Uranium(VI) Adsorption on Goethite and Soil in Carbonate Solutions

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ABSTRACT

Elevated concentrations of U are found in agricultural drainage waters from the San Joaquin Valley, CA, which are often disposed of in evaporation basins that are frequented by waterfowl. To determine the factors that affect aqueous U concentrations in the basins, sorption experiments with U(VI) were performed at various CO_2 partial pressures, dissolved Ca, Mg, and P concentrations, and carbonate alkalinities. Synthetic waters, comparable in inorganic constituents to irrigation and drainage waters, were prepared, spiked with 0.1 (soil) and 2 mg U(VI) L^{-1} (synthetic goethite), and analyzed for U, P (when applicable), and major ions. Total chemical analyses were input into the computer program FITEQL to determine U(VI) speciation and generate U(VI) adsorption constants with the *diffuse layer model* (also referred to as the *two-layer model*). Maximum adsorption occurred in solutions with low carbonate alkalinities (≤ 3 mmol L^{-1}), ionic strengths (≤ 0.03 *M*), Ca concentrations (≤ 4 mmol L^{-1}), and P concentrations (<0.005 mmol L^{-1} for soil). Lesser and negligible adsorption was attributed to the predicted formation of highly soluble, negatively charged U(VI) carbonates [$UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$] that did not strongly adsorb to soil surfaces. Calcium and, to some degree, Mg competition with positively charged U(VI) species for surface sites was observed at low carbonate alkalinities (<3 mmol L^{-1} for goethite; <14 mmol L^{-1} for soil). At high carbonate alkalinities, carbonates competed with anionic U(VI) species for adsorption sites. Study results suggest that elevated U concentrations in the drainage waters are due to the speciation of dissolved U(VI) into negatively charged carbonate complexes.

IN THE SAN JOAQUIN VALLEY (SJV) of California, irrigated agriculture has led to a dilemma that concerns the disposal of drainage waters containing elevated levels of potentially toxic trace elements such as U, Se, As, B, Mo, and V. These high-salinity and high-alkalinity drainage waters are often discharged to on-farm evaporation ponds, which have aqueous concentrations ranging from a few micrograms per liter U L^{-1} to 22.3 mg U L^{-1} and sediment concentrations of up to 290 mg U kg^{-1} (Chilcott et al., 1990a,b). The USEPA-recommended maximum drinking water standard of 20 mg U L^{-1} is exceeded in all but one of the SJV ponds sampled in the survey by Chilcott et al. (1990b). Despite preventative efforts to exclude waterfowl from the ponds, the ponds provide habitat and food resources for many waterfowl and there is concern that U poses a hazard to hatchlings and adult birds that frequent the ponds (J. Skorupa, U.S. Fish and Wildlife, Sacramento, CA, 1992, personal communication).

Uranium(VI) in aqueous solution exists as complexes of the stable linear uranyl ion, UO_2^{2+}, which forms numerous hydrolysis species, for example, UO_2OH^+, $UO_2(OH)_2^0$, and $(UO_2)_2(OH)_2^{2+}$. In the absence of dissolved inorganic ligands (carbonate, fluoride, sulfate, and phosphate), these hydrolysis species often dominate U(VI) speciation. In the presence of dissolved carbonates, U(VI) forms several strong carbonate complexes: $(UO_2)_2CO_3(OH)_3^-$, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, and possibly $(UO_2)_3(CO_3)_6^{6-}$ (Grenthe, 1992; Langmuir, 1978; Ciavatta et al., 1981). A U(VI) species distribution for U(VI) hydrolysis and U(VI) carbonate species is shown for two different total inorganic C values (Ci_{tot}) in Fig. 1a and 1b. The distribution of these mononuclear and polynuclear U(VI) species is strongly concentration and pH dependent (Langmuir, 1978; Baes and Mesmer, 1976). The SJV pond carbonate alkalinities range from <0.1 to 108 $mmol_c$ L^{-1} (Chilcott et al., 1990b) and it is probable that U(VI) carbonate complexes dominate U(VI) speciation. In waters high in both phosphate and U but low in carbonate, it is likely that small amounts of U(VI) phosphate complexes will be present as $UO_2PO_4^-$ and $UO_2HPO_4^0$ and the precipitation of U(VI) phosphates is possible.

Several adsorption studies of the uranyl ion on Fe oxides and Fe oxyhydroxides have been reported (Tripathi, 1983; Ho and Doern, 1984; Hsi and Langmuir, 1985; Ho and Miller, 1986; Payne and Waite, 1991; Waite et al., 1994). Hsi and Langmuir (1985) found that U(VI) adsorption on goethite increases with increasing pH in carbonate-free solutions across a large pH range. Similar adsorption trends with pH in carbonate-free solutions on synthetic hematite, amorphous Fe hydroxides, and other Fe oxides have been observed (Tripathi, 1983; Ho and Doern, 1984; Hsi and Langmuir, 1985; Payne and Waite, 1991; Waite et al., 1994). In low carbonate alkalinity solutions, U(VI) adsorption (above pH 6) on most Fe oxide and oxyhydroxide surfaces abruptly decreases with increasing pH (Tripathi, 1983; Hsi and Langmuir, 1985; Ho and Miller, 1986; Waite et al., 1994). It can be concluded from these studies that U(VI) adsorption to Fe oxide and oxyhydroxide mineral surfaces is influenced by pH and dissolved carbonate.

Many researchers have varying conclusions on what U(VI) species adsorb to clay mineral surfaces and the nature of the adsorption. The EXAFS data of U(VI) adsorbed to ferrihydrite at pH 5.0 and 5.5, in the absence of carbonate, support a bidentate adsorption of a mononuclear U(VI) species on an edge of the Fe oxyhydroxyl octahedron (Waite et al., 1994). Chisholm-Brause et al. (1994) concluded that U(VI) adsorption on smectite (pH 3-3.5) involves multiple surface sites, structurally distinct monomeric adsorbed species, and monodentate surface complexes. Morris et al. (1994) came to similar conclusions using data from Raman and electronic emission spectroscopy. Dent et al. (1992) concluded that spectra from EXAFS studies of polymeric U(VI) species

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Published in Soil Sci. Soc. Am. J. 60:1393-1400 (1996).

Abbreviations: SJV, San Joaquin Valley; EXAFS, extended x-ray absorption fine structure; pCO_2, partial pressure of carbon dioxide; r.c.f., relative centrifugal force; TLB, Tulare Lake Bed; DLM, diffuse layer model.

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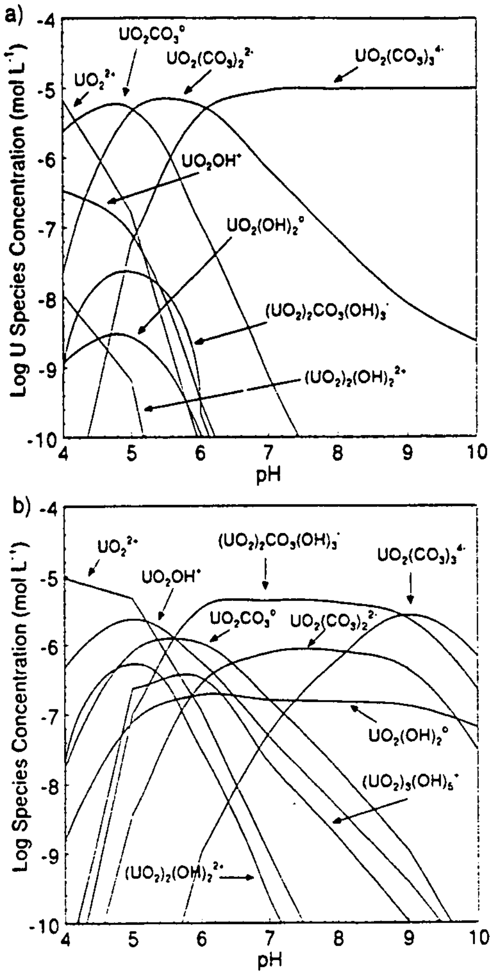

Fig. 1. The species distribution for 2.38 mg U(VI) L^{-1} with respect to pH at (a) total inorganic C (Ci$_{tot}$) = 31.1 mmol$_c$ L^{-1} and (b) Ci$_{tot}$ = 0.2 mmol$_c$ L^{-1}.

could be attributed to monodentate linkages on silica colloids in solutions [pH 5.2, 25 mg U(VI) L^{-1}].

Little information from spectroscopic studies exists on the adsorption of U(VI) species in high-carbonate solutions. But, Dent et al. (1992) compared the EXAFS spectra of a U(VI) species adsorbed on montmorillonite at pH 5.3 and atmospheric CO_2 to spectra from a U(VI) solution at pH 4.3 and atmospheric CO_2. Carbonate ligands tentatively ascribed to the third atomic shell of the U(VI) solution species were found in spectra of the adsorbed U(VI) species. The infrared spectra of adsorbed U(VI) in high-carbonate solutions shows that a U(VI) carbonate species, the hemicarbonate $(UO_2)_2CO_3(OH)_3^-$, adsorbed to hematite (Ho and Miller, 1986). Based on electrophoretic mobility studies, Ho and Miller (1986) concluded that this U(VI) species is specifically adsorbed (i.e., as an inner sphere complex). They also mentioned that other U(VI) species may be involved in adsorption.

The objectives of this study were to determine what conditions favor the adsorption of U(VI) to a calcareous, montmorillonitic, SJV soil and the mineral goethite in systems with a chemical composition similar to the SJV evaporation ponds. We hypothesized that the adsorption of U(VI) involves both cationic and anionic solution species. By using goethite, which has a pH-dependent surface charge and in general is known to adsorb both cationic and anionic dissolved species, we studied the adsorption of U(VI) from solutions of various alkalinity and pCO$_2$, which controlled the pH. Additional U(VI) adsorption studies with goethite and a SJV soil were conducted with synthetic SJV drainage waters of various concentrations of dissolved U(VI), Ca, Mg, Na, SO_4, Cl, CO_3, and P. The negatively charged goethite surface at high pH (low pCO$_2$) and high carbonate alkalinities provided surface conditions similar to the negative charge of 2:1 permanent-charge clays found in the SJV soil.

MATERIALS AND METHODS

Two different groups of waters were prepared for the goethite experiment. Group one consisted of four 100 mmol L^{-1} ionic strength (I) solutions with variable ratios of NaCl/NaHCO$_3$ equilibrated with three different CO_2 partial pressures: 0.22, 5.05, and 92.9 kPa. These waters had U(VI) concentrations of about 2.0 mg L^{-1} from $UO_2(NO_3)_{2(s)}$. A second group of four synthetic SJV drainage waters (labeled 1, 2, 3, and 4) were first prepared from various salts and equilibrated with 0.03 kPa CO_2 (Table 1). Water 4 was made to be approximately one-half the concentration of Water 2 by an equal-volume dilution with deionized water. Water 2 had excess reagent-grade $CaCO_{3(s)}$ and, upon dilution, more $CaCO_{3(s)}$ dissolved resulting in higher dissolved Ca concentrations and carbonate alkalinities. Solutions [prepared with excess reagent-grade $CaSO_4 \cdot 2H_2O_{(s)}$ and $CaCO_{3(s)}$] were decanted from the $CaSO_4 \cdot 2H_2O_{(s)}$ and $CaCO_{3(s)}$ after equilibration with the various CO_2 mixtures and before the addition of U(VI).

According to the Hardie–Eugster Model (Hardie and Eugster, 1970, p. 273–290), synthetic SJV Water 1 was representative of an inlet water with a high Ca/HCO$_3$ ratio that upon concentration, would yield a high-SO$_4$ near-neutral brine. Waters 2 and 4 resembled Water 1, but had lower I values. Water 3 was representative of a water that upon evapoconcentration, would yield a high-pH, high-carbonate brine. (A review on the chemistry of evaporation waters is presented in Drever, 1988.)

The mineral goethite was made using a procedure described by Atkinson et al. (1967). The prepared goethite had a surface area of 58.5 m^2 g^{-1} (BET N_2 adsorption) and was mineralogically confirmed with x-ray diffraction analysis.

In triplicate, 25 mL of the first two groups of waters were equilibrated at their respective CO_2 partial pressures with approximately 2.0 mg U(VI) L^{-1} and 0.2 g of goethite, and shaken for 24 h. Then the samples were centrifuged (17 300 r.c.f.) and the pH was measured. The supernatants were decanted and saved for further analysis (at 4°C) of U, Ca, Mg, Na, SO_4, Cl, and carbonate alkalinity. Analysis of U was done by inductively coupled plasma mass spectrometry in 10 g L^{-1} HNO$_3$ (trace metal grade) with an internal standard of 50 µg L^{-1} Bi. The amount adsorbed was taken as the difference between the amount added and the amount recovered in the equilibrium solution. Calcium and Mg were measured in 1000 mg L^{-1} LaCl$_3$ by atomic absorption spectroscopy and Na was measured by atomic emission spectroscopy. Chloride and SO_4 were determined by anion exchange chromatography with a Dionex Ion Chromatograph (Dionex, Sunnyvale, CA). Carbonate alkalinity was determined by titration with 0.005 mol L^{-1} H_2SO_4 to pH 4.4.

A third group of synthetic SJV irrigation drainage waters

Table 1. The amount of reagent-grade salts used to make the synthetic drainage water compositions at 0.03 kPa CO_2—prior to equilibration with other CO_2 partial pressures, goethite, or Tulare Lake Bed soil.

Water	$MgCl_2 \cdot 6H_2O_{(s)}$	$MgSO_{4(s)}$	$NaHCO_{3(s)}$	$NaCl_{(s)}$	$Na_2SO_{4(s)}$	$CaCO_{3(s)}$	$CaSO_4 \cdot 2H_2O_{(s)}$
	mmol L^{-1}					g L^{-1}	
1	5	2	10	60	15	1	3
2	5	–	–	–	15	1	3
3	–	5	80	–	10	1	0†
4‡	2.5	–	–	–	7.5	0.5	1.5

† Water 3 contained reagent-grade $CaSO_4 \cdot 2H_2O_{(S)}$ (3 g L^{-1})—TLB soil study only.

‡ Estimated based on a 1:1 dilution of Water 2 with deionized water—goethite study only.

similar to Waters 1, 2, and 3 (Table 1) were prepared and equilibrated under 0.03, 0.22, 5.41, and 92.9 kPa CO_2. Reagent-grade $CaSO_4 \cdot 2H_2O_{(s)}$ (3 g L^{-1}) was added in excess to ensure saturation for *all* Group 3 waters. A concentration of approximately 0.1 mg U(VI) L^{-1} from $UO_2(NO_3)_{2(s)}$ was prepared from each water. Solutions [prepared with excess reagent-grade $CaSO_4 \cdot 2H_2O_{(s)}$ and $CaCO_{3(s)}$] were decanted from the $CaSO_4 \cdot 2H_2O_{(s)}$ and $CaCO_{3(s)}$ after equilibration with the various CO_2 mixtures and before the addition of U(VI).

About 100 g of Tulare Lake Bed (TLB) soil (0–25 cm, a fine, montmorillonitic [calcareous], thermic Vertic Fluvaquent) from a berm adjacent to a SJV evaporation pond was washed with 250 mL of each respective U-free water (from Group 3) prior to the adsorption experiment. This washing was done twice to equilibrate cation-exchange sites with each water prior to introducing the U(VI)-containing water. Soil–water mixtures were shaken for 2 h, centrifuged, and the supernatant decanted. Soil samples were oven dried at 100°C for 24 h and gently ground with a mortar and pestle to break up the dried soil sample. Because of native U in the soil prior to the experiment, the soil (after being washed with each respective water) was twice extracted with 20 mL of 0.5 mol L^{-1} $(NH_4)_2CO_3$ to determine initial U values. These background U concentrations were low (<0.1 mg U kg^{-1} dry wt.) relative to the U(VI) concentrations added. Prior to washing, the TLB soil had <1% organic C, 12.3% carbonate, a cation-exchange capacity of 204 mmol$_c$ kg^{-1}, a pH of 8.7, and an electrical conductivity of 10.8 dS m^{-1} on a 1:1 (w/w) water extract.

In triplicate, 25 mL of the synthetic SJV waters (Group 3) were added to 1.0 g of soil and shaken for 24 h. Soluble P as phosphate was determined colorimetrically with ammonium molybdate and ascorbic acid on a Technicon Auto Analyzer (Method no. 94-70 w/b, Tarrytown, New York). All analyses and calculations of the amount of U(VI) adsorbed were performed as described above.

The computer program FITEQL was chosen for modeling with the diffuse layer model (DLM), with the solutions equilibrated with goethite (Dzombak and Morel, 1990; Herbelin and Westall, 1994). The DLM, also referred to as the *two-layer model*, was selected because of its simplicity and its ability to describe specific adsorption (Dzombak and Morel, 1990). The model consists of two layers: (i) a charged surface layer where specific adsorption is allowed and (ii) a diffuse layer of ions of opposite charge that lie between the bulk solution and the charged surface. The second layer is best described as a Gouy–Chapman distribution of ions whose concentrations decrease as the distance from the solid to the bulk solution increases.

We allowed for the competitive adsorption of carbonate and bicarbonate with U(VI) anions. The specific adsorption of carbonate and bicarbonate to goethite was previously studied with the DLM (van Geen et al., 1994). Van Geen et al. (1994) modeled carbonate and bicarbonate adsorption and determined adsorption constants for the following reactions:

	log *K*(int)
$Fe\text{-}OH_{(s)} + H^+ \leftrightarrow Fe\text{-}OH^+_{2(s)}$	7.91
$Fe\text{-}OH_{(s)} \leftrightarrow Fe\text{-}O^-_{(s)} + H^+$	−10.02
$Fe\text{-}OH_{(s)} + CO_3^{2-} + 2H^+ \leftrightarrow Fe\text{-}OCOOH_{(s)} + H_2O$	20.78
$Fe\text{-}OH_{(s)} + CO_3^{2-} + H^+ \leftrightarrow Fe\text{-}OCOO^-_{(s)} + H_2O$	12.71

Surface protonation–deprotonation constants and a site density of 2.3 sites nm^{-2} were taken from van Geen et al. (1994). Our model included several U(VI) complexation reactions and corresponding formation constants in addition to other pertinent reactions, which are listed in Table 2. Solution species activities were calculated using the Davies equation. Adsorbed species and solid phases were assumed to have activity coefficients equal to 1.0 and Ci_{tot} was specified in the input file.

For the adsorption modeling of the SJV waters that were equilibrated with goethite, we were limited to 40 species reactions per input file in FITEQL for the DLM. The following species were removed from the equilibrium speciation: UO_2Cl^+, $UO_2(OH)_3^-$, $(UO_2)_3(OH)_7^-$, and $(UO_2)_4(OH)_7^+$. The formation constants for the following complexes (Grenthe et al., 1992) were added to the program:

	log *K*
$UO_2^{2+} + SO_4^{2-} \leftrightarrow UO_2SO_4^0$	3.2
$UO_2^{2+} + 2\,SO_4^{2-} \leftrightarrow UO_2(SO_4)_2^{2-}$	4.1

For the *solution* U(VI) speciation modeling for the synthetic SJV waters, which, after equilibration with TLB soil consequently contained soluble phosphate, several U(VI)–phosphate

Table 2. Uranium(VI) complexation reactions and other reactions used in modeling with the diffuse layer model and in the absence of an adsorbing solid phase, with MINTEQA2†.

Reaction	log *K*
$2UO_2^{2+} + 3\,H_2O + CO_3^{2-} \leftrightarrow (UO_2)_2CO_3(OH)_3^- + 3H^+$	−1.2‡
$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2CO_3^0$	9.7
$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_2^{2-}$	17.0
$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}$	21.6
$UO_2^{2+} + H_2O \leftrightarrow UO_2OH^+ + H^+$	−5.2
$UO_2^{2+} + 2H_2O \leftrightarrow UO_2(OH)_2^0 + 2H^+$	−12.0
$UO_2^{2+} + 3H_2O \leftrightarrow UO_2(OH)_3^- + 3H^+$	−20.0
$UO_2^{2+} + 4H_2O \leftrightarrow UO_2(OH)_4^{2-} + 4H^+$	−33.0
$2UO_2^{2+} + H_2O \leftrightarrow (UO_2)_2OH^{3+} + H^+$	−2.8
$2UO_2^{2+} + 2H_2O \leftrightarrow (UO_2)_2(OH) + 2H^+$	−5.6
$3UO_2^{2+} + 4H_2O \leftrightarrow (UO_2)_3(OH)_4^{2+} + 4H^+$	−11.9
$3UO_2^{2+} + 5H_2O \leftrightarrow (UO_2)_3(OH)_5^+ + 5H^+$	−15.5
$3UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_3(OH)_7^- + 7H^+$	−31.0
$4UO_2^{2+} + 7H_2O \leftrightarrow (UO_2)_4(OH)_7^+ + 7H^+$	−21.9
$UO_2^{2+} + Cl^- \leftrightarrow UO_2Cl^+$	0.2§

† Stability constants from Grenthe et al. (1992) unless otherwise noted.

‡ Stability constant taken from Tripathi (1983).

§ Stability constant taken from Allison et al. (1991).

Table 3. Uranium(VI)-phosphate complexes and solid reactions used with MINTEQA2 to predict what U(VI) species dominated solution speciation in the absence of a solid phase. The thermodynamic database was updated with equilibrium constants from Grenthe et al. (1992).

Reaction	log *K*
$UO_2^{2+} + PO_4^{3-} \leftrightarrow UO_2PO_4^-$	13.2
$UO_2^{2+} + PO_4^{3-} + H^+ \leftrightarrow UO_2HPO_4^0$	19.6
$UO_2^{2+} + PO_4^{3-} + 2H^+ \leftrightarrow UO_2H_2PO_4^+$	20.7
$UO_2^{2+} + PO_4^{3-} + 3H^+ \leftrightarrow UO_2H_3PO_4^{2+}$	45.1
$UO_2^{2+} + 2PO_4^{3-} + 4H^+ \leftrightarrow UO_2(H_2PO_4)_2^0$	44.0
$UO_2^{2+} + 2PO_4^{3-} + 5H^+ \leftrightarrow UO_2(H_2PO_4)(H_3PO_4)^+$	45.1
$UO_2^{2+} + PO_4^{3-} + H^+ + 4H_2O \leftrightarrow UO_2HPO_4 \cdot 4H_2O_{(s)}$	23.2
$2UO_2^{2+} + 3PO_4^{3-} + 4H_2O \leftrightarrow (UO_2)_3(PO_4)_3 \cdot 4H_2O_{(s)}$	49.4

complexation reactions had to be added to the model. However, FITEQL was limited to 40 species reactions per input file and the computer solution speciation model MINTEQA2 (Allison et al., 1991) was used to calculate what dissolved U(VI) species would be present in the absence of an adsorbing phase. The additional species and their respective equilibrium constants listed in Tables 2 and 3 were added to the MINTEQA2 database files or updated for the U(VI) speciation calculations.

RESULTS AND DISCUSSION

Uranium(VI) Adsorption by Goethite in Sodium Chloride/Bicarbonate Solutions

Figure 2 shows the U(VI) fraction adsorbed to goethite vs. pCO_2 and carbonate alkalinity for the twelve 0.1 *M I* waters whose equilibrium chemical compositions are described in Table 4. With the addition of $CO_{2(g)}$ the solution pH decreased. Uranium(VI) adsorption decreased with increasing carbonate alkalinity for solutions of equivalent pCO_2. Figure 3 presents the same data as a function of pH and shows that U(VI) adsorption decreased with increasing pH above pH 6. Adsorption decreased slightly below pH 5. The adsorption edge increased with decreasing pCO_2 and was attributed to the effect of the carbonate and bicarbonate ions on adsorption. Carbonate forms several strong ion pairs with U(VI), which decreased adsorption.

In contrast, Hsi and Langmuir (1985) found that U(VI) adsorption by goethite increased with increasing pH from 4 to 8 in a carbonate-free system. This trend in adsorption with pH resembled that of a cationic species, which they attributed to the UO_2OH^+ and $(UO_2)_3(OH)_5^+$ species. In carbonate-containing systems, they observed that adsorption increased from pH 4 to 6 and then decreased as the pH increased from 6 to 9 (Hsi and Langmuir, 1985). They interpreted this behavior to the adsorption of both anionic $[UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}]$ and cationic U(VI) species.

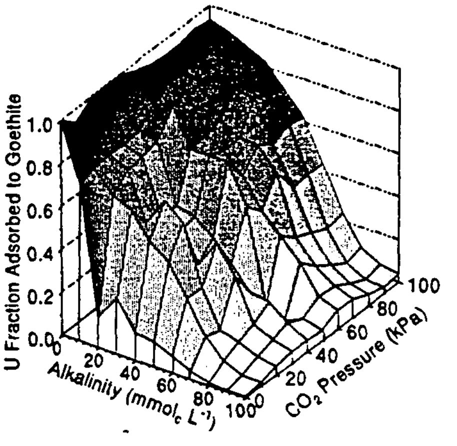

Fig. 2. The U(VI) fraction adsorbed to goethite vs. carbonate alkalinity and CO_2 partial pressure for solutions of constant ionic strength (0.1 *M*), variable NaCl/NaHCO$_3$, with U(VI) concentrations of approx 2.0 mg U(VI) L^{-1}.

Speciation calculations with the DLM for these 0.1 *M I* (Group 1) waters were done with the equilibrium constants for U(VI) species listed in Table 2 for the goethite adsorption studies. The calculations indicated that as carbonate alkalinities increased (for solutions of equal pCO_2), the concentrations of U(VI) di- and tricarbonates $[UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}]$ increased relative to the concentrations of U(VI) hemicarbonate $[(UO_2)_2CO_3(OH)_3^-]$ and U(VI) hydrolysis species $[UO_2OH^+$, $UO_2(OH)_2^0$, and $(UO_2)_2(OH)_2^{2+}]$, which decreased (Table 5). At the highest solution carbonate alkalinities (100 mmol L^{-1}), the U(VI) di- and tricarbonates were the predominant U(VI) species predicted to be in solution—regardless of pH. If negatively charged U(VI) carbonates were the primary forms of U(VI) in solution at pH 6.7 and 100 mmol L^{-1} carbonate alkalinity, one would expect some anionic adsorption of these species because the surface was predominantly positively charged. However, adsorption was quite low. This may

Table 4. The aqueous chemistry of the 0.1 *M* ionic strength solutions containing ≈2 mg L^{-1} U(VI) that were equilibrated with goethite.

Treatment	CO₂	pH	Na	HCO₃	Cl	U(VI) fraction adsorbed	
						Observed	Predicted
	kPa			mmol$_c$ L^{-1}			
1	0.22	6.9	100	0.1	100	0.99	1.00
2	5.05	5.8	100	0.1	100	1.00	1.00
3	92.9	4.1	100	0.1	100	0.93	0.95
2	0.22	8.2	100	7.0	93.0	0.76	0.92
5	5.05	7.0	100	7.0	93.0	0.97	0.98
6	92.9	5.5	100	7.0	93.0	0.97	0.96
7	0.22	8.6	100	20.0	79.8	0.13	0.11
8	5.05	7.4	100	20.1	80.0	0.53	0.52
9	92.9	5.9	100	20.1	79.6	0.79	0.82
10	0.22	9.2	100	100	0.02	0.01	<0.01
11	5.05	8.0	100	100	0.01	0.02	<0.01
12	92.9	6.7	100	100	0.01	0.03	0.01

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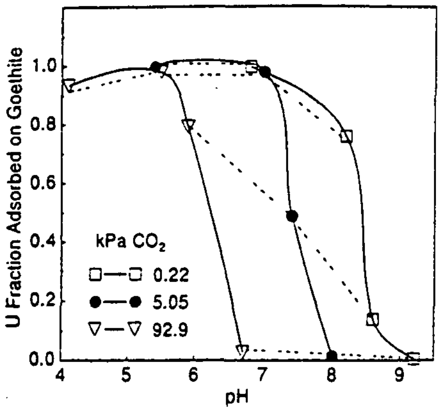

Fig. 3. The U(VI) fraction adsorbed on goethite vs. pH for the solutions of constant ionic strength (0.1 *M*) and variable NaCl/NaHCO$_3$. Solid lines represent solutions equilibrated at the same CO$_2$ pressures. Dashed lines on the plot join data points that have the same carbonate alkalinities but different CO$_2$ partial pressures.

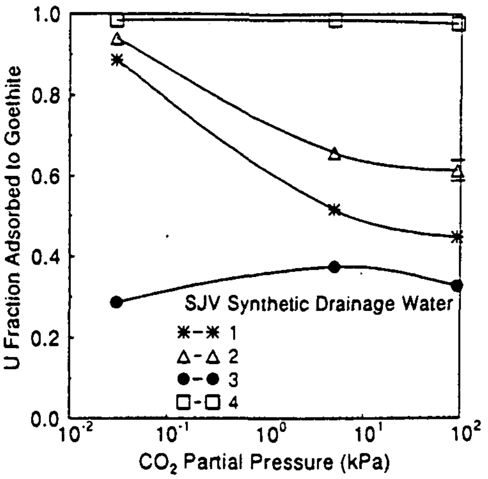

Fig. 4. The U(VI) fraction adsorbed to goethite vs. CO$_2$ partial pressure for the synthetic San Joaquin Valley waters. Solution pH values decrease with increasing CO$_2$ pressure. Waters 1, 2, and 3 contained excess reagent-grade CaCO$_{3(s)}$ and approx. 2.0 mg U(VI) L^{-1}.

have been due to the presence of dissolved carbonates, which competed with U(VI)-carbonate ion pairs for positively charged sites at high carbonate alkalinities. This has been confirmed with adsorption modeling (see below). It was also concluded that the U(VI) tricarbonate species does not adsorb, even though it has a −4 charge. It appears that the adsorption of U(VI) is controlled predominantly by coordination, rather than simple electrostatics.

Uranium(VI) Adsorption by Goethite in Synthetic Drainage Waters

In Fig. 4, U(VI) adsorption is plotted as a function of *p*CO$_2$ for the SJV synthetic drainage waters (Group 2) whose final chemical compositions are described in Table 6. Adsorption decreased with increasing CO$_2$ for Waters 1 and 2, which was different from the earlier studies shown in Fig. 2. Adsorption was not greatly influenced by CO$_2$ pressure for Water 4, which had the lowest carbonate alkalinity of the waters. With increasing CO$_2$ pressure, the solution pH was lowered and CaCO$_{3(s)}$ dissolved. This dissolution contributed carbonate alkalinity to Waters 1, 2, and 3 and promoted a shift in U(VI) complexation, forming more UO$_2$(CO$_3$)$_3^{4-}$. Hence, U(VI) adsorption decreased with increasing *p*CO$_2$ (decreasing pH and increasing carbonate alkalinity), which favored the formation of the U(VI) dicarbonate species and greater competitive adsorption of the bicarbonate ion (van Geen et al., 1994).

At all CO$_2$ pressures, Water 3 had the greatest carbonate alkalinity (Table 6) and the lowest adsorption (Fig. 4). Solution speciation calculations for Water 3 predicted that the U(VI) tricarbonate species [UO$_2$(CO$_3$)$_3^{4-}$] comprised the majority of the U(VI) species in solution at all pH values. Evidence suggests that this species is not adsorbed and the adsorption of bicarbonate and carbonate on the positively charged goethite surface inhibited U(VI) adsorption.

At high pH, dissolved Ca and Mg affected U(VI) adsorption, and competition between these ions and positively charged U(VI) species for surface sites was considered. Adsorption in the carbonate alkalinity range of 2 to 14 mmol$_c$ L^{-1} was lowest in Water 1, which contained higher dissolved Ca than Waters 2 or 4. This indicated

Table 5. The diffuse layer model predicted adsorbed and dissolved species for the first set of solutions that were equilibrated with goethite.

	Adsorbed species†				Solution species‡					
Trtmnt.	Fe-O-$^-$UO$_2$OH$^+_{(s)}$	Fe-OH$_2$-$^+$UHC$^-_{(s)}$	Fe-OCOOH$_{(s)}$	Fe-OCOO$^-_{(s)}$	UO$_2^{2+}$	UO$_2$OH$^+$	UHC	UMC	UDC	UTC
	% of total U(VI) in system		log concentration							
1	99.1	0.9	−4.2	−4.0	−12	−11	−14	−11	−11	−14
2	30.7	69.3	−3.1	−3.8	−9.6	−9.4	−12	−8.7	−9.3	−13
3	0.7	94.5	−2.9	−5.2	−6.3	−7.7	−12	−6.9	−9.0	−13
4	88.8	5.6	−3.6	−3.4	−15	−12	−12	−10	−7.3	−6.2
5	29.6	68.3	−3.0	−3.5	−12	−11	−11	−8.7	−6.9	−6.9
6	0.1	96.1	−2.8	−4.6	−9.0	−9.1	−11	−7.0	−6.7	−8.1
7	10.7	0.1	−3.5	−3.3	−16	−13	−13	−11	−7.0	−5.0
8	19.1	32.4	−3.0	−3.5	−13	−11	−11	−8.8	−6.1	−5.3
9	1.0	81.3	−2.8	−4.4	−10	−9.5	−10	−7.1	−5.8	−6.3
10	<0.1	<0.1	−3.5	−3.3	−20	−16	−20	−13	−8.1	−4.8
11	<0.1	<0.1	−3.0	−3.4	−17	−14	−17	−11	−7.1	−4.9
12	<0.1	0.1	−2.8	−4.0	−13	−12	−13	−8.7	−5.9	−5.0

† UHC is the (UO$_2$)$_2$CO$_3$(OH)$_3^-$ species.
‡ UMC, UDC, and UTC are the UO$_2$CO$_3$°, UO$_2$(CO$_3$)$_2^{2-}$, and UO$_2$(CO$_3$)$_3^{4-}$ species, respectively.

Table 6. Average measured synthetic drainage water compositions after equilibration with goethite and various fixed CO_2 partial pressures. The waters contained approx. 2.0 mg U(VI) L^{-1}.

										U(VI) fraction adsorbed	
Water	CO_2	pH	HCO_3	Mg	Ca	Na	SO_4	Cl	I	Observed†	Predicted‡
	kPa		mmol L^{-1}						M		
1	0.03	7.4	2	4	11	86	28	59	0.14	0.89	0.99
	5.41	7.0	5	4	13	89	29	60	0.14	0.51	0.87
	92.9	6.1	14	5	19	90	28	63	0.14	0.45	0.47
2	0.03	7.6	3	4	2	18	16	3	0.05	0.94	1.00
	5.41	7.2	8	6	5	18	19	3	0.07	0.66	0.94
	92.9	6.3	14	6	12	19	22	3	0.07	0.61	0.62
3	0.03	9.0	47	2	1	91	19	4	0.11	0.29	0.00
	5.41	7.9	50	4	4	93	19	ND§	0.12	0.37	0.01
	92.9	6.6	56	4	4	100	20	ND	0.12	0.33	0.01
4	0.03	7.4	3	0.1	2	21	10	2	0.03	0.99	1.00
	5.41	6.9	3	3	2	18	13	2	0.03	0.99	0.99
	92.9	5.5	3	3	2	18	11	2	0.03	0.98	0.95

† Observed U(VI) fraction adsorbed.
‡ Diffuse layer model values.
§ ND = not determined.

that Ca^{2+} competition with positively charged U(VI) species may account for decreases in U(VI) adsorption. Adsorption was lower in Waters 2 and 3 than in Water 4 at 0.03 kPa CO_2 pressure and 3 mmol L^{-1} HCO_3 due to a higher Mg concentration in Waters 2 and 3, which probably supported competitive adsorption with positively charged U(VI) for adsorption sites (Hsi and Langmuir, 1985), but few studies have investigated the effect of higher dissolved Ca on U(VI) adsorption. Kob (1988) found that the adsorption of U(VI) to sandy groundwater sediments at pH 7.2 decreased with increasing I and the possibility of competing cations (Ca^{2+} and Na^+) was considered. Calcium, Mg, and Ba ions successfully compete with U(VI) species on adsorption sites on montmorillonite, illite, and kaolinite (Borovec, 1981; Tsunashima et al., 1981; Chisholm-Brause et al., 1994).

Modeling Uranium(VI) Adsorption by Goethite

The adsorption of U(VI) on goethite was highly correlated ($P < 0.0001$) with concentrations of the UO_2OH^+ ($R^2 = 0.91$) and $(UO_2)_2CO_3(OH)_3^-$ ($R^2 = 0.93$) species. We assumed that the following monodentate U(VI) adsorption reactions were occurring:

$$\underline{\log K(\text{int})}$$

$$\text{Fe–OH}_{(s)} + UO_2^{2+} + H_2O \leftrightarrow$$

$$\text{Fe–O}^-\text{–}UO_2OH^+_{(s)} + 2H^+ \qquad -3.07$$

$$\text{Fe–OH}_{(s)} + 2UO_2^{2+} + CO_3^{2-} + 3H_2O \leftrightarrow$$

$$\text{Fe–OH}_2^+\text{–}(UO_2)_2CO_3(OH)^-_{3(s)} + 2H^+ \qquad 15.51$$

These two species, the U(VI) hemicarbonate and U(VI) hydroxide, were fitted with the DLM for the adsorption data from Table 4. The overall variance or weighted sum of squares of residuals/degrees of freedom term (WSOS/df) was 0.27, a value characteristic of a model with a significantly high quality of fit.

Caution must be taken when using generalized surface complexation models to describe complex, microscopic systems. Goethite is known to contain at least three surface sites that each have different affinities for ion adsorption (Hiemstra et al., 1989). Our model did not account for this and therefore may not be the best method for predicting the adsorption of U(VI) species. However, modeling adsorption with three or more complexation sites and their surface protonation–deprotonation complexes may require "an unreasonably large number of adjustable parameters" (Goldberg, 1992) and therefore prevent or complicate mathematical convergence.

Some surface complexation modeling and spectroscopic studies support our assumptions concerning the adsorbing species. In low-carbonate solutions, Kob (1988) attributes adsorption to UO_2OH^+ species; Hsi and Langmuir (1985) modeled adsorption with the species UO_2OH^+ and $(UO_2)_3(OH)_5^+$; and Ho and Doern (1984) attributed adsorption to the $(UO_2)_3(OH)_5^+$ species. In our system, the calculated concentrations of the $(UO_2)_3(OH)_5^+$ species were low relative to the other species and adsorption could not be "fitted" with the model using this species. Thus, we did not attribute adsorption to this species. Ho and Miller (1986) associated adsorption with the U(VI) hemicarbonate in low carbonate alkalinity (1 $mmol_c$ L^{-1}) solutions because adsorption across a wide pH range was correlated with the concentrations of the hemicarbonate. They supported their assumptions with infrared spectroscopic evidence for carbonate bands. They stated that more than one adsorbing species was probably present because of a wide U(VI) absorption band. The extensive modeling studies of Tripathi (1983) fit adsorption with the hemicarbonate species across a wide range of U(VI) and solid concentrations, carbonate alkalinities, and pH values. Payne and Waite (1991) fit U(VI) adsorption to goethite at 2.5 $mmol_c$ L^{-1} alkalinity by trial and error to the UO_2OH^+, $UO_2CO_3^0$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ species. We could not attribute adsorption to these carbonate species—particularly the di- and tricarbonates. Adsorption was lowest in the solutions that contained these species.

Conclusions from EXAFS data suggest that both mono- and polynuclear species adsorb to soil minerals (Chisholm-Brause et al., 1994; Dent et al., 1992). The EXAFS data from adsorption studies with ferrihydrite suggested

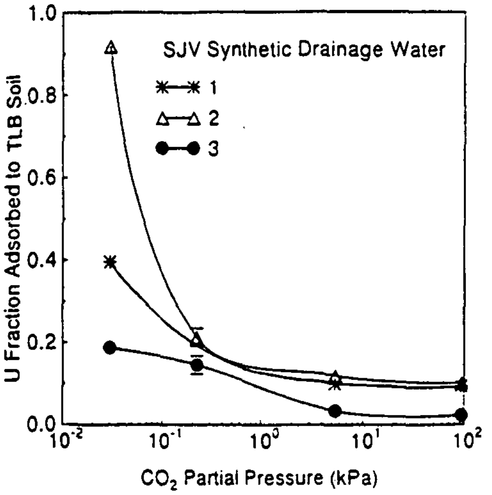

Fig. 5. The U(VI) fraction adsorbed to Tulare Lake Bed soil vs. CO_2 partial pressure for synthetic San Joaquin Valley drainage waters. Solution pH values decrease with increasing CO_2 pressure. All solutions were saturated with reagent-grade $CaCO_{3(s)}$ and contained approx. 0.1 mg U(VI) L^{-1}.

a bidentate as opposed to a monodentate adsorption (Waite et al., 1994). However, no information currently suggests whether U(VI) species exhibit mono- or bidentate adsorption on the more crystalline surface of goethite. The modeling of bidentate adsorption with the DLM was attempted without convergence and monodentate U(VI) adsorption was considered.

Tables 4 and 5 show the DLM-predicted U(VI) fraction adsorbed to goethite in the $NaCl/NaHCO_3$ solutions. The predicted adsorption values describe the trends in adsorption as discussed above. The hemicarbonate accounted for adsorption at high CO_2 pressures (low pH), whereas the U(VI) hydroxyl species accounted for most adsorption at low pCO_2 (high pH). The speciation calculations indicate that at high pH and high carbonate alkalinity, adsorption decreased due to the formation of U(VI) di- and tricarbonates, which did not adsorb. Adsorption was slightly underpredicted in waters with carbonate alkalinities of 100 mmol L^{-1} HCO_3.

Uranium(VI) adsorption to goethite in the synthetic SJV waters in Table 6 were modeled using the DLM adsorption constants generated from the study with the $NaCl/NaHCO_3$ solutions of constant I. Adsorption was overpredicted for Waters 1 and 2 – indicating the inability of the DLM to predict U(VI) adsorption in these waters. Competition between the positively charged adsorbing U(VI) species and Ca^{2+}-Mg^{2+} ions for surface sites above pH 7.0 in Waters 1 and 2 may account for the overprediction of U(VI) adsorption. Considerably lower dissolved Ca and Mg were present in Water 4 and U(VI) adsorption was satisfactorily predicted. Since adsorption was underpredicted with the DLM in Water 3, it is possible that the model is unsatisfactory for the high carbonate alkalinity of Water 3 used in this study.

The specific adsorption of Ca^{2+} and Mg^{2+} (i.e., as inner sphere complexes) to soil and clay minerals has been observed. Dzombak and Morel (1990) have determined surface complexation constants for Ca^{2+} on hydrous ferric oxide, and Charlet and Sposito (1987) have accounted for inner sphere Mg^{2+} and Ca^{2+} adsorption to an Oxisol with the triple-layer model. Goldberg (1992) presents an overview of surface complexation models and their predicted constants for inner sphere Ca^{2+} and Mg^{2+} complexes. Surface complexation constants for Ca^{2+} [which may have improved the model in the presence of Ca^{2+} competition with U(VI)] were not used in this study.

Uranium(VI) Adsorption by Soil in Synthetic Drainage Waters

In Fig. 5 (Group 3 waters), each data point represents a synthetic SJV water at specific pCO_2 (described in Table 7). Waters 1, 2, and 3 exhibited a similar decrease in adsorption with increasing CO_2 pressure that was characteristic of Waters 1, 2, and 3 (Group 2) in the goethite experiment. Adsorption decreased due to higher carbonate alkalinities. At high pCO_2, the dissolution of soil P was greatest due to the low solution pH (see Table 7). Solution speciation calculations with MINTEQA2 predicted that the U(VI) mono-, di-, and tricarbonates were the dominant solution species (in the absence of an adsorbing phase). These calculations did not predict significant amounts of soluble U(VI) phosphate species or saturated U(VI) phosphate solids. Therefore, the data suggest that adsorption was lowest in the waters that were equilibrated at high pCO_2 (low pH values) because of the formation of soluble U(VI) mono-, di-, and tricarbonates.

Table 7. Average measured synthetic drainage water compositions after equilibration with Tulare Lake Bed soil experiment. All waters were saturated with excess $CaCO_{3(s)}$. As the water CO_2 partial pressure was increased, $CaCO_{3(s)}$ and P dissolution occurred and solution carbonate alkalinities consequently increased.

Water	CO_2	pH	HCO_3	Mg	Ca	Na	SO_4	Cl	PO_4	I
	kPa		mmol L^{-1}							M
1	0.03	8.0	2	4	9	94	31	75	0.010	0.12
	5.41	7.0	9	5	11	95	33	74	0.010	0.13
	92.9	6.0	23	5	18	112	28	66	0.038	0.17
2	0.03	8.6	1	4	1	20	14	11	0.003	0.03
	0.22	8.2	7	4	3	26	15	13	0.009	0.06
	5.41	7.3	12	4	3	43	15	12	0.013	0.07
	92.9	6.1	25	5	9	36	14	13	0.039	0.06
3	0.03	9.2	44	3	1	96	31	4	0.016	0.13
	0.22	8.6	44	3	1	98	33	3	0.020	0.13
	5.41	7.7	49	4	2	101	34	2	0.020	0.14
	92.9	6.5	58	2	4	117	30	5	0.044	0.15

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Goethite had a greater adsorption preference for U(VI) than the TLB soil in adsorption studies done with the three SJV waters (from Table 7). At a greater initial U(VI) concentration [2 mg U(VI) L^{-1}], goethite adsorbed six times as much U(VI) as the TLB soil under comparable solution compositions (results not shown).

Although goethite was not an ideal model surface for U(VI) adsorption as it relates to the SJV soil, the goethite study suggested that both cationic and anionic dissolved U(VI) species accounted for adsorption. This was concluded because U(VI) adsorption by goethite was somewhat pH-independent at low and high carbonate alkalinities. Uranium(VI) adsorption by both goethite and TLB soil was considerably more carbonate alkalinity dependent. With increasing carbonate alkalinity, U(VI) most likely formed negatively charged carbonate complexes, which did not strongly adsorb to the soil or goethite in this study. Therefore, U(VI) adsorption to soils dominated by permanently charged clays is not a likely factor controlling U(VI) solubility and partitioning in the evaporation ponds.

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