which has a positive net charge caused by substitution of higher valence cations for lower valence ones, for example $Mg_2Al(OH)_6^+$ (Schulze 2002). These substitutions may occur in either or both octahedral sheets of chlorites, the one that is part of the 2:1 layer or the interlayer sheet. These sheets can contain cations such as Mg^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+}. Chlorite (or ferran clinoch-lore which is a Fe(II)-rich chlorite) is common in some contaminated sites, such as the Hanford site in the State of Washington (Qafoku et al. 2005).

Chlorite (or clinochlore) has a multidimensional role in the complex U(VI) attenuation processes that occur in natural sytems which will be presented below:

(i)   Studies have shown that uranyl sorbs to the clinochlore interlayer (brucite interlayer) by corner and edge sharing bidentate complexes (Muckett et al. 1998). In addition, experiments conducted with granite to investigate the contri-bution of constituent minerals to total U(VI) uptake indicated that U(VI) has a relatively strong affinity for chlorite (Baik et al. 2004b).

(ii) Second, clinochlore, an Fe(II)-bearing 2:1:1 soil mineral, weathers or undergoes dissolution to yield soluble Fe(II) (Qafoku et al. 2003), which then oxidizes to form poorly crystalline Fe(III) oxides such as ferrihydrite (Pabalan and Turner 1997; Arnold et al. 1998, 2001; Pabalan et al. 1998), or other Fe(III) oxides that are strong U(VI) sorbents.

(iii) Aqueous U(VI) may be reduced by soluble Fe(II) released from chlorite upon its dissolution.

(iv) Redox sensitive contaminants such as U(VI) may sorb on hydroxylated edge sites of

chlorite, and serve as electron acceptors of the structural Fe(II).

(v) The migration of U(VI) species may be curtailed by attachment between the expandable layers of chlorite. This diffusion controlled process appears to be driven by a multiple step, coupled sorption and reduction (charge distribution) reactions, which result in U(VI) reduction by structural Fe(II) of the clinochlore's brucite interlayer.

2.4 Calcite

Calcite is a ubiquitous mineral in soils and sediments and usually tends to dominate geosystem's chemical behavior when it is present at a level of 1% or more (Langmuir 1997). However, literature offers relatively few insights on the potential role of natural calcite in controlling U(VI) behavior in contaminated calcite-rich sediments (Kaplan et al. 1998; Zheng et al. 2003; Dong et al. 2005; Wang et al. 2005).

2.4.1 Sorption affinity

The extent and rate of U(VI) sorption to calcite and U(VI) interactions at the calcite:water interface have been studied and reported in the literature (Morse et al. 1984; Carroll and Bruno 1991; Carroll et al. 1992; Geipel et al. 1997; Reeder et al. 2001, 2004; Savenko 2001; Elzinga et al. 2004). These studies have revealed that the extent of U(VI) adsorption in systems open to atmosphere depends on aqueous carbonate aqueous concentrations, which is controlled by calcite solubility. Aqueous carbonate is an important U(VI) ligand in contaminated subsurface pore waters because of the stability of the negatively charged U(VI)-carbonato and neutral Ca-U(VI)-carbonato aqueous species (Kalmykov and Choppin 2000; Bernhard et al. 2001), which dominate U(VI) speciation at slightly alkaline pH.

2.4.2 Contacting aqueous solution

Aqueous U(VI)-carbonate complexes may interact with calcite forming surface complexes, but studies have shown that U(VI) exhibits limited adsorption to calcite and sorption is reversible (Carroll and Bruno 1991; Elzinga et al. 2004). Studies have also demonstrated that multiple adsorption species may form on calcite surfaces. For example, luminescence spectroscopic studies have indicated the presence of at least two adsorption complexes on calcite surfaces, that change proportion with U(VI) loading (Elzinga et al. 2004): one species (the U(VI) triscarbonate complex) dominates at low surface coverage, and the other one (an intermediate between the triscarbonate species found at the lowest loadings and U(VI) incorporated in calcite crystal structure) is observed at higher surface loading.

2.4.3 Calcite mediated U(VI) precipitation and sequestration

A second possible mechanism of U(VI) attenuation in the U(VI)-calcite system is solid-phase mediated U(VI) precipitation. U(VI) precipitation at the calcite-solution interface is observed only when the initial U(VI) concentration is greater than the solubility of rutherfordine, $UO_2CO_{3(solid)}$ (Carroll et al. 1992), or under conditions of unusual pH and carbonate concentration associated with extreme waste chemistry and over-neutralization (Wang et al. 2005).

A third mechanism of U(VI) attenuation in the U(VI)-calcite system is U(VI) sequestration inside calcite crystal structure. Although calcite was initially believed to be an unsuitable host for the long-term sequestration of U(VI) (Reeder et al. 2000), a recent spectroscopic study has shown that uranyl has a stable lattice position within natural calcite (Kelly et al. 2003). It is interesting to note that the stable configuration of uranyl in calcite was found in natural calcite crystals that are quite old. In contrast, incorporation of uranyl in recently-grown calcite in the laboratory does not occur in a stable configuration, and this may be interpreted to mean that uranyl partitioning changes (becomes more stable) with time. This implies that contaminant U(VI) may coprecipitate with calcite and may be sequestered during growth-periods yielding a mineral association that may influence or limit U(VI) migration (Kelly et al. 2003; Reeder et al. 2004). Other spectroscopic studies have shown that some U(VI) substitution sites in calcite may be distorted to exhibit a local, more energetically favorable aragonite structure (Wang et al. 2005).

Because multiple sorbed U(VI) species (adsorbed, precipitated, and sequestered) with different stabilities may simultaneously exist in calcite-bearing contaminated sediments, U(VI) partitioning may be influenced by energetic and possibly mechanistic differences that increase the complexity of U(VI) sorption/desorption behavior. The prediction of this behavior is quite challenging and little information is available in the literature.

3 Soil minerals and kinetics of U(VI) sorption

3.1 Time-dependent soil mineral:aqueous U(VI) interactions

Studies have demonstrated that U(VI) adsorption to single soil mineral phases is typically kinetically controlled and exhibits strong time-dependency, as illustrated by the different uranyl configurations in calcite over time cited above. Examples involving some common soil minerals follow. U(VI) adsorption to hematite demonstrated a rapid initial phase of 30 minutes and a longer phase extending to hundreds of hours (Bargar et al. 2000). In systems that are open to air, the major U(VI) surface species formed were ternary uranyl-carbonate complexes such as $FeO_2UO_2CO_3^{2-}$ and $FeO_2UO_2(CO_3)_2^{4-}$ over the pH range 4–9, in the presence of a total U(VI) concentration of 10^{-5} M. The rates of U adsorption and desorption on a synthetic goethite have been evaluated in batch experiments conducted at constant pH of 6 and ionic strength of 0.1 M (Giammar and Hering 2001). Adsorption and desorption reactions following the perturbation of initial states were completed within minutes to hours. Although the U desorption rate was unaffected by the aging of U-goethite suspensions (6 months), the aging process appears to remove a portion of adsorbed U from a readily exchangeable pool. At faster pore water velocities, U(VI) adsorption in a goethite column was far from equilibrium (Gabriel et al. 1998). A two-step kinetic behavior dominates in both the intact surfaces and natural fracture surfaces of granite (Baik et al. 2004a).

Soils and sediments are heterogeneous and consist of natural assemblages of primary soil minerals at different stages of weathering, secondary soil minerals that are products of weathering and other soil formation processes, organic matter and living organisms.

Properties such as soil mineral abundances, degree of crystallinity, location of the phase along the groundwater flow path, soil mineral associations and aggregation, particle size distribution, and chemical concentration gradients within the network of pores may have quite a remarkable effect on the K_d, and extent and rate of U(VI) sorption reactions.

Because of intraparticle diffusion, rate limited mass transfer, redistribution between sites with differing reactivities or location, and surface precipitation, both U(VI) adsorption and desorption should be kinetically-controlled in soils and sediments (Braithwaite et al. 1997, 2000; Mason et al. 1997; Gamerdinger and Kaplan 2000; Gamerdinger et al. 2001a, b; Qafoku et al. 2005; Qafoku et al. 2008a, b). Decoupling the effects of different reactions and processes, and measuring time scales of the kinetically controlled chemical reactions and physicochemical processes is a challenge researchers are currently facing. On the other hand, time scales of reactions and processes are important parameters to be estimated to accurately predict U(VI) behavior and transport through heterogeneous natural systems.

3.2 Mineralogical, physical and chemical heterogeneities

3.2.1 Mineralogical heterogeneities

There are two types of mineralogical heterogeneities in soils and sediments: (i) Sediments are heterogeneous media because they may contain a variety of sorbents each exhibiting different sorption properties, and (ii) precipitated U minerals undergo a paragenetic sequence of phases (Catalano and Brown 2004; Liu et al. 2004a; Wang et al. 2005; Arai et al. 2007).

In the first case, the general belief is that the type of sorbents and especially the degree of crystallinity may be important determinants of U(VI) sorption extent and rate (Rosentreter et al. 1998). Sorbed U in deep vadose zone sediments at Hanford 200 Area was associated with intragrain fractures of granitic lithic clasts (McKinley et al. 2006). Although the granitic clasts are the minor components of the sediments (<4%), they are the exclusive host for sorbed U(VI), most likely resulting from preferential interactions between U(VI) in the waste fluids and the sediments, and diffusive mass transfer limitations (Liu et al. 2006; McKinley et al. 2006).

The second type of heterogeneity emphasizes progressive formation of multiple U solid phases with different solubilities (Catalano and Brown 2004; Liu et al. 2004a; Wang et al. 2005; Arai et al. 2007). The most common U precipitates include oxyhydroxides, carbonates, silicates and phosphates that evolve in this order (Finch and Murakami 1999). Recent studies involving X-ray absorption spectroscopy and cryogenic laser induced fluorescence spectroscopy (CLIFS) demonstrated that U(VI) may coprecipitate with calcite (Kelly et al. 2003; Wang et al. 2005). The study by Kelly et al. reported results for a single calcite crystal. Whether or not their results can be universally applied to all calcium carbonates is an open question and may very well depend on the precipitation kinetics of calcite. The type of U neophases, their physical location and mineral phase associations depend on the existing and newly created specific conditions as a result of the aqueous and solid phase interactions in the inter- and intra-aggregate network of micro and nanopores. The neo or existing U solid phases are difficult to identify when they occur in remote microscopic domains. U behavior observed in macroscopic desorption experiments would actually be a complex, time-dependent process and would be difficult to describe and predict.

3.2.2 Physical heterogeneities

U(VI) adsorption/desorption behavior will strongly depend on the physical location of potential U(VI) sorbent domains within the macro, meso, and micropore network of the heterogeneous soil matrix. When these domains are located in the remote areas in relation to the advective pores, U(VI) movement is then controlled by time-dependent intraparticle diffusion and rate limited mass transfer. In addition, physical properties of the solid phase such as particle size distribution and reactive surface area (Rosentreter et al. 1998) may have an effect on the time-dependent U(VI) mobility and transport. A finer texture is commonly associated with a greater surface area per unit weight of sorbent and a greater concentration of sorbing surface sites available for U(VI) sorption, with different sorption properties. We emphasize that soil minerals that exhibit high affinity for aqueous U(VI) typically occur in the fine fraction. Studies are required to investigate separately the surface area and affinity effects on U sorption.

3.2.3 Chemical heterogeneities

The chemical composition and pH of the aqueous phase in sediments is controlled by time-dependent dissolution and precipitation reactions of different solid phases that compose the sediment. Pockets or microcosmos of aqueous phase with a different elemental composition and pH of that of the advective pore water may be formed within the sediment pore network. The aqueous phase chemical heterogeneity may affect the rate of U(VI) sorption and desorption reactions through the effects associated with pH and ionic composition. In addition, the solid phase chemical heterogeneity may also affect rates of U(VI) sorption and desorption. For example, sorbed U beneath the 300 Area is associated with secondary particle coatings and microporous aggregates of clay-sized phyllosicates (Qafoku et al. 2005; Zachara et al. 2005). The solid phase speciation of U(VI) is complex and exhibits continuous transitions from multi-component precipitated phases near the contaminated fluid source, to adsorbed complexes in underlying deeper sediments (Wang et al. 2005; Catalano et al. 2006). Changes in speciation across the soil profile increase the complexity of the system, promoting multiple-rate adsorption and desorption, and make difficult the overall prediction of the time-dependent U(VI) sorption.

3.3 Diffusion and mass transfer

In many contaminated sites U has been in contact with the sediments for relatively long periods of time, allowing U movement towards remote regions within sediments matrix that are influenced by diffusion-limited mass transfer. Recent research has revealed that sorbed U(VI) in the sediments exists in complex, microscopic, intragrain domains (McKinley et al. 2006).

U(VI) sorbed in intragrain remote regions may desorb (de-adsorb and/or undergo dissolution) with varying release rates and extent, which may be controlled by chemical reactions that occur inside these regions, and the reactants mass transfer to and products mass transfer from these microscopic domains to advective flow pores (Liu et al. 2004a; Qafoku et al., 2005). Pore waters flow through permeable layers or regions, while pore water in less permeable or intragrain regions remains virtually

immobile. The exchange of mass between regions with different dynamic properties occurs via diffusion or mass transfer driven by concentration or thermo-dynamic potential gradients.

Diffusion is the movement of an aqueous chemical species of a contaminant from regions of higher concentration to regions of lower concentration due to the ceaseless random thermal motion of molecules (molecular diffusion), or random motion of the water that carries the chemical (turbulent diffusion), or a combination of the two (Hemond and Fechner-Levy 2000). Another term, microscale mass transfer, is commonly used in the contemporary literature to describe the same physical phenomenon. A specific case of diffusion or microscale mass transfer is when aqueous phase concentration gradients are created as a result of a sorption reaction at the solid:solution interfaces. In this case, the mass transfer of a chemical is driven by a combination of two sequential chemical (sorption) and physical (gradient of concentration) processes. This coupling controls the overall rate and extent of the exchange of mass between regions of different fluid residence times. Decoupling these steps is essential in understanding the reactivity and stability of U(VI) intragrain complexes and phases, predicting the mobility of intragrain U(VI) following the intragrain and inter-grain gradient of concentration, and finding the most suitable remediation strategy for site-specific conditions.

Mass-transfer to and from poorly accessible sorbent domains was responsible for the non-equilibrium sorption–desorption behavior of U(VI) in a contaminated site at Hanford (Liu et al. 2004a, 2006; Qafoku et al. 2005). Microscopic evaluation of thin sections of the sediments from this and other sites show that sand grains and lithic fragments of various sizes are coated with films of the phyllosilicates that were identified in the clay-sized fraction (e.g., smectite, vermiculite, chlorite). These silt and clay films represent sorbent domains with limited diffusivity that impacted U(VI) sorption rate and extent.

Some literature sources on the role of diffusion and the mass transfer phenomenon in soils and sediments are available to investigators seeking to understand this phenomenon better (van Genuchten and Wierenga 1976, 1977; Lichtner 1993, 1996; Li et al. 1994; Haggerty and Gorelick 1995, 1998; Harvey and Gorelick 1995; Reedy et al. 1996; Culver

et al. 1997; Steefel and van Cappellen 1998; Hollenbeck et al. 1999; Li and Brusseau 2000; Wang et al. 2003; Zinn and Harvey 2003; Haggerty et al. 2004; Liu et al. 2004a, 2004b, 2006; Harvey et al. 2005; Steefel et al. 2005; Lichtner and Carey 2006; Liu 2007; Yabusaki et al. 2007).

3.4 Importance of kinetics

The kinetic aspects of U(VI) mobility may be important in natural assemblages of soil minerals, but unfortunately the literature offers few insights on this important subject. The kinetics of U(VI) adsorption and desorption could be an important factor in controlling the long-term evolution and dissipation of contaminant plumes. U(VI) adsorption during unsaturated transport experiments with two sediments, a silt loam (56% silt) and sand (98% sand) textured Hanford sediment, was affected by rate-limited mass transfer (Gamerdinger et al. 2001a, b). Recent transport studies conducted with simulated Hanford groundwater and vadose zone sediments from the 200 (BX tank farms) and 300 Areas at Hanford, have shown that U(VI) was significantly retarded and exhibited strong time dependency (Qafoku et al. 2005; Ilton et al. 2008). Even in coarse-textured sediments with limited sorption capacities, U(VI) migration was kinetically controlled by pore-scale, mass transfer processes.

Soil mineralogy plays an important role in determining system behavior during U(VI) adsorption and desorption. Examples from recent research conducted with sediments with different mineralogical composition will be presented below. The contaminated sediments from the 300 Area at Hanford contained primarily adsorbed U(VI) (Qafoku et al. 2005; Bond et al. 2007). These investigators concluded that mass-transfer of U(VI) to and from poorly accessible sorbent domains within the sediment fine fraction was responsible for the non-equilibrium sorption-desorption. Microscopic evaluation of thin sections of this and other related sediments from the site (by McKinley JP, personal communication) showed that sand grains and lithic fragments of various sizes were coated with thin layers of the phyllosilicates in the silt and clay-sized fractions (e.g., smectite, vermiculite, chlorite). They represented sorbent domains with limited diffusivity that impacted U(VI) sorption rate and extent. We note, however, that our fitting of the

two-region, physical nonequilibrium model to the Br-breakthrough curves (BTC) implied that the entire aqueous volume in the columns of sand-textured sediment was mobile. Perhaps the fluid volumes of the poorly accessible domains were too small to influence the macroscopic details of Br-BTC, or that negative charge on the phyllosilicates inhibited inward anion diffusion. In contrast, the neutrally-charged, predominant U(VI) species [$Ca_2UO_2(CO_3)_{3(aq)}$] would have not been excluded from these domains.

The extent and rate of U(VI) desorption and adsorption was studied in two vadose zone sediments below the TX tank farm at Hanford site, WA. Waste tank-related saline fluids migrated through the sediments of the Hanford formation (45 to 105 feet below ground surface (bgs)), reaching a depth of approximately 115 feet bgs (Cold Creek unit) (Serne et al. 2004). The pore waters maintained circumneutral pH values between 7.69 and 7.48, but the results from many experiments and modeling studies clearly indicated that various U(VI) attenuation mechanisms were operative in these sediments. Sediments had similar mineralogy, but they differed markedly in terms of calcite content (2.4 vs. 32.8%). The morphology of calcite is also significantly different in these two sediments. Small calcite particles that form aggregates and thin coatings ($\sim$10–30 μm) are partially agglomerated around larger size particles present in one sediment from the Hanford formation, while larger calcite particles (>200 μm diameter) and thick Ca carbonate coatings ($\sim$100–150 μm) are manifested in the other one (the sediment from the Cold Creek unit).

Large soil particle aggregates were present in both sediments, but they exhibited different characteristics. The thick calcite coatings in the calcite-rich sediment filled all available space between grains that make up the aggregates, whereas amorphous Si was the likely cement holding the soil particles together in the aggregates found in calcite-poor sediment. Unlike pedogenic carbonate, which cements by engulfing soil particles like mortar between bricks (Monger and Kelly 2002), pedogenic silica cements by bonding soil particles at grain contact points like glue (Chadwick and Nettleton 1990). For this reason, and because the degree of Si cementation may vary greatly, the aggregates of calcite-poor sediment were porous. The remote adsorption sites and/or domains within the aggregate pore network were most likely responsible for the kinetic behavior observed during U(VI) desorption and adsorption in this sediment, under various experimental conditions.

The TRLIFS measurements demonstrated that U(VI) was associated with calcite in both sediments. In calcite-poor sediment, U(VI) was either adsorbed to calcite and/or incorporated into calcite structures. The spectra changed little after removal of U(VI) labile fraction, indicating that a significant mass of U(VI) remained in this sediment, either as adsorbed complexes in remote (not easily accessible) locations, or incorporated into calcite. It is likely that U(VI) sequestration/stabilization via either slow growth that allows for ordering of incorporated U(VI) within calcite structure, or structural transformations of calcite over time (Kelly et al. 2003), may have occurred in the calcite-poor sediment that was exposed for years to U(VI)-bearing fluids. Sorption of U(VI) to calcite by either a surface adsorption/exchange reaction or coprecipitation may occur under the pH and carbonate concentration conditions present in these sediments (Meece and Benninger 1993; Reeder et al. 2000).

U(VI) was also associated with calcite in the calcite-rich sediment but experimental data confirmed that U(VI) was present only as an adsorbed complex. These results were consistent with those from the extraction of U(VI) by a dilute bicarbonate/carbonate solution at pH = 9.37 (conditions under which crystalline calcite dissolution is not promoted; Kohler et al. 2004), which demonstrated that the labile U(VI) fraction comprised about 48 and 99 % of total U(VI) content in calcite-poor and -rich sediments, respectively. This was also consistent with other X-ray microprobe, XAFS and XANES studies conducted in the same sediments, which indicated that betafite C, a U(IV) mineral, was also present in the calcite-poor sediment representing a portion of the background, non-labile and unleachable contaminant U that was presents in this sediment (Shelly Kelly, personal communications).

The calcite-rich paleosol exhibited high sorptive capacity for U(VI) and had effectively arrested the downward migration of the U(VI) vadose zone plume, probably because calcite content in this sediment was so high and adsorption to other soil minerals was insignificant. U(VI)-carbonate aqueous complexes may interact with calcite forming ternary

surface complexes, although studies have shown that U(VI) exhibits limited adsorption to calcite and sorption is reversible (Carroll and Bruno 1991; Elzinga et al. 2004).

A disparate effect was observed in another study conducted with two other soils with 0.1 and 10% calcium carbonate contents, where it was demonstrated that higher concentrations of soil calcium carbonate caused a pronounced suppression of the U(VI) pH-dependent sorption curve in the neutral pH range (Zheng et al. 2003). A study conducted with a Hanford sediment exposed to a calcite saturated solution (Dong et al. 2005), also demonstrated that although calcite was a minor ($\sim 3\%$) component of the silt/clay fraction, carbonate removal from this material caused substantial increases in U(VI) adsorption ($\sim 50\%$).

4 Soil minerals and U(VI) redox reactions

4.1 U as a redox sensitive contaminant

Oxidation–reduction reactions are important in both inorganic and biological processes and regardless of the system under investigation this involves an electron-transfer (ET) mechanism which is integral to the overall redox process. The ET reaction has been the center of considerable experimental study in inorganic, organic, and organometallic systems for the last 50 years. For aqueous redox reactions, three ET reaction mechanisms have been delineated: (1) inner-sphere ET, (2) outer-sphere ET, and (3) diffusion-controlled (Newton 1975; Jordan 1998 and references therein). The most common is the outer-sphere pathway (formally known as Marcus theory) and the ET reaction is typically rate-limiting. The inner-sphere ET process (Traube theory) is unique in that the ET reaction is not the rate limiting step. As one would expect, the diffusion-controlled reaction rate (a special case in Marcus theory) is typically outer-sphere, but is limited only by the rate of formation of encounter complexes because for each collision an ET reaction occurs.

Surface redox reactions usually follow a sequence of reactions or processes, initiated by inner-sphere surface complexation of either the oxidant or the reductant; then a complex forms between the adsorbed species and its counterpart reactant as a precursor to an electron transfer step, after which the ternary surface complex becomes destabilized by the production of newly reduced and oxidized species (Sposito 2004). The adsorbent itself may not participate directly in the redox reaction (Sposito 2004), although there are recent reports in the literature that clearly demonstrate that even structural elements may participate in these heterogeneous redox reactions (Dodge et al. 2002; Missana et al. 2003; Williams and Scherrer 2004). The mechanisms responsible for the catalytic effect of soil mineral or organic surfaces have not been fully explored and understood.

Similar to other elements in the early actinide series (Th–Pu), U can exist at several oxidation states from II to VI with varying degree of reductive potentials through ionization of the electrons of the 5f, 6d and 7s shells. Because of the hard acid character, U prefers to bind to hard bases such as oxygen, and the higher oxidation states (V,VI) cations occur exclusively as dioxide, UO_2^+ and UO_2^{2+}. Uranyl ion is a strong oxidant ($E^0 = 2.6$ V) and undergoes redox reactions with many species.

It is generally believed that the reduction of U(VI) to U(IV) results in the formation of the sparingly soluble U(IV) solids, such as uraninite, in reduced environments (Duff et al. 1999). Because of its sensitivity to varying oxidation/reduction (redox) conditions (natural or manmade) U(VI) often exhibits very complex migration behavior in natural systems. Current scientific understanding of the natural redox systems is inadequate to predict the attenuation mechanisms, rates or the extent of reaction, and future migration pattern of this redox sensitive contaminant.

Many important redox reactions in soils, sediments, and waters are microbially mediated (Wang et al. 2003), and therefore, chemical parameters cannot be used alone to predict reaction rates (Morel and Hering 1993). Direct bacterial reduction of U(VI) has been reported by a number of investigators (Gorby and Lovley 1992; Lovley and Phillips 1992; Fredrickson et al. 2000). These reactions can proceed in systems dominated by soluble U carbonates [e.g. $UO_2(CO_3)_2^{2-}$(aq)]. Additionally, biogenic reduction of U(VI) can be a secondary, heterogeneous reaction resulting from microbially reduced Fe(II) (O'Loughlin et al. 2003) but the efficacy of this mechanisms on uranyl-carbonato complexes is not known. Importantly, introduction of dissolved Ca into these systems

leads to the formation of soluble $Ca_2UO_2(CO_3)_3$ which inhibits microbial reduction (Brooks et al. 2003). While it is not known if this latter species is susceptible to heterogeneous reduction, it is likely that lacking a net charge it has a higher propensity to interact with particle surfaces than its Ca-free, anionic counterparts. The presence of aqueous $Ca_2UO_2(CO_3)_3$ in the pore-waters of many contaminated sites warrants an assessment of the redox reactivity of this molecule.

4.2 Soil mineral role in U(VI) redox reactions

While the redox energetics and kinetics of uranyl coordination complexes in the aqueous phase are relatively well studied (Morris 2002), this appears to be not true for the soil mineral mediated U(VI) reduction reaction. A slow homogeneous reaction may be accelerated in the presence of solids because reactants may be concentrated on surfaces allowing for longer lives of the encounter complexes. Surfaces may also increase the reaction driving force.

Redox processes are by nature a series of coupled reactions, which may in turn be coupled with other reactions (adsorption/desorption, dissolution/precipitation) and processes (hydrologic, physical and chemical) that occur in soils, sediments and vadose zones during the transport of contaminants. This coupling will affect the extent of these reactions in geochemical systems, and the overall mobility of U. The role of soil minerals in the redox reactions that occur in soils, sediments and aquifers is multifarious, and their chemical (sorption capacity, surface charge and composition), and physical properties (with or without expandable layers) are important determinants of the extent of their participation in transport controlled, coupled adsorption/desorption, dissolution/precipitation and redox reactions of contaminants, although the extent of their involvement is not well understood or studied.

Stumm et al. have emphasized the importance of coupled geochemical processes and reactions with the Fe(II) and Fe(III) redox transformations (Stumm 1992; Stumm and Morgan 1996), and numerous studies have shown that sorbed Fe(II) is involved in redox reactions with carbon tetrachloride (Elsner et al. 2004b), pentachloronitrobenzene (Klupinski et al. 2004), polyhalogenated methanes (Pecher et al. 2002), oxime carbamate pesticides (Strathmann and

Stone 2003), and organic contaminants such as 4-chloronitrobenzene and hexachloroethane (Elsner et al. 2004a). The catalytic role of soil minerals in the redox reactions that occur in soils, sediments and aquifers is, therefore, clearly demonstrated in the recent literature (Liger et al. 1999; Strathmann and Stone 2003; Elsner et al. 2004a, 2004b; Fredrickson et al. 2004; Ilton et al. 2004; Klupinski et al. 2004).

Potentially important U(VI) reductants in low-temperature geochemical systems are aqueous and structural Fe(II), sulfides, and organic matter (Liger et al. 1999). Fe(II) is abundant in many suboxic and anoxic soils and sediments (Anderson et al. 1994) and numerous observations indicate that reduction of redox sensitive elements can occur in soils and sediments in the presence of inorganic Fe(II).

Aqueous U(VI) is not involved in homogeneous redox reactions with aqueous Fe(II) in near neutral and basic pH (Liger et al. 1999). However, with Fe(II) sorbed to a surface (Charlet et al. 1998; Liger et al. 1999; Boyanov et al. 2007) or as a constituent in a smectite clay (Giaquinta et al. 1997) and biotite (Ilton et al. 2004), U(VI) reduction proceeds faster. Sorbed or structural Fe(II) may be also present or formed when strong reductants (such as dithionite, H_2S gas and Ca-polysulfide liquid) react with Fe(III) oxides or other soil minerals, such as phyllosilicates.

Heterogeneous, abiotic reduction of U(VI) by Fe(II) has been observed in zero valent iron (Noubactep et al. 2003), mixed Fe(II)/Fe(III) green rust (O'Loughlin et al. 2003), nano-magnetite (Missana et al. 2003) and biotite (Ilton et al. 2004) in acid to circumneutral pH, and in anoxic-CO_2-free systems. Little information is available on U(VI) reduction by these Fe(II)-containing phases in alkaline fluids were anionic uranyl-carbonates and neutral Ca-uranyl-carbonate are the dominant aqueous U(VI) species.

Unlike the kinetically inert Cr(III), oxidation of reduced U(IV) with the intrusion of O_2 may occur in sediments. However, the oxidation of the reduced species appears to be diffusion and residence time controlled. U(IV) oxidation from reduced ISRM sediments shows a slow process that may be confounded by other reduced species (Szecsody et al. 1998). In a more recent study (Moon et al. 2007), reoxidation of microbially reduced U with either O_2 or nitrate supplied as the oxidant, was investigated. They found that U reduction occurred simultaneously with Fe reduction as the dominant electron accepting

process. Both O_2 and nitrate remobilized the majority (88 and 97%, respectively) of the U precipitated during bioreduction within 54 days. Although O_2 is more thermodynamically favorable an oxidant than nitrate, U oxidation by nitrate occurred significantly faster at the beginning of the experiments, due to O_2 reacting more strongly with other reduced compounds (Moon et al. 2007).

Regardless of whether the redox process is homogeneous or heterogeneous, near-field or far-field, or whether the reactive surfaces are neoformed or a natural part of the sediment mineral assemblage, hydrologic flow characteristics will affect reactions, reaction rates, and extent of reaction via the transport of either oxidants or reductants to or away from an Fe(II) source. The processes, reactions and conditions that affect the rate of the surface (soil mineral) mediated redox reactions under advection, mass transfer and/or diffusion limiting condition, are not well studied in natural mixtures of soil minerals.

4.3 Recent findings and future trends

There are interesting developments in the area of U redox reactions in the presence of solid phases. We previously mentioned that in the presence of soil mineral catalysts, the redox reaction may occur on the Fe(II) exchanged surface of a solid phase, or on the surface of a Fe(II)-bearing mineral. However, the explanation for the enhanced reactivity of sorbed Fe(II) remains ambiguous, although recent studies have shed some light on this subject (Boyanov et al. 2007). These authors conducted experiments to gain further insights into the U–Fe redox process at a complexing, non-conducting surface such as carboxyl-functionalized polystyrene. It was reported that in the Fe + surface carboxyl system, a transition from monomeric to oligomeric Fe(II) surface species was observed between pH 7.5 and pH 8.4 (Boyanov et al. 2007). In the U + surface carboxyl system, the U(VI) cation was adsorbed as a mononuclear uranyl-carboxyl complex at both pH 7.5 and 8.4. In the ternary U + Fe + surface carboxyl system, U(VI) was not reduced by the solvated or adsorbed Fe(II) at pH 7.5 over a 4-month period, whereas complete and rapid reduction to U(IV) nanoparticles occurred at pH 8.4 (Boyanov et al. 2007).

Boyanov et al. (2007) also reported that the U(IV) product reoxidized rapidly upon exposure to air, but it was stable over a 4-month period under anoxic conditions. The U(IV)–Fe coordination was consistent with an inner-sphere electron transfer mechanism between the redox centers and involvement of Fe(II) atoms in both steps of the reduction from U(VI) to U(IV). The inability of Fe(II) to reduce U(VI) in solution and at pH 7.5 in the U + Fe + carboxyl system was explained by the formation of a transient, "dead-end" U(V)–Fe(III) complex that blocked the U(V) disproportionation pathway after the first electron transfer. These authors suggested that the increased reactivity at pH 8.4 relative to pH 7.5 could be attributed to the reaction of U(VI) with an Fe(II) oligomer, whereby the bonds between Fe atoms facilitated the transfer of a second electron to the hypothetical U(V)–Fe(III) intermediate, which may explain the commonly observed higher efficiency of uranyl reduction by adsorbed or structural Fe(II) relative to aqueous Fe(II) (Boyanov et al. 2007).

However, recent results have shown that at low Fe(II) concentrations, sorbed Fe(II) species on hematite are transient and quickly undergo interfacial electron transfer with structural Fe(III) (Larese-Casanova and Scherrer 2007), forming a Fe(III) surface coating layer. The formation of a stable, sorbed Fe(II) phase in hematite was observed only at higher Fe(II) concentrations and coincided with the macroscopically observed change in isotherm slope, and with the estimated surface site saturation, suggesting that the finite capacity for interfacial electron transfer is influenced by surface properties (Larese-Casanova and Scherrer 2007).

Definitely, the heterogeneous reduction of U(VI) by sorbed Fe(II) is an important pathway for immobilization of aqueous U(VI) species in subsurface environments, where the homogeneous redox reaction of the aqueous U(VI):Fe(II) couple is slow. However, many questions remain unanswered:

(i)   What is the extent of sorbed U(VI) reduction by sorbed Fe(II) on hematite or other Fe(III) oxides and hydroxide surfaces?

(ii) Is sorbed U(VI) more competitive than structural Fe(III) for the electrons of sorbed Fe(II) on hematite?

(iii) What are the conditions that may control the competition between sorbed U(VI) and structural Fe(III) for sorbed Fe(II) electrons?

(iv) How do other Fe(III) oxides behave?

5 In lieu of conclusions

U(VI) interactions with the soil minerals is an exciting area of research which is evolving on a daily basis. Studies conducted over the last few years have provided evidence for such interactions and have described U geochemical behavior in complex natural systems under different physical, biogeochemical, hydrological, and reducing or oxidizing conditions. This review covers important aspects of the aqueous U(VI) interactions with the soil minerals in natural systems under oxic and slightly alkaline conditions.

The physical and chemical complexity of the natural systems complicate the development of a mechanistic understanding of the interactions of the aqueous U(VI) species with soil minerals. Nevertheless information from carefully designed and executed experiments conducted with such materials provide helpful information to better understand the nature of aqueous U(VI) interactions with soil minerals, and to predict system's behavior and U contaminant mobility and transport. Areas that warrant further attention and study are also provided in this review paper.

References

Allison JD, Brown DS, Novo-Gradac KJ (1991) MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: version 3.0 user's manual. Environmental Protection Agency, Athens

Allison JD, Brown DS, Novo-Gradac KJ (1998) MINTEQA2/PRODEFA2, A geochemical assessment model for environmental systems: user manual supplement for version 4.0. Environmental Protection Agency, Athens

Ames LL, McGarrah JE, Walker BA (1983) Sorption of uranium and radium by biotite, muscovite, and phlogopite. Clays Clay Miner 31:343–351. doi:10.1346/CCMN.1983.0310503

Anderson LD, Kent DB, Davis JA (1994) Batch experiments characterizing the reduction of Cr(VI) using suboxic material from a mildly reducing sand and gravel aquifer. Environ Sci Technol 28:178–185. doi:10.1021/es00050a025

Anderson RT, Vrionis HA, Ortiz-Bernad I, Resch CT, Long PE, Dayvault R et al (2003) Stimulating the in situ activity of *Geobacter* species to remove uranium from the groundwater of a uranium-contaminated aquifer. Appl Environ Microbiol 69:5884–5891. doi:10.1128/AEM.69.10.5884-5891.2003

Arai Y, McBeath M, Bargar JR, Joye J, Davis JA (2006) Uranyl adsorption and surface speciation at the imogolite-water interface: self-consistent spectroscopic and surface complexation models. Geochim Cosmochim Acta 70:2492–2509. doi:10.1016/j.gca.2006.02.013

Arai Y, Marcus MK, Tamura N, Davis JA, Zachara JM (2007) Spectroscopic evidence for uranium bearing precipitates in vadose zone sediments at the Hanford 300-area site. Environ Sci Technol 41:4633–4639. doi:10.1021/es062196u

Arnold T, Zorn T, Benhard G, Nitsche H (1998) Sorption of uranium(VI) onto phyllite. Chem Geol 151:129–141. doi:10.1016/S0009-2541(98)00075-8

Arnold T, Zorn T, Zanker H, Bernhard G, Nitsche H (2001) Sorption behavior of U(VI) on phyllite: experiments and modeling. J Contam Hydrol 47:219–231. doi:10.1016/S0169-7722(00)00151-0

Arnold T, Utsunomiya S, Geipel G, Ewing RC, Baumann N, Brendler V (2006) Adsorbed U(VI) surface species on muscovite identified by laser fluorescence spectroscopy and transmission electron microscopy. Environ Sci Technol 40:4646–4652. doi:10.1021/es052507l

Baik MH, Cho WJ, Han PS (2004a) Sorption of U(VI) onto granite surfaces: a kinetic approach. J Radioanal Nucl Chem 260:495–502. doi:10.1023/B:JRNC.0000028207.55356.ec

Baik MH, Hyun SP, Cho WJ, Hahn PS (2004b) Contribution of minerals to the sorption of U(VI) on granite. Radiochim Acta 92:663–669. doi:10.1524/ract.92.9.663.54980

Bargar JR, Reitmeyer R, Davis JA (1999) Spectroscopic confirmation of uranium(VI)-carbonato adsorption complexes on hematite. Environ Sci Technol 33:2481–2484. doi:10.1021/es990048g

Bargar JR, Reitmeyer R, Lenhart JJ, Davis JA (2000) Characterization of U(VI)-carbonate ternary complexes on hematite: EXAFS and electrophoretic mobility measurements. Geochim Cosmochim Acta 64:2737–2749. doi:10.1016/S0016-7037(00)00398-7

Baumann N, Brendler V, Arnold T, Geipel G, Bernhard G (2005) Uranyl sorption onto gibbsite studied by time-resolved laser-induced fluorescence spectroscopy (TRUS). J Coll Inter Sci 290:318–324

Benes P, Kratzer K, Vlckova S, Sebestova E (1998) Adsorption of uranium on clay and the effect of humic substances. Radiochim Acta 82:367–373

Bernhard G, Geipel G, Reich T, Brendler V, Amayri S, Nitsche H (2001) Uranyl(VI) carbonate complex formation: validation of the $Ca_2UO_2(CO_3)_3$ (aq.) species. Radiochim Acta 89:511–518. doi:10.1524/ract.2001.89.8.511

Bigham JM, Fitzpatrick RW, Schulze DG (2002) Iron oxides. In: Dixon JB, Schulze DG (eds) Soil mineralogy with environmental applications, vol SSSA Book Series No. 7. Soil Science Society of America, Inc., Madison, WI, pp 323–366

Bond DL, Davis JA, Zachara JM (2007) Uranium(VI) release from contaminated vadose zone sediments: estimation of potential contributions from dissolution and desorption. In: Barnett MO, Kent DB (eds) Adsorption of metals by Geomedia II. Academic Press, San Diego, pp 379–420

Bostick BC, Fendorf S, Barnett MO, Jardine PM, Brooks SC (2002) Uranyl surface complexes formed on subsurface media from DOE facilities. Soil Sci Soc Am J 66:99–108

Boyanov MI, O'Loughlin EJ, Roden EE, Fein JB, Kemner KM (2007) Adsorption of Fe(II) and U(VI) to carboxyl-functionalized microspheres: the influence of speciation on uranyl reduction studied by titration and XAFS. Geochim Cosmochim Acta 71:1898–1912. doi:10.1016/j.gca.2007.01.025

Braithwaite A, Livens FR, Richardson S, Howe MT, Goulding KWT (1997) Kinetically controlled release of uranium from soils. Eur J Soil Sci 48:661–673. doi:10.1046/j.1365-2389.1997.00121.x

Braithwaite A, Richardson S, Moyes LN, Livens FR, Bunker DJ, Hughes CR (2000) Sorption kinetics of uranium-238 and neptunium-237 on glacial sediment. Czech J Phys 50:265–269. doi:10.1023/A:1022842808820

Brooks SC, Fredrickson JK, Carroll SL, Kennedy DW, Zachara JM, Plymale AE et al (2003) Inhibition of bacterial U(VI) reduction by calcium. Environ Sci Technol 37:1850–1858. doi:10.1021/es0210042

Carroll SA, Bruno J (1991) Mineral-solution interactions in the U(VI)-CO_2-H_2O system. Radiochim Acta 52(53):187–193

Carroll SA, Bruno J, Petit J-C, Dran J-C (1992) Interactions of U(VI), Nd, and Th(IV) at the calcite-solution interface. Radiochim Acta 58(59):245–252

Catalano JG, Brown GE (2004) Analysis of uranyl-bearing phases by EXAFS spectroscopy: interferences, multiple scattering, accuracy of structural parameters, and spectral differences. Am Min 89:1004–1021

Catalano JG, Brown GE (2005) Uranyl adsorption onto montmorillonite: evaluation of binding sites and carbonate complexation. Geochim Cosmochim Acta 69:2995–3005. doi:10.1016/j.gca.2005.01.025

Catalano JG, McKinley JP, Zachara JM, Heald SM, Smith SC, Brown GE (2006) Changes in uranium speciation through a depth sequence of contaminated Hanford sediments. Environ Sci Technol 40:2517–2524. doi:10.1021/es0520969

Chadwick O, Nettleton WD (1990) Micromorphologic evidence of adhesive and cohesive forces in soil cementation. Soil Sci 19:207–212. doi:10.1016/S0166-2481(08)70332-5

Charlet L, Silvester E, Liger E (1998) N-compound reduction and actinide immobilization in surficial fluids by Fe(II):the surface $=Fe^{II}OFe^{II}OH^0$ species, as major reductant. Chem Geol 151:85–93. doi:10.1016/S0009-2541(98)00072-2

Cheng T, Barnett MO, Roden EE, Zhuang JL (2006) Effects of solid-to-solution ratio on uranium(VI) adsorption and its implications. Environ Sci Technol 40:3243–3247. doi:10.1021/es051771b

Clark DL, Hobart DE, Neu MP (1995) Actinide carbonate complexes and their importance in actinide environmental chemistry. Chem Rev 95:25–48. doi:10.1021/cr00033a002

Cornell RM, Schwertmann U (1996) The iron oxides. VCH Publ, Weinheim

Cornell RM, Schwertmann U (2003) The iron oxides. Structure, properties, reactions, occurrences and uses, 2nd edn. WILEY-VCH

Culver TB, Hallisey SP, Sahoo D, Deitsch JJ, Smith JA (1997) Modeling the desorption of organic contaminants from long-term contaminated soil using distributed mass transfer rates. Environ Sci Technol 31:1581–1588. doi:10.1021/es9600946

Curtis GP, Fox P, Kohler M, Davis JA (2004) Comparison of in situ uranium K_d values with a laboratory determined surface complexation model. Appl Geochem 19:1643–1653. doi:10.1016/j.apgeochem.2004.03.004

Curtis GP, Davis JA, Naftz DL (2006) Simulation of reactive transport of uranium(VI) in groundwater with variable chemical conditions. Water Resour Res 42:W04404. doi:10.1029/2005WR003979

Davis JA (2001) Surface complexation modeling of uranium(VI) adsorption on natural mineral assemblages. U.S. Geological Survey, NUREG/CR–6708

Davis JA, Curtis GP (2003) Application of surface complexation modeling to describe uranium(VI) adsorption and retardation at the uranium mill tailings site at Naturita, Colorado. NUREG Report CR-6820. U.S. Nuclear Regulatory Commission, Rockville

Davis JA, Meece DE, Kohler M, Curtis GP (2004) Approaches to surface complexation modeling of Uranium(VI) adsorption on aquifer sediments. Geochim Cosmochim Acta 68:3621–3641. doi:10.1016/j.gca.2004.03.003

Davis JA, Curtis GP, Wilkins MJ, Kohler M, Fox P, Naftz DL et al (2006) Processes affecting transport of uranium in a suboxic aquifer. Phys Chem Earth 31:548–555

de Jong WA, Apra E, Windus TL, Nichols JA, Harrison RJ, Gutowski KE et al (2005) Complexation of the carbonate, nitrate, and acetate anions with the uranyl dication: density functional studies with relativistic effective core potentials. J Phys Chem A 109:11568–11577. doi:10.1021/jp0541462

Dodge CJ, Francis AJ, Gillow JB, Halada GP, Eng C, Clayton CR (2002) Association of uranium with iron oxides typically formed on corroding steel surfaces. Environ Sci Technol 36:3504–3511. doi:10.1021/es011450+

Dong WM, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) using anion exchange method. Environ Sci Technol 40:4689–4695. doi:10.1021/es0606327

Dong W, Ball WP, Liu C, Wang Z, Stone AT, Bai J et al (2005) Influence of calcite and dissolved calcium on uranium(VI) sorption to a Hanford subsurface sediment. Environ Sci Technol 39:7949–7955. doi:10.1021/es0505088

Dong WM, Xie GB, Miller TR, Franklin MP, Oxenberg TP, Bouwer EJ et al (2006) Sorption and bioreduction of hexavalent uranium at a military facility by the Chesapeake Bay. Environ Pollut 142:132–142. doi:10.1016/j.envpol.2005.09.008

Duff MC, Amrhein C (1996) Uranium(VI) adsorption on goethite and soil in carbonate solutions. Soil Sci Soc Am J 60:1393–1400

Duff MC, Hunter DB, Bertsch PM, Amrhein C (1999) Factors influencing uranium reduction and solubility in evaporation pond sediments. Biogeochem 45:95–114

Duff MC, Coughlin JU, Hunter DB (2002) Uranium co-precipitation with iron oxide minerals. Geochim Cosmochim Acta 66:3533–3547. doi:10.1016/S0016-7037(02)00953-5

Elsner M, Schwarzenbach RP, Haderlein SB (2004a) Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. Environ Sci Technol 38:799–807. doi:10.1021/es0345569

Elsner M, Haderlein SB, Kellerhais T et al (2004b) Mechanisms and products of surface-mediated reductive dehalogenation of carbon tetrachloride by Fe(II) on goethite. Environ Sci Technol 38:2058–2066. doi:10.1021/es034741m

Elzinga EJ, Tait CD, Reeder RJ, Rector KD, Donohoe RJ, Morris DE (2004) Spectroscopic investigation of U(VI) sorption at the calcite-water interface. Geochim Cosmochim Acta 68:2437–2448. doi:10.1016/j.gca.2003.09.023

Finch RJ, Murakami T (1999) Systematics, Paragenesis of U Minerals. In: Burns PC, Finch RJ (eds) Uranium: mineralogy, geochemistry and the environment, vol 38. Mineralogical Society of America, Washington, pp 91–179

Fox PM, Davis JA, Zachara JM (2006) The effect of calcium on aqueous uranium(VI) speciation and adsorption to ferrihydrite and quartz. Geochim Cosmochim Acta 70:1379–1387. doi:10.1016/j.gca.2005.11.027

Fredrickson JK, Zachara JM, Kennedy DW, Duff MC, Gorby YA, Li SMW et al (2000) Reduction of U(VI) in goethite (alpha-FeOOH) suspensions by a dissimilatory metal-reducing bacterium. Geochim Cosmochim Acta 64:3085–3098. doi:10.1016/S0016-7037(00)00397-5

Fredrickson JK, Zachara JM, Kennedy DW, Kukkadapu R, McKinley JP, Heald SM et al (2004) Reduction of TcO_4^- by sediment-associated biogenic Fe(II). Geochim Cosmochim Acta 68:3171–3187. doi:10.1016/j.gca.2003.10.024

Froideval A, Del Nero M, Barillon R, Hommet J, Mignot G (2003) pH dependence of uranyl retention in a quartz/solution system: an XPS study. J Coll Inter Sci 266:221–235. doi:10.1016/S0021-9797(03)00528-9

Fuller CC, Bargar JR, Davis JA, Piana MJ (2002) Mechanisms of uranium interactions with hydroxyapatite: implications for groundwater remediation. Environ Sci Technol 36:158–165. doi:10.1021/es0108483

Fuller CC, Bargar JR, Davis JA (2003) Molecular-scale characterization of uranium sorption by bone apatite materials for a permeable reactive barrier demonstration. Environ Sci Technol 37:4642–4649. doi:10.1021/es0343959

Gabriel U, Gaudet JP, Spadini L, Charlet L (1998) Reactive transport of uranyl in a goethite column: an experimental and modeling study. Chem Geol 151:107–128. doi:10.1016/S0009-2541(98)00074-6

Gamerdinger AP, Kaplan DI (2000) Application of a continuous-flow centrifugation method for solute transport in disturbed, unsaturated sediments and illustration of mobile-immobile water. Water Resour Res 36:1747–1755. doi:10.1029/2000WR900063

Gamerdinger AP, Kaplan DI, Wellman DM, Serne JN (2001a) Two-region flow and decreased sorption of uranium(VI) during transport in Hanford groundwater and unsaturated sands. Water Resour Res 37:3155–3162. doi:10.1029/2001WR000247

Gamerdinger AP, Kaplan DI, Wellman DM, Serne JN (2001b) Two-region flow and rate-limited sorption of uranium(VI) during transport in an unsaturated silt loam. Water Resour Res 37:3147–3153. doi:10.1029/2001WR000244

Geipel G, Reich T, Brendler V, Bernhard G, Nitsche H (1997) Laser and X-ray spectroscopic studies of uranium-calcite interface phenomena. J Nucl Mater 248:408–411. doi:10.1016/S0022-3115(97)00136-0

Giammar DE, Hering JG (2001) Time scales for sorption-desorption and surface precipitation of uranyl on goethite.

Environ Sci Technol 35:3332–3337. doi:10.1021/es0019981

Giaquinta DM, Soderholm L, Yuchs SE, Wasserman SR (1997) The speciation of uranium in a smectite clay: evidence for catalysed uranyl reduction. Radiochim Acta 76:113–121

Gorby YA, Lovley DR (1992) Enzymatic uranium precipitation. Environ Sci Technol 26:205–207. doi:10.1021/es00025a026

Gorman-Lewis D, Elias PE, Fein JB (2005) Adsorption of aqueous uranyl complexes onto *Bacillus subtilis* cells. Environ Sci Technol 39:4906–4912. doi:10.1021/es047957c

Greathouse JA, Cygan RT (2005) Molecular dynamics simulation of uranyl(VI) adsorption equilibria onto an external montmorillonite surface. Phys Chem Chem Phys 7:3580–3586. doi:10.1039/b509307d

Greathouse JA, Cygan RT (2006) Water structure and aqueous uranyl(VI) adsorption equilibria onto external surfaces of beidellite, montmorillonite, and pyrophyllite: results from molecular simulations. Environ Sci Technol 40:3865–3871. doi:10.1021/es052522q

Greathouse JA, O'Brien RJ, Bemis G, Pabalan RT (2002) Molecular dynamics study of aqueous uranyl interactions with quartz(010). J Phys Chem B 106:1646–1655. doi:10.1021/jp013250q

Grenthe I, Fuger J, Konings RJM, Lemire RJ, Muller AB, Nguyen-Trung C et al (1992) Chemical thermodynamics of uranium. North Holland, Amsterdam

Haggerty R, Gorelick SM (1995) Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. Water Resour Res 31:2383–2400

Haggerty R, Gorelick SM (1998) Modeling mass transfer processes in soil column with pore-scale heterogeneity. Soil Sci Soc Am J 62:62–74

Haggerty R, Harvey CF, von Schwerin CF, Meigs LC (2004) What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results. Water Resour Res 40:W01510. doi:10.1029/2002WR001716

Harvey CF, Gorelick SM (1995) Temporal moment-generating equations: modeling transport and mass transfer in heterogeneous aquifers. Water Resour Res 31:1895–1911. doi:10.1029/95WR01231

Harvey JW, Saiers JE, Newlin JT (2005) Solute transport and storage mechanisms in wetlands of the Everglades, south Florida. Water Resour Res 41(W05009):1–14. doi:10.1029/2004WR003507

Hemond HF, Fechner-Levy EJ (2000) Chemical fate and transport in the environment. Academic Press, San Diego

Ho CH, Miller NH (1986) Adsorption of uranyl species from bicarbonate solution onto hematite particles. J Colloid Interface Sci 110:165–171. doi:10.1016/0021-9797(86)90365-6

Hollenbeck KJ, Harvey CF, Haggerty R, Werth CJ (1999) A method for estimating distribution of mass transfer rate coefficients with application to purging and batch experiments. J Contam Hydrol 37:367–388. doi:10.1016/S0169-7722(98)00165-X

Hsi CD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxides: application of the surface complexation site-binding model. Geochim Cosmochim Acta 49:1931–1941. doi:10.1016/0016-7037(85)90088-2

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 250:55–62. doi:10.1023/A:1013212130177

Ilton ES, Haiduc A, Moses CO, Heald SM, Elbert DC, Veblen DR (2004) Heterogeneous reduction of uranyl by micas: crystal chemical and solution controls. Geochim Cosmochim Acta 68:2417–2435. doi:10.1016/j.gca.2003.08.010

Ilton ES, Qafoku NP, Liu CX, Moore DA, Zachara JM (2008) Advective removal of intraparticle uranium from contaminated Vadose zone sediments, Hanford, US. Environ Sci Technol 42:1565–1571. doi:10.1021/es071113m

Jang JH, Dempsey BA, Burgos WD (2007) A model-based evaluation of sorptive reactivities of hydrous ferric oxide and hematite for U(VI). Environ Sci Technol 41:4305–4310. doi:10.1021/es070068f

Jordan RB (1998) Reaction mechanisms of inorganic and organometallic systems, 2nd edn. Oxford University Press Oxford, New York

Kalmykov SN, Choppin GR (2000) Mixed $Ca^{2+}/UO_2^{2+}/CO_3^{2-}$ complex formation at different ionic strengths. Radiochim Acta 88:603–606. doi:10.1524/ract.2000.88.9-11.603

Kampf N, Scheinost AC, Schulze DG (2000) Oxide minerals. In: Sumner ME (ed) Handbook of soil science. CRC Press, Boca Raton

Kaplan DI, Gervais TL, Krupka KM (1998) Uranium(VI) sorption to sediments under high pH and ionic strength conditions. Radiochim Acta 80:201–211

Kelly SD, Newville M, Cheng L, Kemner KM, Sutton SR, Fenter P et al (2003) Uranyl incorporation in natural calcite. Environ Sci Technol 37:1284–1287. doi:10.1021/es025962f

Kelly SD, Kemner KM, Brooks SC (2007) X-ray absorption spectroscopy identifies calcium-uranyl-carbonate complexes at environmental concentrations. Geochim Cosmochim Acta 71:821–834. doi:10.1016/j.gca.2006.10.013

Kilislioglu A, Bilgin B (2002) Adsorption of uranium on halloysite. Radiochim Acta 90:155–160. doi:10.1524/ract.2002.90.3_2002.155

Klupinski TP, Chin YP, Traina SJ (2004) Abiotic degradation of pentachloronitrobenzene by Fe(II): reaction on goethite and iron oxide nanoparticles. Environ Sci Technol 38:4353–4360. doi:10.1021/es035434j

Kohler M, Curtis GP, Kent DB, Davis JA (1996) Experimental investigation and modeling of uranium(VI) transport under variable chemical conditions. Water Resour Res 32:3539–3551

Kohler M, Curtis GP, Meece DE, Davis JA (2004) Methods for estimating adsorbed uranium(VI) and distribution coefficients of contaminated sediments. Environ Sci Technol 38:240–247. doi:10.1021/es0341236

Kohut CK, Warren CJ (2002) Chlorites. In: Dixon JB, Schulze DG (eds) Soil minerals with environmental applications. Soil Science Society of America, Inc., Madison, pp 531–584

Kowal-Fouchard A, Drot R, Simoni E, Ehrhardt JJ (2004) Use of spectroscopic techniques for uranium(VI)/montmorillonite interaction modeling. Environ Sci Technol 38:1399–1407. doi:10.1021/es0348344

Krepelova A, Sachs S, Bernhard G (2006) Uranium(VI) sorption onto kaolinite in the presence and absence of humic acid. Radiochim Acta 94:825–833. doi:10.1524/ract.2006.94.12.825

Krepelova A, Brendler V, Sachs S, Baumann N, Bernhard G (2007) U(VI)-kaolinite surface complexation in absence and presence of humic acid studied by TRLFS. Environ Sci Technol 41:6142–6147. doi:10.1021/es070419q

Langmuir D (1997) Aqueous environmental geochemistry. Prentice Hall, Upper Saddle River

Larese-Casanova P, Scherrer MM (2007) Fe(II) sorption on hematite: new insights based on spectroscopic measurements. Environ Sci Technol 41:471–477. doi:10.1021/es0617035

Lefevre G, Noinville S, Fedoroff M (2006) Study of uranyl sorption onto hematite by in situ attenuated total reflection-infrared spectroscopy. J Coll Inter Sci 296:608–613. doi:10.1016/j.jcis.2005.09.016

Li Z, Brusseau ML (2000) Nonideal transport of reactive solutes in heterogeneous porous media. 6. Microscopic and macroscopic approaches for incorporating heterogeneous rate-limited mass transfer. Water Resour Res 36:2853–2867. doi:10.1029/2000WR900089

Li Z, Barry DA, Culligan-Hensley PJ, Bajracharya K (1994) Mass transfer in soils with local stratification of hydraulic conductivity. Water Resour Res 30:2891–2900. doi:10.1029/94WR01218

Lichtner PC (1993) Scaling properties of time-space kinetic mass-transport equations and the local equilibrium limit. Am J Sci 293:257–296

Lichtner PC (1996) Continuum formulation of multicomponent-multiphase reactive transport. Reactive transport in porous media, vol 34. pp 1–81

Lichtner PC, Carey JW (2006) Incorporating solid solutions in reactive transport equations using a kinetic discrete-composition approach. Geochim Cosmochim Acta 70:1356–1378. doi:10.1016/j.gca.2005.11.028

Liger E, Charlet L, Van Cappellen P (1999) Surface catalysis of uranium(VI) reduction by iron(II). Geochim Cosmochim Acta 63:2939–2955. doi:10.1016/S0016-7037(99)00265-3

Lindberg JW, Peterson RE (2004) 300-FF-5 operable unit, Chapter 1.12 PNNL-14548. Pacific Northwest National Laboratory, Richland

Liu CX (2007) An ion diffusion model in semi-permeable clay materials. Environ Sci Technol 41:5403–5409. doi:10.1021/es0624117

Liu C, Zachara JM, Qafoku OS, McKinley JP, Heald SM, Wang Z (2004a) Dissolution of uranyl microprecipitates in subsurface sediments at Hanford Site, WA. Geochim Cosmochim Acta 68:4519–4537. doi:10.1016/j.gca.2004.04.017

Liu CX, Zachara JM, Felmy A, Gorby Y (2004b) An electrodynamics-based model for ion diffusion in microbial polysaccharides. Colloids Surf B Biointerfaces 38:55–65. doi:10.1016/j.colsurfb.2004.08.003

Liu C, Zachara JM, Yantasee W, Majors PD, McKinley JP (2006) Microscopic reactive diffusion of uranium in the contaminated sediments at the Hanford site, USA: characterization and modeling. Water Resour Res 42(12):W12420. doi:10.1029/2006WR005031

Livens FR, Jones MJ, Hynes AJ, Charnock JM, Mosselmans JFW, Hennig C et al (2004) X-ray absorption

spectroscopy studies of reactions of technetium, uranium, and neptunium with mackinawite. J Environ Radioact 74:211–219. doi:10.1016/j.jenvrad.2004.01.012

Lovley DR, Phillips EJP (1992) Bioremediation of uranium contamination with enzymatic uranium reduction. Environ Sci Technol 26:2228–2234. doi:10.1021/es00035a023

Mason CFV, Turney WRJR, Thomson BM, Lu N, Longmire PA, Chisholm-Brause CJ (1997) Carbonate leaching of uranium from contaminated soils. Environ Sci Technol 31:2707–2711. doi:10.1021/es960843j

McKinley JP, Zachara JM, Liu CX, Heald SC, Prenitzer BI, Kempshall BW (2006) Microscale controls on the fate of contaminant uranium in the vadose zone, Hanford Site, Washington. Geochim Cosmochim Acta 70:1873–1887. doi:10.1016/j.gca.2005.10.037

Meece DE, Benninger LK (1993) The coprecipitation of Pu and other radionuclides with CaCO$_3$. Geochim Cosmochim Acta 57:1447–1458. doi:10.1016/0016-7037(93)90005-H

Missana T, Maffiotte C, Garcia-Gutierrez M (2003) Surface reactions kinetics between nanocrystalline magnetite and uranyl. J Coll Inter Sci 261:154–160. doi:10.1016/S0021-9797(02)00227-8

Monger HC, Kelly EE (2002) Silica minerals. In: Dixon JB, Schulze DG (eds) Soil mineralogy with environmental applications. Soil Science Society of America, Inc., Madison, pp 611–636

Moon HS, Komlos J, Jaffe PR (2007) Uranium reoxidation in previously bioreduced sediment by dissolved oxygen and nitrate. Environ Sci Technol 41:4587–4592. doi:10.1021/es063063b

Morel FMM, Hering JG (1993) Principles and applications of aquatic chemistry. Wiley, New York

Morris DE (2002) Redox energetics and kinetics of uranyl coordination complexes in aqueous solution. Inorg Chem 41:3542–3547. doi:10.1021/ic0201708

Morse JW, Shanbbag PM, Saito A, Choppin GR (1984) Interaction of uranyl ions in carbonate media. Chem Geol 42:85–99. doi:10.1016/0009-2541(84)90007-X

Moyes LN, Parkman RH, Charnock JM, Vaughan DJ, Livens FR, Hughes CR et al (2000) Uranium uptake from aqueous solution by interaction with goethite, lepidocrocite, muscovite, and maskinawite: an X-ray absorption spectroscopy study. Environ Sci Technol 34:1062–1068. doi:10.1021/es990703k

Muckett C, Sherman D, Rognarsdottir V (1998) The adsorption of uranium onto goethite and clinochlore, pp 118–119. The Synchrotron Radiation Source Scientific Reports, Geology and Mineralogy: http://srs.dl.ac.uk/Annual_Reports/AnRep97_98/Annexe/118_Muskett.pdf

Murakami T, Sato T, Ohnuki T, Isobe H (2005) Field evidence for uranium nanocrystallization and its implications for uranium transport. Chem Geol 221:117. doi:10.1016/j.chemgeo.2005.04.004

Neal AL, Amonette JE, Peyton BM, Geesey GG (2004) Uranium complexes formed at hematite surfaces colonized by sulfate-reducing bacteria. Environ Sci Technol 38:3019–3027. doi:10.1021/es030648m

Newton TW (1975) The kinetics of the oxidation-reduction reactions of uranium, neptunium, plutonium, and americium in aqueous solutions. ERDA Critical Review Series (TID-26506), NTIS, Springfield, Virginia, ERDA Critical Review Series (TID-26506), NTIS, Springfield, Virginia

Noubactep C (2005) Effect of selected ligands on the U(VI) immobilization by zerovalent iron. J Radioanal Nucl Chem 267:13–19. doi:10.1007/s10967-006-0003-2

Noubactep C, Meinrath G, Dietrich P, Merkel B (2003) Mitigating uranium in groundwater: prospects and limitations. Environ Sci Technol 37:4304–4308. doi:10.1021/es034296v

Noubactep C, Meinrath G, Merkel BJ (2005) Investigating the mechanism of uranium removal by zerovalent iron. Environ Chem 2:235–242. doi:10.1071/EN05003

Noubactep C, Sonnefeld J, Sauter M (2006) Uranium release from a natural rock under near-natural oxidizing conditions. J Radioanal Nucl Chem 267:591–602. doi:10.1007/s10967-006-0092-y

O'Loughlin EJ, Kelly SD, Cook RE, Csencsits R, Kemner KM (2003) Reduction of uranium(VI) by mixed iron(II)/iron(III) hydroxide (green rust): formation of UO$_2$ nanoparticles. Environ Sci Technol 37:721–727. doi:10.1021/es0208409

Pabalan RT, Turner DR (1997) Uranium(+6) sorption on montmorillonite: experimental and surface complexation modeling study. Aquat Geochem 2:203–226. doi:10.1007/BF00119855

Pabalan RT, Turner DR, Bertetti FP, Prikryl JD (1998) Uranium(VI) sorption onto selected mineral surfaces. In: Jenne EA (ed) Adsorption of metals by geomedia. Academic Press, San Diego, pp 99–130

Payne TE, Airey PL (2006) Radionuclide migration at the Koongarra uranium deposit, Northern Australia—Lessons from the Alligator Rivers analogue project. Phys Chem Earth 31:572–586

Payne TE, Lumpkin GR, Waite TD (1998) Uranium(VI) adsorption on model minerals. In: Jenne EA (ed) Adsorption of metals by geomedia. Academic Press, San Diego, pp 75–99

Payne TE, Davis JA, Lumpkin GR, Chisari R, Waite TD (2004) Surface complexation model of uranyl sorption on Georgia kaolinite. Appl Clay Sci 26:151–162. doi:10.1016/j.clay.2003.08.013

Pecher K, Haderlein SB, Schwarzenbach RP (2002) Reduction of polyhalogenated methanes by surface-bound Fe(II) in aqueous suspensions of iron oxides. Environ Sci Technol 36:1734–1741. doi:10.1021/es011191o

Phillippi JM, Loganathan VA, McIndoe MJ, Barnett MO, Clement TP, Roden EE (2007) Theoretical solid/solution ratio effects on adsorption and transport: uranium(VI) and carbonate. Soil Sci Soc Am J 71:329–335. doi:10.2136/sssaj2006.0159

Prikryl JD, Jain A, Turner DR, Pabalan RT (2001) Uranium(VI) sorption behavior on silicate mineral mixtures. J Contam Hydrol 47:241–253. doi:10.1016/S0169-7722(00)00153-4

Qafoku NP, Amonette JE (2003) Iron oxides. In: Lal R (ed) Encyclopedia of soil science, vol. Marcel Dekker, Inc., New York. doi:10.1081/E-ESS 120006595

Qafoku NP, Ainsworth CC, Szecsody JE, Bish DL, Young JS, McCready DE et al (2003) Aluminum effect on dissolution and precipitation under hyperalkaline conditions: II. Solid phase transformations. J Environ Qual 32:2364–2372

Qafoku NP, Zachara JM, Liu C, Gassman PL, Qafoku OS, Smith SC (2005) Kinetic desorption and sorption of U(VI) during reactive transport in a contaminated Hanford sediment. Environ Sci Technol 39:3157–3165. doi:10.1021/es048462q

Qafoku NP, Zachara JM, Liu C, Smith SC, Kukkadapu R, Gassman P et al (2008a) Factors controlling U(VI) adsorption and desorption rate and extent in two subsurface sediments of common provenance. Geochim Cosmochim Acta (to be submitted)

Qafoku NP, Zachara JM, Liu C, Wang Z, Arey B, Gassman P et al (2008b) Evaluation of U(VI) mobility in advancing and retreating zones of a deep vadose zone plume: the role of natural calcite. Geochim Cosmochim Acta (to be submitted)

Read D, Lawless TA, Sims RJ, Butter KR (1993) Uranium migration through intact sandstone cores. J Contam Hydrol 13:277–289. doi:10.1016/0169-7722(93)90066-2

Reeder RJ, Nugent M, Lamble GM, Tait CD, Morris DE (2000) Uranyl incorporation into calcite and aragonite: XAFS and luminescence studies. Environ Sci Technol 34:638–644. doi:10.1021/es990981j

Reeder RJ, Nugent M, Tait CD, Morris DE, Heald SM, Beck KM et al (2001) Coprecipitation of uranium(VI) with calcite: XAFS, micro-XAS, and luminescence characterization. Geochim Cosmochim Acta 65:3491–3503. doi:10.1016/S0016-7037(01)00647-0

Reeder RJ, Elzinga EJ, Tait CD, Rector KD, Donohoe RJ, Morris DE (2004) Site-specific incorporation of uranyl carbonate species at the calcite surface. Geochim Cosmochim Acta 68:4799–4808. doi:10.1016/j.gca.2004.05.031

Reedy OC, Jardine PM, Wilson GV, Selim HM (1996) Quantifying the diffuse mass transfer of nonreactive solute in columns of fractured saprolite using flow interruption. Soil Sci Soc Am J 60:1376–1384

Reich T, Moll H, Arnold T, Denecke MA, Henning C, Geipel G et al (1998) An EXAFS study of uranium(VI) sorption onto silica gel and ferrihydrite. J Electron Spectrosc Relat Phenom 96:237–243. doi:10.1016/S0368-2048(98)00242-4

Riley RG, Zachara JM, Wobber FJ (1992) Chemical contaminants on DOE lands and selection of contaminant mixtures for subsurface science research; DOE/ER-0547T DOE/ER-0547T. U.S. Department of Energy, Office of Energy Research, Washington, DC

Rosentreter JJ, Quarder HS, Smith RW, McLing T (1998) Uranium sorption onto natural sands as a function of sediment characteristics and solution pH. In: Jenne EA (ed) Adsorption of metals by geomedia. Academic Press, San Diego, pp 181–208

Rovira M, El Aamrani FZ, Duro L, Casas I, de Pablo J, Brouno J et al (2000) Experimental study and modeling of uranium(VI) transport through ferrous olivine rock columns. Radiochim Acta 88:6665–6671. doi:10.1524/ract.2000.88.9-11.665

Rovira M, El Aamrani S, Duro L, Gimenez J, de Pablo J, Bruno J (2007) Interaction of uranium with in situ anoxically generated magnetite on steel. J Hazard Mater 147:726–731. doi:10.1016/j.jhazmat.2007.01.067

Savenko AV (2001) Sorption of UO_2^{2+} on calcium carbonate. Radiochemistry 43:193–196. doi:10.1023/A:1012827617901

Schulze DG (2002) An introduction of soil mineralogy. In: Dixon JB, Schulze DG (eds) Soil mineralogy with environmental applications. Soil Science Society of America, Inc., Madison, pp 1–36

Schwertmann U, Taylor RM (1989) Iron oxides. In: Dixon JB, Weed SB (eds) Minerals in soil environments. Soil Science Society of America, Madison

Serne RJ, Schaef HT, Bjornstad BN, Williams BA, Lanigan DC, Horton DG et al (2001) Characterization of uncontaminated sediments from the Hanford Reservation-RCRA borehole core and composite samples PNNL-2001-1. Pacific Northwest National Laboratory, Richland

Serne JN, Brown CF, Schaef HT, Pierce EM, Lindberg MJ, Wang Z et al (2002) 300 Area uranium leach and adsorption project PNNL-14022. Pacific Northwest National Laboratory, Richland

Serne JN, Bjornstad BN, Horton DG, Lanigan DC, Lindenmeier CW, Lindberg JW et al (2004) Characterization of vadose zone sediments below the TX Tank Farm: Boreholes C3830, C3831, C3832 and RCRA borehole 299-W10-27. Report Number PNNL-14594. Pacific Northwest National Laboratory, Richland, WA

Sposito G (1984) The surface chemistry of soils. Oxford University Press, New York

Sposito G (1989) The chemistry of soils. Oxford University Press, New York

Sposito G (2004) The surface chemistry of natural particles. Oxford University Press, New York

Steefel CI, Van Cappellen P (1998) Reactive transport modeling of natural systems—Preface. J Hydrol (Amst) 209:1–7. doi:10.1016/S0022-1694(98)00182-6

Steefel CI, DePaolo DJ, Lichtner PC (2005) Reactive transport modeling: an essential tool and a new research approach for the Earth sciences. Earth Planet Sci Lett 240:539–558. doi:10.1016/j.epsl.2005.09.017

Strathmann TJ, Stone AT (2003) Mineral surface catalysis of reactions between Fe-II and oxime carbamate pesticides. Geochim Cosmochim Acta 67:2775–2791. doi:10.1016/S0016-7037(03)00088-7

Stumm W (1992) Chemistry of the solid-water interface. Processes at the mineral-water and particle-water interface in natural systems. Wiley, New York

Stumm W, Morgan JJ (1996) Aquatic chemistry: chemical equilibria and rates in natural waters, 3rd edn. Wiley, New York

Sylwester ER, Hudson EA, Allen PG (2000) The structure of uranium(VI) sorption complexes on silica, alumina, and montmorillonite. Geochim Cosmochim Acta 64:2431–2438. doi:10.1016/S0016-7037(00)00376-8

Szecsody JE, Cantrell KJ, Krupka KM, Resch CT, Williams MD, Fruchter JS (1998) Uranium mobility during in situ redox manipulation of the 100 area of the Hanford site. PNNL-12048-UC-2000. Pacific Northwest National Laboratory, Richland, WA

Todorov PT, Ilieva EN (2006) Contamination with uranium from natural and anthropological sources. Rom J Phys 51:27–34

Tripathi VS (1983) Uranium transport modeling: geochemical data and sub-models. Stanford University, Stanford

Ulrich KU, Rossberg A, Foerstendorf H, Zanker H, Scheinost AC (2006) Molecular characterization of uranium(VI)

sorption complexes on iron(III)-rich acid mine water colloids. Geochim Cosmochim Acta 70:5469–5487. doi:10.1016/j.gca.2006.08.031

Um W, Serne RJ, Brown CF, Last GV (2007a) U(VI) adsorption on aquifer sediments at the Hanford Site. J Contam Hydrol 93:255–269. doi:10.1016/j.jconhyd.2007.03.002

Um W, Mattigod S, Serne RJ, Fryxell GE, Kim DH, Troyer LD (2007b) Synthesis of nanoporous zirconium oxophosphate and application for removal of U(VI). Water Res 41:3217–3226. doi:10.1016/j.watres.2007.05.030

van Geen A, Robertson AP, Leckie JO (1994) Complexation of carbonate species at the goethite surface: implications for adsorption of metal ions in natural waters. Geochim Cosmochim Acta 58:2073–2086. doi:10.1016/0016-7037(94)90286-0

van Genuchten MT, Wierenga PJ (1976) Mass transfer studies in sorbing porous media: I. Analytical solutions. Soil Sci Soc Am J 40:473–480

van Genuchten MT, Wierenga PJ (1977) Mass transfer studies in sorbing porous media. II. Experimental evaluation with tritium-labeled water. Soil Sci Soc Am J 41:272–278

Villalobos M, Trotz MA, Leckie JO (2001) Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II) and U(VI) on goethite. Environ Sci Technol 35:3849–3856. doi:10.1021/es001748k

Waite TD, Davis JA, Payne TE, Waychunas GA, Xu N (1994) Uranium(VI) adsorption to ferrihydrite: application of a surface complexation model. Geochim Cosmochim Acta 58:5465–5478. doi:10.1016/0016-7037(94)90243-7

Waite TD, Davis JA, Fenton BR, Payne TE (2000) Approaches to modelling uranium(VI) adsorption on natural mineral assemblages. Radiochim Acta 88:687–693. doi:10.1524/ract.2000.88.9-11.687

Wang S, Jaffe PR, Li G, Wang SW, Rabitz HA (2003) Simulating bioremediation of uranium-contaminated aquifers; uncertainty assessment of model parameters. J Contam Hydrol 64:283–307. doi:10.1016/S0169-7722(02)00230-9

Wang Z, Zachara JM, Yantasee W, Gassman PL, Liu C, Joly AG (2004) Cryogenic laser induced fluorescence characterization of U(VI) in Hanford vadose zone pore waters. Environ Sci Technol 38:5591–5597. doi:10.1021/es049512u

Wang Z, Zachara JM, McKinley JP, Smith SC (2005) Cryogenic laser induced U(VI) fluorescence studies of the U(VI) substituted natural calcite: implications to U(VI) speciation in contaminated Hanford sediments. Environ Sci Technol 39:2651–2659. doi:10.1021/es048448d

Wazne M, Korfiatis GP, Meng XG (2003) Carbonate effects on hexavalent uranium adsorption by iron oxyhydroxide. Environ Sci Technol 37:3619–3624. doi:10.1021/es034166m

Wazne M, Meng XG, Korfiatis GP, Christodoulatos C (2006) Carbonate effects on hexavalent uranium removal from water by nanocrystalline titanium dioxide. J Hazard Mater 136:47–52. doi:10.1016/j.jhazmat.2005.11.010

Webb SM, Fuller CC, Tebo BM, Bargar JR (2006) Determination of uranyl incorporation into biogenic manganese oxides using X-ray absorption spectroscopy and scattering. Environ Sci Technol 40:771–777. doi:10.1021/es051679f

Williams AGB, Scherrer MM (2004) Spectroscopic evidence for Fe(II)–Fe(III) electron transfer at the iron oxide–water interface. Environ Sci Technol 38:4782–4790. doi:10.1021/es049373g

Yabusaki SB, Fang Y, Long PE, Resch CT, Peacock AD, Komlos J et al (2007) Uranium removal from groundwater via in situ biostimulation: field-scale modeling of transport and biological processes. J Contam Hydrol 93:216–235. doi:10.1016/j.jconhyd.2007.02.005

Zachara JM, Davis JA, Liu C, McKinley JP, Qafoku NP, Wellman DM, Yabusaki SB (2005) Uranium geochemistry in vadose zone and aquifer sediments from the 300 Area uranium plume PNNL-15121

Zheng Z, Tokunaga TK, Wan J (2003) Influence of calcium carbonate on U(VI) sorption to soils. Environ Sci Technol 37:5603–5608. doi:10.1021/es0304897

Zinn B, Harvey CF (2003) When good statistical models of aquifer heterogeneity go bad: a comparison of flow, dispersion, and mass transfer in connected and multivariate Gaussian hydraulic conductivity fields. Water Resour Res 39:1051. doi:10.1029/2001WR001146