Uranium Fate in Hanford Sediment Altered by Simulated Acid Waste Solutions

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July 2015

Resubmitted to: *Applied Geochemistry*

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Abstract

Infiltration of aqueous acidic waste to the subsurface may induce conditions that alter contaminant transport. Experiments were conducted to examine the effects of low pore water pH and associated changes to sediment properties on U(VI) behavior in sediments. Macroscopic batch experiments were combined with a variety of bulk characterization studies (Mössbauer and laser spectroscopy), micron-scale inspections (μ -XRF), and molecular scale interrogations (XANES) with the objectives to: 1) determine the extent of U(VI) partitioning to Hanford sediments exposed to acidic waste simulants and held at pH = 2, pH = 5, or under neutral conditions (pH = 8) at varying ionic strength, and in the presence of air [bench-top (BT) experiments] or in the absence of air [glove-box (GB) experiments]; and 2) determine the uranium micron-scale solid phase and associated valence state resulting from the experimental conditions. The investigation showed minimal overall changes in Fe mineralogy as a result of sediment exposure to acid solutions, but an increase in the highly reactive nano Fe fraction of the sediment. Greater uranium partitioning was observed at pH = 5 than at pH = 2 and 8. The μ -XRF inspections and XANES analyses confirmed that high concentration areas on sediment surfaces were rich in U(VI) in the BT experiments, and both U(IV) and U(VI) in the GB experiments. The laser spectroscopy data showed that uranyl phosphates {*e.g.*, metaautunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}]$ and phosphuranylite $[\text{KCa}(\text{H}_3\text{O})_3(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_4 \cdot 8\text{H}_2\text{O}]$ } may have formed in the BT experiments. In the GB experiments, in addition to U(IV) phases, U(VI) phases may have also formed similar to those that are naturally present in the sediment, but at higher concentrations. The results provide insights about U(VI) mobility beneath acidic waste disposal sites.

1. Introduction

Hexavalent uranium [U(VI)] is a common subsurface contaminant throughout the world, including the vadose zone at the Department of Energy Hanford Site in Washington State (Hanford site). Vadose zone U(VI) contamination is of concern with respect to the potential to cause future contaminant plumes in groundwater (GW). Key to predicting future migration from the vadose zone to the GW is an understanding of geochemical processes that control U(VI) mobility.

Mineral-U(VI) contaminant interactions have been the subject of many studies [see for example (Qafoku and Icenhower, 2008) and references therein]. It is well-established in the literature that contaminant U(VI) may interact via adsorption and/or reduction reactions with 1) organic matter (Bruggeman et al., 2012; Joseph et al., 2011; Joseph et al., 2013a; Joseph et al., 2013b; Schmeide et al., 2000; Schmeide et al., 2003; Steudtner et al., 2011); 2) Fe oxides (Bargar et al., 1999; Dodge et al., 2002; Duff and Amrhein, 1996; Ho and Miller, 1986; Hsi and Langmuir, 1985; Jang et al., 2007; Lefevre et al., 2006; Moyes et al., 2000; Reich et al., 1998; Rovira et al., 2007; van Geen et al., 1994; Villalobos and Leckie, 2001; Waite et al., 1994; Wazne et al., 2003); 3) phyllosilicates (Catalano and Brown, 2005); 4) micas (Ilton et al., 2006); 5) titanium oxide (Lefevre et al., 2008); 6) calcite (Kelly et al., 2003); 7) quartz (Ilton et al., 2012); 8) chlorite (Singer et al., 2009); 9) biogenic mackinawite (Veeramani et al., 2013); and 10) framboid pyrite (Qafoku et al., 2009). Uranium adsorption has also been studied in sediments from the Hanford site [see, for example, (Dong et al., 2005; Zachara et al., 2005)], and other DOE contaminated sites, such as the one in Rifle, CO (Campbell et al., 2012; Qafoku et al., 2014). However, the properties of the sediments may be significantly altered when they are

exposed to waste streams with acidic or basic chemistries (Szecsody et al., 2013), affecting U(VI) behavior and mobility.

At some locations at the Hanford site, U(VI) was previously co-disposed in acidic waste and an understanding of geochemical processes beneath these sites is relevant to predicting future fate and transport of the disposed U(VI). There have been research efforts in the past to study uranium interaction with the subsurface sediments of the central plateau at Hanford (Ilton et al., 2008; Wellman et al., 2008; Zachara et al., 2007). However, behavior of U(VI) in sediments that have been exposed to acidic waste fluids is not well documented.

A series of macroscopic batch experiments were combined with a variety of microscopic inspections and spectroscopic measurements with the objectives to: 1) determine the extent of U(VI) partitioning to Hanford sediments exposed to acidic waste simulants and held at pH = 2 and 5, or under neutral conditions (pH = 8) at varying ionic strength and for experiments in air and in a controlled oxygen- and carbon-dioxide-free atmosphere; and 2) determine the uranium micron-scale solid phase and associated valence state resulting from the experimental conditions. Sediment analysis techniques included bulk characterization (Mössbauer and laser spectroscopy), micron-scale inspections (μ -XRF), and molecular-scale interrogations (XANES) of the pre- and post-treatment sediment samples. The results provide insights about U(VI) mobility beneath acidic waste disposal sites.

2. Materials and Methods

2.1. Sediment Material

Sediment used in the experiments was collected in the portion of the Hanford site known as the Hanford Central Plateau. The Hanford Central Plateau is underlain by a sequence of supra-basaltic sediments of Pleistocene and Pliocene age (Serne et al., 2001). These sediments include four primary units: 1) coarse-grained glacio-fluvial gravels and sands in the Hanford formation; 2) Cold Creek upper subunit; 3) Cold Creek lower subunit; and 4) fluvial-lacustrine gravel/sand/silt lithofacies of the Ringold formation. The Hanford formation represents upper 50 to 100% of the 60-90-m thick vadose zone.

An uncontaminated coarse sand sediment was collected at approximately 7 m depth and it is similar to the sediments underneath the former waste disposal areas. This sediment has been previously characterized [e.g., (Qafoku et al., 2003; Szecsody et al., 2013)]. The < 2 mm size-fraction separated from this sediment was used in this study. Previous characterization of similar Hanford sediments indicated that the mineralogy of these sediments was dominated by quartz (30–80%) and plagioclase feldspar (5–20%), with minor amounts (<10%) of K feldspar and amphibole; illite, smectite, chlorite and kaolinite were present in the clay fraction (<2 μ m) (Serne et al., 2001).

2.2. Batch Experiments

These experiments were conducted in the presence of air [bench-top (BT) experiments] or under strict anaerobic conditions inside a controlled-atmosphere (100% Argon gas with undetectable amounts of O₂ and CO₂) [glove-box (GB) experiments]. The presence of O₂ was an experimental variable because it may have an effect on the uranium oxidation state. In addition, O₂ may also control the rate of Fe(III) (hydr)oxide precipitation in a system where the Fe(II) is expected to be released into the aqueous phase from dissolving Fe(II) bearing minerals. The

presence of CO₂ may affect the uranium aqueous speciation and overall adsorption. A total of six batch experiments were conducted:

- 1.) Fixed pH = 2, BT, 3 background solutions, 5 uranium concentrations
- 2.) Fixed pH = 2, GB, 5 background solutions, 5 uranium concentrations
- 3.) Variable pH (initial pH ~ 2), BT, 2 background solutions
- 4.) Fixed pH = 5, BT, 3 background solutions, 5 uranium concentrations
- 5.) Fixed pH = 5, GB, 5 background solutions, 5 uranium concentrations
- 6.) Natural pH = 8, BT, 3 background solutions, 5 uranium concentrations

2.2.1 U(VI) partitioning at fixed pH values (BT and GB experiments)

These experiments were conducted to determine the extent of U(VI) partitioning to the Hanford sediment at three predetermined pH values (pH = 2, 5 and 8), different ionic strengths (using NaNO₃ to vary ionic strength, Table S1), and five U(VI) concentrations (0.1, 0.2, 0.5, 1 and 10 mg/L), in both BT (pH = 2, 5, and 8) and GB (pH = 2 and 5) experiments. The sediments were equilibrated for a relatively long time (weeks) with acid solutions before exposure to the U(VI)-rich solutions. Changes in pH values during equilibration period and the total amount of acid/base added are presented in Figs. S1 and S2 and Tables S2 and S3. The initial solid to solution ratio for each of the batch reactors was 5 g: 9 mL of the background solution. The background solution was Hanford GW mixed with varying concentrations of NaNO₃. The major elemental composition of the GW was: 23.88 mg/L Ca, 5.91 mg/L Mg, 4.75 mg/L K, 20.84

mg/L Si and 14.01 mg/L Na. All experiments were conducted with two replicates. In addition, solution blanks [only the U(VI)-free contacting solutions], soil blanks [soil plus the U(VI)-free contacting solutions], and U(VI) blanks [contacting solutions spiked with the highest U(VI) concentration, i.e., 10 mg/L], were used for each pH and background solution concentration.

The aqueous phase pH of all batch reactors included in the experimental design was continuously adjusted with a nitric acid solution or sodium hydroxide base (0.1M or 1M), as needed, until the solution pH was close to the target pH (i.e., pH = 2 and 5) (Figs. S1 and S2). The process of adjusting pH by addition of adequate amounts of acid or base was continued for weeks depending on the system's ability to reach a new equilibrium when exposed to different background solutions. When the targeted new equilibrium pH was reached, 1 mL of the respective U-rich solutions was spiked into the batch reactors. The pH was checked and readjusted immediately after the U(VI) spike was added. In addition, the aqueous pH was measured and adjusted daily, as needed, to maintain the targeted pH (± 0.1 pH units) in each batch reactor during the 7-day duration of the U(VI) partitioning experiment. In the BT experiment conducted at pH = 8, the initial pH of the background solutions in contact with the sediment was close to 8. There was therefore no need for an initial pH adjustment. The pH was checked and adjusted every day during the seven day time period of the uranium sorption experiment.

At the end of the experiments, the pH was adjusted again to ± 0.1 pH units of the target pH and centrifugation was applied for 5 minutes at 2000 rpm to separate the solid from the liquid phase. The liquid suspensions were then filtered using a 0.2 μm filter and aliquots were taken for chemical analysis (ICP-OES and ICP-MS). The samples for ICP analyses were immediately

acidified using concentrated nitric acid (1% of the total volume). The sediment-associated uranium concentrations were calculated based on the results of the aqueous phase analyses at the end of the experiments and the initial aqueous U(VI) concentration (which accounted for the uranium contribution from the sediment). The initial U(VI) concentration in each batch reactor was based on the total volume of solution, including the volume of acid/base added for pH adjustment (included in Table S1). Uranium isotherms were plotted and the uranium distribution coefficients (K_d) were calculated from these data.

One gram of the solid phase was used for further solid phase mineralogical characterization studies, uranium valence state, and solid phase uranium speciation determinations. For experiments in the absence of air, solid phase samples were stored in the controlled-atmosphere chamber until analysis. The remaining four grams of soil in each batch reactor were used for sequential wet chemical extractions. A bicarbonate/carbonate solution (0.0144 mol/L NaHCO_3 and 0.0028 mol/L Na_2CO_3) with pH = 9.45 and an oxalic acid solution (0.1 mol/L ammonium oxalate and 0.1 mol/L oxalic acid) with pH = 3 were applied for the sequential wet chemical extractions. Eight mL of the bicarbonate/carbonate extracting solution were added in each batch reactor including the blanks in each experimental set. The reactors were shaken for one hour and the solid and liquid phases were then separated via centrifugation. The solutions were filtered (0.2 μm) and liquid samples were prepared for ICP analyses as described above. Eight mL of the second extracting solution were added in each batch reactor to perform extraction in the dark (Al-foil was used to cover the batch reactors). The reactors were continuously shaken for one hour and centrifugation was then used to separate the liquid and

solid phases. The solutions were filtered (0.2 μm) and liquid samples were prepared for ICP analyses as described above.

2.2.2. U(VI) partitioning at variable pH (BT experiments)

The variable-pH BT experiment was conducted with simultaneous addition of acid and U(VI) solutions. After the addition of these solutions into the batch reactors, the pH was not adjusted as in the previously described experiments, but it was measured each day during the 7-day duration of the U(VI) partitioning experiment. Background electrolyte concentrations were 0.1 and 5 mol/L NaNO_3 and were made using a 0.2 mol/L HNO_3 solution and not the GW which was used in the other experiments.

2.3. Geochemical Modeling

Geochemical modeling was performed with the Geochemical Workbench software (Aqueous Solutions, LLC, Champaign, IL). The model calculated the percent distribution of the aqueous phase species and the saturation index for various solid phases based on the input aqueous chemical element concentrations from the experimental data. For the experiments conducted under atmospherically controlled conditions (i.e., inside the anaerobic chamber), the pCO_2 and pO_2 input values were set as functionally zero. The redox couple Fe(II)/Fe(III) was also considered in these modeling simulations because the experiments were conducted in the absence of the O_2 .

2.4. Solid Phase Characterization

2.4.1. Mössbauer Spectroscopy

Mössbauer spectroscopy analyses were performed to quantify the Fe speciation. Mössbauer spectra were collected using either a WissEl Elektronik (Germany) or Web Research Company (St. Paul, MN) instrument that included a closed-cycle cryostat SHI-850 obtained from Janis Research Company, Inc (Wilmington, MA), a Sumitomo CKW-210 He compressor unit, and an Ar-Kr proportional counter detector with WissEl setup or a Ritverc (St. Petersburg, Russia) NaI detection system. A $^{57}\text{Co/Rh}$ source (50-mCi to 75-mCi, initial strength) was used as the gamma energy source. With the WissEl setups, the transmitted counts were stored in a multichannel scalar (MCS) as a function of energy (transducer velocity) using a 1024-channel analyzer. In both the setups (WissEl and Web Research Company) the raw data were folded to 512 channels to provide a flat background and a zero-velocity position corresponding to the center shift (CS) of a metal alpha-Fe foil at room temperature (RT). Calibration spectra were obtained with a 25- μm -thick Fe foil (Amersham, England) placed in the same position as the samples to minimize any geometry errors. The Mössbauer data were modeled with RecoilTM software (University of Ottawa, Canada) using a Voigt-based structural fitting routine (Rancourt and Ping, 1991). Sample preparation procedures (type of sample holder, etc) was described in Peretyazhko et al. (2012).

2.4.2. X-ray Absorption Near Edge Structure (XANES) and Micro- X-ray Fluorescence (μ -XRF)

Polished thin sections were prepared for analysis at the Advanced Photon Source (APS) of the Argonne National Laboratory for elemental mapping using μ -XRF and molecular-scale interrogations using XANES spectra. Sediment samples were imbedded in epoxy, wafered using a diamond saw, and prepared as 100- μm -thin sections on fused quartz slides. These samples were analyzed at the PNC/XSD beamline 20-ID-A at the Advanced Photon Source. Rh coated K-

B mirrors operating at 3 mrad incident angles were used to focus the beam to $5.6\ \mu\text{m} \times 4.8\ \mu\text{m}$. The sediment samples were placed in the x-ray beam at a 45° angle with respect to the incident x-ray beam direction and were inspected to find uranium rich areas. The sample fluorescence was measured using a four element Vortex detector from SII Nanotechnology. The signals for the various elements were separated using electronic regions of interest around their corresponding peaks, and then they were corrected for dead-time and normalized to I_0 measured in a N_2 gas filled miniature ion chamber located just in front of the sample. A U(VI) standard reference sample was measured using scattered radiation (Cross and Frenkel, 1999) using a uranyl nitrate standard. The peak of the first derivative of the uranyl standard was calibrated to 17171 eV. The XANES spectra from the sample were aligned to the standard collected simultaneously with the sample. The spectra were then compared to the U(VI) standard and a natural uraninite as the U(IV) standard. The incident x-ray energy of 17200 eV was used for the μ -XRF maps to excite uranium within the sample. Element distributional maps (e.g., Ca, Cu, Fe, K, Mn, S and Zn) were also developed to study spatial correlations of these elements with the uranium.

2.4.3. Laser Spectroscopy Analyses

Cryogenic time-resolved laser induced fluorescence spectroscopic (TRLIFS) measurements were performed on both treated and untreated sediments at near liquid helium temperature (LHeT, $6 \pm 2\ \text{K}$) using methods described previously (Wang et al., 2005; Wang et al., 2004). The sediment samples were from the experiments conducted at $\text{pH} = 2$ and 5 in the presence (samples BT2 and BT5) and absence (samples GB2 and GB5) of air. In brief, the sediments were placed inside a $2\ \text{mm} \times 4\ \text{mm} \times 25\ \text{mm}$ fused quartz cuvette, sealed with a

silicone stopper, and attached to the cold-finger of a Cryo Industries model RC-152 cryogenic workstation. The sample cuvette was directly exposed to the flow of helium vapors near liquid temperatures (6-8 °K) during measurement and excited with a MOPO-730 laser at 415 nm (Spectra-Physics Nd:YAG). The emitted light was detected with a thermoelectrically cooled PIMAX intensified CCD camera (Princeton Instruments, Inc., Trenton, NJ) after dispersing the emitted light using an Acton SpectroPro 300 spectrograph (Princeton Instruments Inc.). Data analysis was performed using IGOR™ (WaveMetrix Inc., Lake Oswego, OR). All spectra were corrected for the background emission observed for the pure sediment prepared under the same conditions as those of the U(VI)-bearing samples except that no U(VI) was spiked.

3. Results and Discussion

3.1. U(VI) partitioning in batch experiments

The effects of the evaluated experimental variables on the extent of U(VI) partitioning to sediment are presented in the following sections.

3.1.1. GB experiments (absence of air)

In the GB experiments conducted at pH = 2, the U(VI) sorption isotherms were linear in the range of the U(VI) concentrations tested in these experiments (i.e., 0.1-10 mg/L) (Fig. 1A, B, C, D and E). A Freundlich isotherm parameter, “n”, of 0.77 was calculated using the linearized (logarithmic) version of the Freundlich isotherm [$\log(S) = \log K + n \times \log(C)$] (Langmuir, 1997). This value compared well with literature values for U(VI) adsorption to quartz [0.52 and 0.55 (Pabalan et al., 1998) and 0.75 (Davis, 2001; Kohler et al., 1996)], and a Hanford sediment [between 0.80 and 0.88 (Dong et al., 2005)].

The K_d values (Fig. 2A) and associated percent of uranium associated with the solid phase (Table S4) increased with the concentration of NaNO_3 in the background solution. The K_d values also increased with initial U(VI) concentration at the lower range of U(VI) concentrations, but then decreased at higher initial U(VI) concentrations, with similar trends in all background solutions.

In the experiments conducted at $\text{pH} = 5$, essentially all of the uranium was associated with the sediment for all tested background solutions [99-100 % (Table S5)]. The bicarbonate extraction at the end of these sorption experiments removed between 36-67% of the sediment-associated uranium. A subsequent extraction with oxalic acid removed the remaining sediment-associated uranium. The greater U(VI) partitioning of the sediments at $\text{pH} = 5$ could be attributed to either the formation of stable uranium bearing solids, or both adsorption and precipitation.

3.1.2. BT experiments (presence of air)

The BT experiments were conducted at three pH values (i.e., $\text{pH} = 2$, 5, and ~ 8) and three background NaNO_3 concentrations (0.1M, 1M, and 8M) (Tables S6, S7, and S8). At $\text{pH} = 2$, the percent of uranium associated with the sediment increased with the concentration of NaNO_3 in the background solution, with 9.36-27.63 %, 10.84-27.15 %, and 72.93-77.03 % in the 0.1M, 1M, and 8M NaNO_3 solutions, respectively. The U(VI) sorption isotherms (Fig. 1A, C and E) were linear for all conditions, but the K_d values were different at different initial U(VI) concentrations (Fig. 2B). In the experiment conducted at $\text{pH} = 5$, again essentially all of uranium was associated with the sediment for all tested background solutions.

In the BT experiment conducted at near neutral conditions (pH ~ 8) no pH adjustment was necessary. Therefore, dissolution of existing phases was likely at minimum. The percent of uranium associated with the sediment was 15-25 %, 14-18 %, and 37-62 % in the 0.1M, 1M, and 8M NaNO₃ solutions, respectively. However, the percent of uranium associated with the sediment decreased with increasing U(VI) concentration (from 61 % with a uranium concentration of 0.1 mg/L to 37 % with a uranium concentration of 10 mg/L). This suggests a finite capacity of the sediment for sorbed U(VI). The sorption isotherms were linear across all conditions (Fig. 1A, C and E) and K_d values were higher at high ionic strength (Fig. 3). A comparison of all data collected from experiments conducted at pH = 8 is presented in Table S11.

3.1.3. Variable pH

In the variable-pH experiments, the percent of uranium associated with the sediment was 50-58 %, and 85-87% in the 0.1M and 5M NaNO₃ solutions, respectively (Table S9). The overall sediment-associated uranium was greater in these experiments than in the experiments conducted with the acid-pretreated sediment and fixed pH = 2 (Table S10). The trend was linear in both the 5M NaNO₃ and 0.1M NaNO₃ experiments (Fig. S3), and the K_d values increased with the concentration of NaNO₃ in the background solution (Fig. S4).

3.3. Mössbauer Spectroscopy

A series of Mössbauer analyses were conducted to investigate changes in sediment Fe mineralogy after exposure to acid waste simulants. The Mössbauer spectra of the untreated sediment sample were complex. The spectral features, nevertheless, are in agreement with the

presence of phyllosilicates and Fe oxides. These spectra were modeled using: i) fit parameters from the modeled magnetic separate (about 0.5 to 1 wt% of the total sediment), where Fe-oxide and phyllosilicate peaks are distinct (Fig. S5 a), ii) qualitative differences evident between RT and 77 K (not shown) and 77 K and 12 K spectra (Fig. S5 d), that are due to changes in Fe-oxide magnetic behavior with temperature, and iii) XRD observations and chemical data. Room temperature and 77 K spectra modeled using these assumptions are shown in Figs. S5 b and c. A similar approach was used in other studies to characterize the Fe-mineralogy of sediments (Peretyazhko et al., 2012).

Spectral features due to Ti-magnetite, ilmenite, hematite, Al-goethite/nanomagnetite, nano Fe-oxide, phyllosilicates and pyroxene were evident in RT spectra of both whole sediment and magnetic separate of the untreated sample, albeit of different Fe-mineral compositions, as anticipated (Figs. S5 a and b). Although the presence of nano Fe-oxide (nano Fe) is not apparent in the RT spectrum because its peaks and Fe(III)-phyllosilicate peaks are unresolved from each other, the nano Fe presence is noticeable from differences in RT, 77 K and 12 K spectra. The decrease in combined spectral area of nano Fe + Fe(III)-phyllosilicates doublet from 22 to 18% of the total spectral area (Figs. S5 b and c), and, more importantly, the simultaneous increase in combined sextet spectral areas with decreasing temperature, which is apparent from a qualitative comparison of 77 K and 12 K spectra (see marked * peaks in Fig. S5 d), are in agreement with the presence of nano Fe oxide.

This is because ferrihydrite doublet transformed to sextet below 77 K (Murad and Cashion, 2004), while nanogoethite displayed a well-defined sextet at 77 K (Cook et al., 1999). The precise nature of this oxide (or this mixture of oxides), however, is not certain because: i)

type and extent of metal substitution (e.g., Al for Fe in goethite) and organic matter coatings (Eusterhues et al., 2008) significantly affect Mössbauer spectral parameters of Fe-oxides, and ii) overlap of nano Fe oxide sextet in spectra collected below RT with Ti-magnetite and Al-goethite/nanomagnetite peaks. In a recent publication, the nano Fe-oxide feature was assigned to a mix of Al-goethite, nanogoethite, and ferrihydrite (Lee *et al.*, 2012). Based on a comparison of RT and 77 K modeled spectra, the model-derived Fe mineral composition of the sediment is (% of the total Fe): Ti-magnetite (~20%), hematite (2-3%), Al-goethite/nanomagnetite (~8%); ilmenite (<5%), phyllosilicate (PS) Fe(III) + nano Fe (20%), phyllosilicate Fe(II) + pyroxene (Py) M1 Fe(II) (25%), and pyroxene M2 Fe(II) (24%). However, the percent contributions of various species are not unique and should therefore be considered semi-quantitative.

From a qualitative comparison of untreated and treated 77 K spectra, small changes in 77 K spectra (0 to -1mm/sec; marked + in Fig. S5 e) are apparent. The phyllosilicate Fe(II) high energy peak (sharp peak at -2.85 mm/sec marked with “o” in Fig. S5 e) was used in all the spectra for normalization. The changes, although minor, are in agreement with the presence of relatively higher amounts of nano Fe-oxides in the treated samples than in the untreated one. This change can be attributed to the acid treatment of the sediment. The changes in Fe speciation due to U(VI) reduction by Fe^{2+} (magnetite or clay) would be insignificant, given the small U/Fe molar ratio in the sediment [U(VI) concentration is 10 mg/L or 0.04 μM and will only oxidize ~0.8 μM of Fe(III) in a system containing mM concentrations of Fe]. Adsorption of U(VI) on the clay/oxide surfaces would also have no significant bearing on Fe speciation. The increase in nano Fe phases demonstrates an increase in the sediment’s adsorption capacity for uranium. The increase in the nano Fe fraction may also imply that some uranium may have been sequestered in

secondary nano Fe oxide that may have precipitated due to transformation of intrinsic nano Fe oxide by Fe^{2+} released from magnetite dissolution (Missana et al., 2003) or clinocllore, which has been shown to have a strong affinity for U(VI) (Baik et al., 2004)]. Finally, the fact the spectra obtained in the glove-box and bench-top sediments are similar (Fig. S5 f) is intriguing and implies rapid precipitation of the stable secondary nano Fe oxide in both systems.

3.4. *X-ray Absorption Near Edge Structure (XANES) and Micro- X-ray Fluorescence (μ -XRF)*

The sediment samples were interrogated with the beam and it was found that the concentration of solid phase associated uranium was low. Only a few uranium concentrated areas were located in the samples from the experiments conducted at pH = 5 and contacted with the 0.1 M NaNO_3 background solution spiked with a 10 mg/L U(VI)-rich solution. XANES spectra were collected in two uranium rich areas, which were found in each of the sediment samples from the BT and GB experiments. In addition, μ -XRF elemental maps ($60\ \mu\text{m} \times 60\ \mu\text{m}$) were collected in parallel to study uranium association with other elements at the micron scale.

The XANES spectra for the samples from the GB experiments showed that uranium occurred both as U(VI) and U(IV) in one of the hotspots (Fig. 4, green), and mostly as U(VI) in the other hotspot (Fig. 4, pink). Because mineral dissolution was allowed to take place for an extended period of time (the acid pre-treatment period) there is the potential for redox reactions or co-precipitation on the surface of different minerals [such as those on Al-oxyhydroxides (Luo, 2009)]. XANES analysis for the samples from the BT experiments determined that the uranium present was U(VI) (Fig. 4, black and blue).

The 60 $\mu\text{m} \times 60 \mu\text{m}$ elemental maps (e.g., Ca, Cu, Fe, K, Mn, S, and Zn) (Figs. S6 and S7) showed low concentrations of these elements in the hotspots or in the vicinity of the uranium hotspots. These data suggest that the uranium in the hotspots was not associated with common minerals containing some of these elements (such as Fe/Mn oxides or calcite).

3.5. Time-resolved laser spectroscopy

Sediment samples from the experiments in the presence of air (samples BT2 and BT5) displayed almost identical luminescence spectra with vibronic band positions located at 504.6 nm, 526.7 nm, 550.0 nm, and 576.0(3) nm, and with vibronic band spacing of 819 cm^{-1} for BT2 and 822 cm^{-1} for BT5 (Fig. 5 and Table S12). Time-resolved spectra at different delay times also displayed similar pattern of variations with a poorly resolved spectra emerged at long delay times (Figs. S8 and S9). Taking into consideration the measurement errors, the band positions and general spectral profiles of both samples resemble those of uranyl phosphates {e.g. metaautunite $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}]$ and phosphuranylite $[\text{KCa}(\text{H}_3\text{O})_3(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_4 \cdot 8\text{H}_2\text{O}]$ }, uranyl silicates (e.g. boltwoodite, soddyite and uranophane), and zellerite (Wang et al., 2008). In confirmation, the vibronic band spacings (819 cm^{-1} for sample BT2 and 822 cm^{-1} for BT5) were significantly different from those of uranophane and boltwoodite (Wang et al., 2008). Under the acidic conditions, the concentration of carbonate was likely too low to form uranyl-carbonate precipitates. The poorly resolved spectra that appeared at long delay times were absent in the steady-state spectra, an indication of its negligible concentration. Because the spectral profile of the steady-state spectra could not be accounted for by the weak background emission from the sediments (data not shown), other minor U(VI) species such as uranyl oxyhydroxide, which typically show poorly resolved and red-shifted emission spectra, may have also contributed

(Wang et al., 2008). The luminescence lifetime data (Table S11) were consistent with the presence of both a long-lived uranyl-phosphate species (major) and short-lived luminescence species (likely, surface uranyl-hydroxyl complexes).

The luminescence spectra of samples from experiments conducted in the absence of air (samples GB5 and GB2, Figs. S10 and S11) appeared to be distinctively different from the BT samples (Fig. 5b). While both spectra were poorly resolved, the presence of well-defined band shoulders for sample GB5 allowed determination of the individual band positions through spectral deconvolution using Lorentzian band profiles (Table S12). Even though the band positions of GB5 were shifted 0.8 nm to 3.8 nm compared with those of the BT samples with smaller vibronic band spacing and lifetimes, errors in deriving the parameters prevent definitive assignments of the underlying U(VI) species. The broad spectral profiles of the GB samples were similar to those observed for the sediment background (Fig. 5a) with much higher intensities. Likely, similar U(VI) species were present in both, though at higher concentrations in the GB sample. The broad luminescence spectra are indications of multiple U(VI) bonding environments, leading to overlapped spectra, and the red-shifted spectra suggested the presence of U(VI)-oxyhydroxide type of bonding character.

4. Summary of the Results and Implications

For the pH = 2 experiments, an increase in sediment-associated uranium is observed as the NaNO₃ concentration is increased. Modeling simulations conducted with the Geochemical Workbench software reveal similar trends (Fig. S12). In addition, these simulations clearly show that U(VI) concentrations are below solubility of uranium minerals that might be formed under

these conditions (Fig. S13), suggesting adsorption is the predominant partitioning mechanism (although uranyl phosphate species were present in the sediment at the end of the experiments conducted in the presence of air, as indicated by the laser spectroscopy data). Similar results are obtained at pH = 8. The uranium aqueous speciation at this pH is dominated by calcium uranyl carbonate species [the neutral species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ and anionic species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{2-}$], with relative concentrations depending on the concentration of NaNO_3 in the background solutions.

Conversely, the uranium partitioning at pH = 5 is much greater than observed at pH = 2 or pH = 8, and likely includes precipitation mechanisms in addition to adsorption. This observation is consistent with other published studies. For example, Tang et al., (2013) showed that decreasing aqueous U(VI) concentrations were related to adsorption onto Fe hydroxides (pH < 5) and the formation of liebigite [$\text{Ca}_2\text{UO}_2(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$], at pH > 5. Another study suggested uranium co-precipitation on the surface of Al oxyhydroxide particles of sediments in the presence of $\text{Ca}(\text{NO}_3)_2$ and at pH close to 5 (Luo, 2009). In addition, our data showed only partial extraction of uranium by the bicarbonate/carbonate solution for the pH = 5 experiment, and full uranium release was only possible through extraction with oxalic acid, suggesting precipitation in addition to adsorption. The results from modeling calculations with Geochemical Workbench were consistent with these experimental results. They showed that 93 % of the initial U(VI) concentrations were above solubility of the uranyl phosphate phases, with final U(VI) concentrations below solubility, suggesting uranium precipitation at pH = 5.

However, the reasons for the differences observed in U(VI) partitioning at different pH values in our experiments are difficult to entirely decipher because of many competing or coupled pH-dependent reactions such as adsorption, reduction, and precipitation. An example of

a pH-dependent reaction is that of uranium adsorption to different minerals. On one side, ferrihydrite, magnetite, and hematite that are present in the Hanford sediment have lower affinity towards U(VI) at pH = 5 than at pH = 8 (Liger et al., 1999; Missana et al., 2003; Payne et al., 1998); on the other side, phyllosilicates may exhibit opposite behavior and montmorillonite is found to adsorb relatively more U(VI) at pH = 5 than pH = 8 (Pabalan and Turner, 1997). Magnetite, which is a major Fe-oxide in the Hanford sediment, is also an effective uranium sorbent. The study conducted by Missana et al. (2003) suggests that relatively more uranium is sorbed at pH = 7 than pH = 5 but a higher degree of the sorbed uranium exists in the reduced state at pH = 5 than at pH = 7.

The overall amount of sediment-associated uranium is greater in the variable-pH experiments where the acid and U(VI) are added simultaneously. Further investigations are required to determine the mechanisms of U(VI) partitioning in this system. Potentially, partitioning could be related to the increasing role of the solubility control on aqueous U(VI) attenuation as the pH is buffered toward less acidic values (which is prevented in the other experiments conducted at pH = 2). This mechanism is consistent with the geochemical modeling results.

Only a few differences are observed in the BT vs. GB experiments in terms of U(VI) partitioning, although the mechanisms of partitioning could have been different. In the absence of air, the amount of aqueous and/or sorbed Fe(II) is expected to be greater. However, this important difference was not manifested in significant differences in uranium partitioning between these two systems. The micron-scale sediment assays show that in areas with relatively high uranium concentrations most of the uranium that is added as U(VI) is not reduced to U(IV).

The laser spectroscopy data, however, indicate the dominant uranium phases are different for the BT and GB experiments.

In summary, this research effort documents the U(VI) partitioning behavior in a sediment that is exposed to acidic waste fluids at fixed and variable pH conditions. The results from this study are intended to support the development of conceptual models and interpretation of waste site characterization data.

Acknowledgments

Funding for this work was provided by the U.S. Department of Energy (DOE) Office of Environmental Management and Richland Operations Office. The Pacific Northwest National Laboratory (PNNL) is operated by Battelle Memorial Institute for the Department of Energy (DOE) under Contract DE-AC05-76RL01830. The research presented in the paper was conducted in part in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. DOE Office of Biological and Environmental Research and located at PNNL in Richland, WA, USA. Use of the Advanced Photon Source (APS) at the Argonne National Laboratory (ANL) is supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences under contract DE-AC02-06CH11357. The authors appreciate the support and help of Dr. Steve Heald at APS/ANL during collection of the μ -XRF and XANES data.

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Figure 1. Uranium sorption isotherms measured at pH = 2 (GB and BT experiments) and pH = 8 (BT experiments). The NaNO_3 background solution concentrations were A) 0.1M, B) 0.5M, C) 1M, D) 5M, and E) 8M.

Figure 2. Distribution coefficient (K_d) as a function of initial U concentration in the contacting solution and five background solutions (pH= 2; A: GB experiments, and B: BT experiments).

Figure 3. Distribution coefficient (K_d) as a function of initial U concentration in the contacting solution and the background solution (pH= 8, BT experiments).

Figure 4. Uranium L_3 XANES measured in the GB (solid lines) and BT (dotted lines) experiments for sediment contacted with the 0.1M NaNO_3 background solution containing 10 mg/L U(VI) in experiments conducted at pH = 5, compared to spectra for U(IV) (purple) and U(VI) (red) reference compounds. Spectra were shifted along the y-axis for clarity. Spectra show partially reduced (GB experiments, green and pink) and oxidized U(VI) (BT experiments, black and blue).

Figure 5. LHeT luminescence spectra of U(VI) treated sediments from the BT and GB experiments: a: BT5 (pH = 5); b: BT2 (pH = 2); c: GB (pH = 5); d: GB2 (pH = 2). All spectra were normalized to the same maximum intensity and offset along the Y-axis for clarity. $\lambda_{\text{ex}} = 415$ nm.