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Effects of sulfate ligand on uranyl carbonato surface species on ferrihydrite surfaces

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ABSTRACT

Understanding uranium (U) sorption processes in permeable reactive barriers (PRB) are critical in modeling reactive transport for evaluating PRB performance at the Fry Canyon demonstration site in Utah, USA. To gain insight into the U sequestration mechanism in the amorphous ferric oxyhydroxide (AFO)-coated gravel PRB, U(VI) sorption processes on ferrihydrite surfaces were studied in 0.01 M Na_2SO_4 solutions to simulate the major chemical composition of U-contaminated groundwater (i.e., $[SO_4^{2-}]$ $\sim$13 mM L^{-1}) at the site. Uranyl sorption was greater at pH 7.5 than that at pH 4 in both air- and 2% pCO_2-equilibrated systems. While there were negligible effects of sulfate ligands on the pH-dependent U(VI) sorption (<24 h) in both systems, X-ray absorption spectroscopy (XAS) analysis showed sulfate ligand associated U(VI) surface species at the ferrihydrite–water interface. In air-equilibrated systems, binary and mono-sulfate U(VI) ternary surface species co-existed at pH 5.43. At pH 6.55–7.83, a mixture of mono-sulfate and bis-carbonato U(VI) ternary surface species became more important. At 2% pCO_2, there was no contribution of sulfate ligands on the U(VI) ternary surface species. Instead, a mixture of bis-carbonato inner-sphere (38%) and tris-carbonato outer-sphere U(VI) ternary surface species (62%) was found at pH 7.62. The study suggests that the competitive ligand (bicarbonate and sulfate) coordination on U(VI) surface species might be important in evaluating the U solid-state speciation in the AFO PRB at the study site where pCO_2 fluctuates between 1 and 2 pCO_2%.

1. Introduction

Metal contamination from mining and processing activities has resulted in an increasing threat to potable water supplies in the United States. Development of effective remediation techniques is critical for protecting drinking water supplies and for mitigating existing contamination problems. Permeable reactive barriers provide a means for passive remediation of groundwater for both organic and inorganic contaminants [1,2]. In its simplest form, a PRB is a trench filled with reactive solid materials, which interact with dissolved groundwater contaminants to reduce their solubility, thus remediating the aquifer. The long-term (9 years) performance of an amorphous ferric oxyhydroxide (AFO)-based PRB has been tested at the Fry Canyon demonstration site in southeastern Utah, USA, the site of an abandoned uranium upgrader operation [3]. The AFO barrier installed in August 1997, consisted of 2 weight percent commercial food grade AFO mixed with pea gravel to produce a solid with high U sorptive capacity, while maintaining permeability that greatly exceeds the surrounding colluvial aquifer. The shallow ground water in the aquifer is contaminated by leaching of uranium from impounded mine tailings resulting in elevated concentrations of U that can exceed 20,000 $\mu g\ L^{-1}$. Groundwater (GW) entering the AFO PRB had dissolved U (as U(VI)) concentrations that ranged from 4 to 130 $\mu M\ L^{-1}$ and averaged 65 $\mu M\ L^{-1}$ over the 10 year demonstration period. The U removal efficiency for the AFO PRB averaged 60% with an estimated 10,700 pore volumes treated during the 10-year deployment. However, the release of U was observed during periods of lower influent U concentration, suggesting that U was approaching sorption equilibrium with the AFO [3]. Evaluating the reaction processes resulting in U sequestration by the AFO PRB, such as determining surface complex species, is critical to development and application of meaningful reaction terms in solute transport models for U at the site. In addition, because iron oxide coatings in many aquifers likely dominate uranium sorption, bulk U concentrations (<20 $\mu g/g$ U in aquifer sediment) are typically well below the threshold for EXAFS measurement ($\sim$200 mg L^{-1}). The AFO PRB, thus, provides an analog for characterizing the speciation and geometry of uranium sorbed by ferric oxyhydroxide under environmental conditions using extended X-ray absorption fine structure spectroscopy (EXAFS). It is well-known knowledge that U(VI) sorbs to AFO surfaces via formation of inner-sphere U(VI) surface species [4]. Since dissolved uranium aqueous speciation is dominated by uranyl carbonato complexes at the alkalinity (avg. 3.4 mM L^{-1}) and pH (avg. 7.1) of Fry Canyon GW, one could expect the formation of U(VI)-carbonato

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Table 1
Average and range of groundwater influent concentrations to the Fry Canyon AFO PRB August 1997 to April 2006.

AFO PRB input	Average (M)	Max. (M)	Min. (M)
Ca	9.3E−03	1.4E−02	2.2E−03
Mg	5.4E−03	7.8E−03	1.8E−03
K	2.4E−04	3.8E−04	1.3E−04
Na	8.1E−03	1.3E−02	3.9E−03
SO_4	1.3E−02	1.8E−02	3.9E−03
Cl	2.0E−03	4.0E−03	2.5E−04
Alkalinity (as CO_3)	3.4E−03	6.4E−03	2.4E−03
Si	2.5E−04	3.5E−04	8.2E−05
U	6.5E−05	1.3E−04	4.1E−06

ternary surface species on AFO surfaces, as previously reported for hematite surfaces [5]. In addition to carbonate alkalinity, the GW has elevated levels of dissolved sulfate (4–18 mM L^{-1}, avg.13 mM L^{-1}) (see Table 1 for GW chemical composition). It is not well understood how sulfate ligands affect the U(VI) partitioning processes on AFO surfaces. While sulfate is known to readily react with iron (oxyhydr) oxides via formation of inner-sphere and outer-sphere complexes, e.g., [6], sulfate is also known to complex with dissolved uranyl to form the uranyl sulfate aqueous species [7]. Sulfate may influence uranyl sorption processes (as U(VI)-carbonato anionic species) on AFO surfaces via (1) competitive adsorption between sulfate and the anionic U(VI)-carbonato aqueous species and/or (2) competitive formation of U(VI)-sulfate/carbonato ternary surface species.

Although the contribution of Ca would be of our future interest to understand Ca-sulfate/carbonato-U quaternary surface species on AFO surfaces (e.g., [8]), we first investigated the competitive ligand effect of sulfate on U(VI) adsorption and U(VI)-carbonato ternary surface species on a model mineral component in the AFO (two-line ferrihydrite) PRB. This paper specifically examines U(VI) reactivity and surface speciation as a function of pH (4 and 7.5) and pCO_2 (air and 2% pCO_2), using batch adsorption experiments and X-ray absorption spectroscopy (XAS) analyses.

2. Materials and methods

2.1. Materials

Two-line ferrihydrite was synthesized according to the method described by Schwertmann and Cornell [9]. To eliminate nitrate ligands, ferrihydrite was prepared using ferric sulfate salts. The pH of the solution was titrated to pH 7.5 and maintained at the pH value for 1 h by addition of 1–2 M CO_2-free NaOH. The ferrihydrite precipitate was washed with deionized (DI) water several times and then kept in ∼0.001 M Na_2SO_4 solutions. The five-point Brunauer–Emmett–Teller (BET) surface area was 99.6 ± 0.8 $m^2\,g^{-1}$. Powder X-ray diffraction (XRD) analysis revealed the diagnostic two broad peaks for two-line ferrihydrite (0.24 and 0.15 nm). The point of zero salt effect (PZSE), as determined by potentiometric titration method [10], was ∼8.

2.2. Uranyl adsorption kinetics

U(VI) adsorption kinetics on ferrihydrite ($[U(VI)]_{tot}$: 7 μM, suspension density: 1.23 g L^{-1}, and *I*: 0.01 M Na_2SO_4) was studied as a function of pH (4 and 7.5) and partial pressure of pCO_2 (air and 2%). A 0.01 M U(VI) stock solution at pH ∼3 was prepared by dissolving $UO_3(s)$ (Alfa Aesar) in conc. H_2SO_4. Ferrihydrite suspensions were prepared in 500 mL polypropylene centrifuge bottles containing 0.01 M Na_2SO_4 solution. Sufficient amounts of 10 mM $NaHCO_3$ solution were added to achieve the desired bicarbonate concentration in equilibrium with the partial pressure of carbon dioxide gas in air (pCO_2: $10^{-3.8}$ atm) or 2% pCO_2 at specified experimental pH values. After 24 h of equilibration with humidified air or 2% CO_2 gas, a sufficient quantity of the U(VI) stock solution was added to the ferrihydrite suspensions to assure $[U_{tot}] = 7$ μM L^{-1}. While the addition of 0.1 M H_2SO_4 was required to maintained the pH values in the air-equilibrated system at 7.5 ± 0.08 or 4.0 ± 0.03, pH values in the 2% pCO_2 system were stable during the experiments. The samples were reacted on a stir plate at room temperature. 10 ml of suspension samples was periodically (5 min–24 h) taken and was filtered through 0.45 μm Millex®-GX filters (Millipore Corp., Bedford, MA). Filtrates were analyzed for $[U_{tot}]$ using kinetic phosphorescence analyzer (Chemchek Instruments, Richland, WA). Dissolved Fe concentrations were analyzed using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). They were <0.02 μM/L at pH 4 and below detection limit at pH 7.5.

2.3. Extended X-ray absorption fine structure spectroscopic measurements

U(VI)-reacted ferrihydrite samples were prepared in 0.01 M Na_2SO_4 as a function of pH (5–8) and pCO_2 (air and 2% pCO_2), according to the method described above (see Table 2 for specific reaction conditions). Using aqueous thermodynamic speciation calculations, these systems were undersaturated with respect to β-$(UO_2)(OH)_2(s)$ under all conditions (see Table 2). For the XAS analyses, the U(VI)-reacted ferrihydrite paste was recovered via centrifugation at >20,000*g* for 10 min. Paste samples were loaded in 3 mm polyChloroTriFluoroEthylene (PCTEF) sample holders, which were then sealed with Mylar tape with polycarbonate windows. The samples were wrapped with moist tissues and kept at ∼3–5 °C prior to XAS data collection. Samples that were prepared under 2% pCO_2 were loaded and kept in a 2% pCO_2 environment prior to the measurements. Room temperature U L_{III} edge (17 166 eV) fluorescence spectra were collected within 48 h of sample preparation at beamline 11–2 at Stanford Synchrotron Radiation Laboratory, Menlo Park, CA. The storage ring was operated at 3 GeV energy with current of 80–100 mA. A uranium reference foil was used to calibrate at the U L_{III} absorption edge energy position every 12 h. A Sr 3 μx filter was used to remove elastically scattered radiation from the fluorescence emissions from samples. Si(2 2 0) double-crystal monochromators were used to tune the incident X-ray beam to the desired energy. A total of 5–8 scans were collected using a Canberra 30-element Ge array detector.

An experiment was conducted at pH ∼5 in argon atmosphere to understand the presence of U(VI)-sulfate ternary species on ferrihydrite surfaces in the absence of carbonate ligand. Deionized water was first boiled and then acidified at pH 3.9 using 0.1–1 M H_2SO_4, and the solution was purged with argon for 24 h to remove dissolved carbonate. The CO_2-free DI water was used to prepare all reagents in 0.01 M Na_2SO_4. To minimize adsorbed/dissolved carbonate ions on ferrihydrite surfaces, the pH of the ferrihydrite suspensions was initially adjusted to ∼4 and purged with humidified argon gas for 24 h. pH values were re-adjusted using a CO_2-free 0.1 M NaOH solution and then kept under the humidified argon purge prior to the CO_2-free U(VI) adsorption experiments. After the centrifugation, the XAS sample was loaded in an argon-filled glove bag.

The program FEFF 6 [11] was used to estimate backscattering phases and amplitude functions of single scattering (SS) $U{-}O_{ax}$, $U{-}O_{eq}$, U—C, U—Fe, and transdioxo uranium multiple scattering paths (MS), which were derived from structural refinement data for andersonite ($Na_2CaUO_2(CO_3)_3{\cdot}5.33H_2O$) and Fe-substituted phuralumite ($Al_2(OH)_2(PO_4)_2(UO_2)_3(OH)_4$ $10H_2O$) [12,13]. A U—S SS paths was obtained from the structural refinement data of zinczippeite, $Zn[UO_2]_2[SO_4]O_2{\cdot}3.5H_2O$ [14]. XAS data reduction and