

Sequestering Uranium and Technetium through Co-Precipitation with Aluminum in a Contaminated Acidic Environment

WENSUI LUO,[†] SHELLY D. KELLY,^{†,‡}
KENNETH M. KEMNER,[‡] DAVID WATSON,[†]
JIZHONG ZHOU,[§] PHILIP M. JARDINE,[†]
AND BAOHUA GU^{*†}

Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, Biosciences Division, Argonne National Laboratory, Argonne, Illinois 60439, and Institute for Environmental Genomics, Department of Botany and Microbiology, University of Oklahoma, Norman, Oklahoma 73019

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This research evaluated a method of controlled base addition for immobilizing uranium (U) and technetium (Tc) through co-precipitation with aluminum (Al) and other metal ions which co-exist in a highly contaminated acidic environment. The batch and column experiments indicate that the addition of strong base (NaOH) provided a rapid yet effective means of sequestering U, Tc, and toxic metal ions such as nickel (Ni²⁺) and cobalt (Co²⁺) in the sediment and groundwater. Greater than 94% of soluble U (as UO₂²⁺) and >83% of Tc (as TcO₄⁻) can be immobilized at pH above 4.5 by co-precipitation with Al-oxyhydroxides. The presence of sediment minerals appeared to facilitate co-precipitation of these contaminants at lower pH values than those in the absence of sediments. The immobilized U and Tc were found to be stable against dissolution in Ca(NO₃)₂ solution (up to 50 mM) because of the formation of strong surface complexes between U or Tc and Al-oxyhydroxides. This research concludes that, as long as a relatively high pH (>5) and a low carbonate concentration are maintained, both U and Tc can be effectively immobilized under given site-specific conditions.

Introduction

During the cold war era, massive amounts of acidic and radioactive wastes were disposed of in four unlined S-3 Ponds at the Y-12 National Security Complex in Oak Ridge, Tennessee (1, 2). The leakage from the S-3 Ponds created a groundwater plume of contamination in the underlying unconsolidated residuum and shale bedrock, which extends more than 2 km along the geologic strike both east and west of the Ponds. The groundwater is characterized with a low pH (~3.5) but high contents of uranium (U, as high as 0.2 mM), technetium (Tc, ~47 nM), aluminum (Al, ~18 mM), nitrate and sulfate (~100 mM). The dominant forms of U

and Tc in groundwater and sediments are U(VI) [as uranyl (UO₂²⁺)] and Tc(VII) [as pertechnetate (TcO₄⁻)], as described previously (1, 3). However, uranyl could be associated with nitrate (as UO₂NO₃⁺) or sulfate [as UO₂SO₄ or UO₂(SO₄)₂²⁻] at such a low pH due to high nitrate and sulfate concentrations (1, 4–8). Pertechnetate is poorly retained by the sediment and thus has often been observed along with nitrate in the groundwater (1, 3). On the other hand, reduced forms of U(IV) and Tc(IV) are known to be particle reactive or readily immobilized in the sediment under strong reducing conditions (1, 3, 9). The extreme acidity also caused the dissolution of the shale and carbonate bedrocks, releasing high concentrations of Ca²⁺ (as high as 25 mM), Mg²⁺ (~8 mM), and toxic metal ions such as Ni²⁺ (0.2 mM) and Co²⁺ (~0.02 mM) (1, 10).

The low pH, high metal ion, and nitrate concentrations pose formidable challenges to successful implementation of remediation technologies such as in situ bioremediation and ex situ pump-and-treat at the site (3, 9, 11–14). For example, in a pilot-scale bioremediation study, the groundwater had to be treated or neutralized above-ground and then recirculated to the subsurface to create conditions that are favorable for microbially mediated reduction and immobilization of U (15, 16). The treatment resulted in production of large quantities of precipitated, mixed wastes containing radioactive materials and toxic metal ions, which had to be treated and stored separately. However, by taking advantage of the high Al content in groundwater, studies have shown that more than 90% of U and Tc could be removed or co-precipitated with Al-oxyhydroxides by the base addition (1). A survey of groundwater from this contaminated site also indicates that U and Al concentrations are inversely correlated to pH, possibly due to the co-precipitation of U and Al at higher pH conditions (10). We thus hypothesized that the addition of base (e.g., NaOH) or in situ subsurface pH manipulation could provide an effective means of sequestering U and Tc at the site. Additionally, an increased pH in the subsurface can potentially enhance microbial activity, leading to increased microbial denitrification (to be evaluated in future studies).

The present study was therefore aimed at evaluating the mechanisms and effectiveness of immobilizing U and Tc through precipitation or co-precipitation with Al and developing a controlled pH manipulation technique to remediate the contaminated groundwater and sediment under given site-specific conditions. We show that a large percentage of soluble U and Tc can be removed at pH above 4.5 by co-precipitation with Al-oxyhydroxides. The immobilized U and Tc are stable against dissolution in Ca(NO₃)₂ because of the specific sorption and surface complexation of uranyl and pertechnetate with Al-oxyhydroxides.

Methods and Materials

Groundwater and Sediment Samples. Sediments were collected from borehole FWB103 (11–12 m deep) by rotasonic drilling and characterized as interbedded Nolichucky shale and sandstone (10). This highly weathered clayey sediment was selected for the study because of its relatively high U content among all sediment core samples. The mineralogical composition of the sediment consists of primarily vermiculite > mica > hydroxyl-interlayered-vermiculite, and the sandstone material consists of mainly quartz > calcite > feldspar. The sediment was homogenized and sieved through a 4-mm sieve before use. The major elemental composition of the sediment (Table 1) was determined using an inductively coupled plasma–mass spectrometer (ICP–MS) following the

* Corresponding author phone: (865)-574-7286; fax: (865)-576-3989; e-mail: gub1@ornl.gov.

[†] Oak Ridge National Laboratory.

[‡] Argonne National Laboratory.

[§] University of Oklahoma.

^{||} Current Address: EXAFS Analysis, Bolingbrook, Illinois 60440.

TABLE 1. Major Elemental or Ionic Composition of the Groundwater and Sediment Used in This Study (ND = Not Determined, NA = Non-Applicable, TOC = Total Organic Carbon, and DO = Dissolved Oxygen)

	groundwater (mmol/L)	sediment (mmol/kg)
U	0.2	2.7
Tc	1.1×10^{-5}	3.5×10^{-5}
Al	6.3	1.4×10^3
Si	1.2	ND
Fe	8.9×10^{-3}	8.4×10^2
Mn	0.5	ND
Co	8.0×10^{-3}	0.5
Ni	1.6×10^{-2}	1.3
Mg	2.1	4.8×10^2
Ca	7.6	5.2×10^2
nitrate	50.2	21.0
sulfate	32.0	10.0
chloride	9.1	ND
DO	0.3	NA
TOC	4.1	35.7
CEC	NA	135.5
AEC	NA	14.0

digestion of the sediment using EPA method 3050. The cation- and anion-exchange capacities (CEC and AEC) of the sediment were 135.3 and 14.0 mmol/kg, respectively, determined according to methods of Hendershot et al. (17). Nitrate and sulfate were extracted by 0.03 M KCl solution and determined by ion chromatography (IC). The pH of the sediment suspension was measured in 0.1 M CaCl₂ at a 1:2 soil to solution ratio. Groundwater was collected in polyethylene bottles from the same location as sediment core samples, and its major ionic species also were analyzed by ICP-MS or IC (for anions) (Table 1).

Column pH Manipulation, Batch Titration, and Stability Studies. The column flow experiment was performed by packing homogenized sediments (340 g dry weight) into a glass column (50 × 140 mm) and continuously recirculating contaminated groundwater (1.8 L in a reservoir) through the column at a flow rate of 1.5 mL/min. The experiment is to simulate field remedial scenarios, in which the groundwater is titrated slowly and recirculated within the subsurface treatment zone. While the reservoir was being stirred, NaOH (1.35 M) was added at 0.5–1 mL daily for 31 days. The process was designed to avoid rapid precipitation of Al-oxyhydroxides, which could potentially cause clogging of the sediment column during titration. On the other hand, Al ions tend to form soluble hydroxyl-Al species (at OH⁻/Al ratio <2.8) (18, 19) that are subsequently transported and precipitate slowly within the sediment column. No significant amounts of precipitate were observed in the reservoir for the duration of the experiment. Effluent samples (about 1 mL) were taken periodically through a 3-way valve and then centrifuged at 8000g for 20 min to obtain the clear supernatant solution. The operationally defined dissolved ionic species in the supernatant solution were determined either by ICP-MS (for metal ions) or ion chromatography (for anions). Technetium was assayed by liquid scintillation counting, as described previously (20, 21). Analytical errors were estimated to be better than ± 10%. A control column (without pH adjustment) also was performed in the same manner. However, data are not presented because no significant changes in the effluent water chemistry were noted.

A series of contaminated groundwater samples (20 mL each in separate polyethylene vials) was titrated to pH 9.5 by the addition of varying amounts of NaOH (1.35 M) under aerobic conditions. Similarly, sediment samples (5 g each) were first suspended in 25 mL of 0.03 M KCl background electrolyte in 50-mL polyethylene vials, to which various

amounts of NaOH were added to give a pH ranging from about 3.5 to 9. The final volume was made up to 30 mL for all groundwater and sediment samples, which were then equilibrated on an end-to-end shaker for 48 h. The supernatant solutions were subsequently collected by centrifugation, the final pH was recorded, and the ionic composition was determined as described earlier.

To evaluate the stability and dissolution of precipitated U and Tc, selected sediment and groundwater precipitate samples from the above batch experiments (titrated to pH ~7) were equilibrated with 20 mL of either KHCO₃ or Ca(NO₃)₂ at 5 or 50 mM concentrations. These electrolyte solutions were selected to simulate conditions in which a high ionic strength and carbonate concentration could cause the desorption (through ion exchange) or dissolution (through complexation) of U and Tc. After 7 days of equilibration, the supernatant solution was collected by centrifugation and analyzed for U and Tc contents.

X-ray Absorption Spectroscopy and Mineralogical Characterization. The extended X-ray absorption fine structure (EXAFS) spectra were collected at MR-CAT (22) at the Advanced Photon Source of Argonne National Laboratory. Selected sediment samples from the batch titration experiment were processed in a controlled chamber (N₂ atmosphere) by packing the moist paste (after centrifugation) into a plastic sample holder that was sealed with Kapton film and tape. The sample was stored in the chamber and subsequently transferred to the beamline for the X-ray measurements. The spectra were collected at room temperature in quick scanning fluorescence mode. The beamline parameters and analysis procedures have been previously described (23, 24), and additional details were provided in Supporting Information ((SI) Table S1 and Figure S1). In addition, selected samples (groundwater precipitates and sediments before and after pH adjustment) were analyzed for mineralogical and morphological characteristics by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) spectroscopy. Details are provided in SI (Figures S2–S4).

Results and Discussion

Immobilization of U and Tc in the Sediment Column. During the column-flow experiment, the effluent pH and concentration profiles of U and Tc were continuously monitored along with other major cations and anions (Figure 1). As can be expected, with the addition of NaOH, the pH increased slowly from ~3.5 to 4.4. (Figure 1a), largely due to the hydrolysis of both dissolved and sorbed Al species and the buffering of the sediment in the column (1, 25). The estimated amount of base needed for hydrolyzing Al was about 34 mmol based on the Al concentration (6.3 mM) and the volume of the groundwater used in the experiment. This amount accounted for nearly 67% of the total amount of NaOH consumed (50.9 mmol). In addition to Al species, other polyvalent cationic species such as dissolved and sorbed Fe(III) and Mn(IV) should have contributed to the consumption of NaOH because of their relatively high contents in the sediment (Table 1). They are known to hydrolyze much like Al³⁺ within the pH range studied (26). The presence of natural humic substances may further contribute to the buffering capacity of the system because of their polyelectrolytic characteristics with varying acidic functional groups (7, 27, 28).

The concentrations of U, Tc, Al, and Si in the column effluent decreased consistently as the pH increased (Figure 1b). At the end of the experiment (at pH ~4.4), >90% of the initial groundwater U (0.15 mM) and >80% of Tc (10.5 nM) were removed. This decrease in the U and Tc concentrations coincided with the removal or co-precipitation of Al and Si, in which the groundwater Al concentration decreased from about 6.3 to 0.2 mM and Si decreased from 1.2 to 0.1 mM,

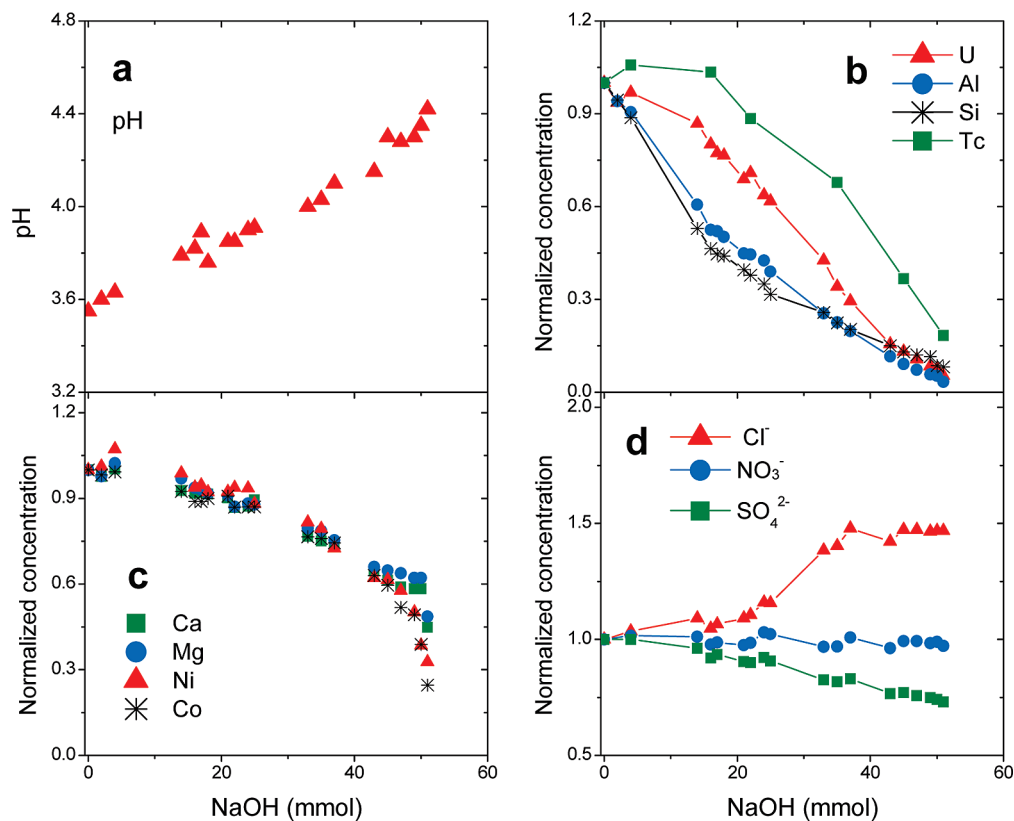


FIGURE 1. pH and normalized concentrations of dissolved U, Tc, and other major cations and anions in column effluent solutions. The groundwater (1.5 L in a reservoir) was added with 0.5–1 mL of NaOH (1.35 M) daily and circulated continuously through the column for 31 days.

respectively. On the basis of the speciation calculations (1, 4, 25, 29), UO_2^{2+} , $\text{UO}_2\text{SO}_4(\text{aq})$, and TcO_4^- should be the dominant aqueous species in the pH range of about 3.5–5 and would have remained in the solution phase. It is the sorption and co-precipitation with Al-oxyhydroxides and/or hydroxyaluminosilicates which caused the sequestration of U and Tc (1, 30). The precipitated Al-oxyhydroxides after pH adjustment formed coatings on minerals as revealed by the SEM analysis, which were also evidenced by increased intensities of Al and U in the EDX spectra (SI Figures S3–S4). Tc cannot be detected because of its low concentrations in the sample.

At the end of the titration, the concentration profiles of Ca^{2+} , Mg^{2+} , Co^{2+} , and Ni^{2+} ions also showed a decrease from initial concentrations of about 7.6 and 2.1 mM to 3.4 and 1.0 mM (for Ca^{2+} and Mg^{2+}) and from 8.0 and 16.1 μM to 2.3 and 5.4 μM (for Co^{2+} and Ni^{2+}) (Figure 1c). However, it was somewhat surprising that the decrease in the concentrations of Ca^{2+} , Mg^{2+} , Co^{2+} , and Ni^{2+} occurred at pH below 4.0 (or after the addition of ~40 mmol of NaOH), under which these cations would be expected to exist as soluble ionic species (1, 25). Even at pH 5 and in the presence of Al (but without sediments), previous studies showed that these ions remained in solution, except Co^{2+} (1). These observations could not be explained by the hydrolysis and precipitation of Ca^{2+} , Mg^{2+} , Co^{2+} , and Ni^{2+} but are attributed to complex interactions such as sorption, ion exchange, and co-precipitation with Al-oxyhydroxides, as will be discussed in detail below. Previous studies reported that Al-oxyhydroxides are particularly effective in sorbing Co^{2+} and Ni^{2+} by forming double hydroxide phases (31–33).

Among major anionic species, the concentration of nitrate remained relatively constant at about 50 mM during the titration (Figure 1d). On the other hand, the sulfate concentration decreased from 31 to 22.6 mM, but the chloride concentration increased from about 9 to 13.2 mM. These

results indicate complex interactions and competition among various anions for sorption and complexation with minerals and precipitated Al-oxyhydroxides. Specifically, because of a relatively low pH and the presence of large quantities of Al and Fe (10), the sediment contains a significant amount of variable positive charges with a measured AEC of 14 mmol/kg at pH = 3.5. With an increase of pH, the AEC of the sediment is expected to decrease (34) and thus results in the desorption or release of previously sorbed anions such as chloride in solution. Nitrate has a low tendency to form surface complexes with mineral surfaces (1, 35); thus its effluent concentration remained relatively constant during the titration (Figure 1d). Although sulfate is a divalent anion and more strongly sorbed than chloride and nitrate by variably charged sites in the sediment (36), the decrease in the sulfate concentration could not be explained by its competitive sorption onto the sediment because sulfate desorption should also be expected as the pH increased or AEC decreased (1, 25). On the other hand, the decrease in the sulfate concentration can be attributed to the co-precipitation and the formation of the Al- SO_4 -OH minerals. The co-precipitation of sulfate with Al and the formation of minerals such as basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$) and jurbanite [$\text{AlSO}_4(\text{OH}) \cdot 5\text{H}_2\text{O}$ or $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 5\text{H}_2\text{O}$] have been reported previously (37–39). However, because of the amorphous nature of these precipitates, the presence of basaluminite and jurbanite minerals could not be detected by the XRD analysis (SI Figure S2). On the other hand, the formation of Al-OH- SO_4 precipitates can be validated by the activity-ratio analysis based on methods of Sposito (34) (SI Figure S5). Results indicate that the formation of basaluminite and jurbanite is thermodynamically favored under given experimental conditions (1, 34).

Batch Titration of the Sediment and Groundwater.

Previous studies (1) using a similar contaminated groundwater showed that the precipitation or co-precipitation of

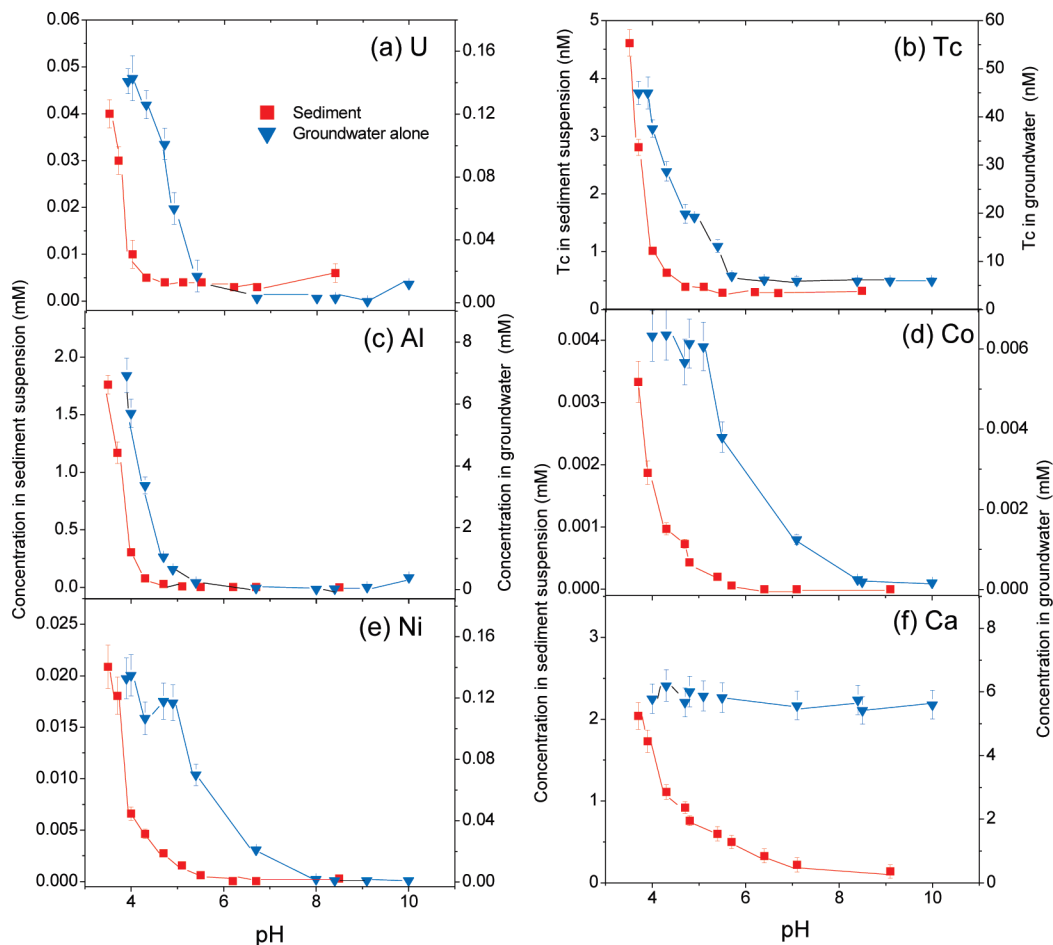


FIGURE 2. Aqueous concentrations of U (a), Tc (b), Al (c), Co (d), Ni (e), and Ca (f) during the batch titration of a contaminated sediment and a groundwater. The error bars represent one standard deviation of triplicate samples.

metal ions (e.g., U, Tc, Al, Ca, Ni, Co) occurred at relatively higher pH values than was observed in the present study (Figure 1). A major difference was the presence of the sediments (in addition to groundwater) in the column experiment, and it suggests that mineral surfaces played an important role in causing the sorption and/or co-precipitation of these metal ions. To evaluate these processes during the pH titration, a series of batch experiments were performed either in the groundwater or the contaminated sediment suspension obtained from the same location. Similarly, results (Figure 2) indicate that U and Tc were rapidly removed as the pH increased. However, the removal of uranium was found to occur at a lower pH (~4) in the presence of sediments than in the groundwater alone (at pH ~5.2) (Figure 2a). The removal of Tc and Al also occurred at slightly lower pH values in the sediment suspension than in the groundwater (Figure 2b, c). The differences in the removal of Ca^{2+} , Ni^{2+} , and Co^{2+} were even more pronounced, in which these ions were hardly removed at pH < 5 during the titration of the groundwater. However, in the presence of sediments, significant portions of Ni^{2+} (>90%), Co^{2+} (>90%), and Ca^{2+} (>60%) were removed at pH above neutral, again indicating the importance of the presence of mineral surfaces in causing the removal of these ions. The different removal patterns of cations in the sediment and the groundwater again suggest that different mechanisms may be responsible, including ion-exchange, adsorption, precipitation, and co-precipitation. The sediment contains substantial amounts of iron oxyhydroxides such as ferrihydrite, goethite, and phyllosilicates (e.g., illite, kaolinite, and vermiculite) (10, 40). These

minerals can act as reactive surfaces for the sorption of these ions and hydroxyl-metal ions [e.g., $\text{Al}(\text{OH})_2^+$ or $\text{Al}(\text{OH})_2^+$, UO_2^{2+} or $\text{UO}_2(\text{OH})^+$, Ca^{2+} or $\text{Ca}(\text{OH})^+$] or oxyanions such as TcO_4^- onto positively charged mineral surfaces under acidic pH conditions (5, 10, 41–43). They may also facilitate the hydroxylation and thus the growth and precipitation of Al-oxyhydroxide solid phases at lower pH values, resulting in the sorption and co-precipitation of U and Tc at lower pH values in the sediment.

It is important to note that most of U and Tc were removed at pH above 5.5 in groundwater, whereas little or no removal of Ca^{2+} or nitrate occurred even though their concentrations were much higher (Table 1). This indicates that the removal of U and Tc is not a simple cation or anion exchange process because concentrations of U and Tc in solution were orders of magnitude lower than those of competing cations or anions in the system. The removal of U and Tc is attributed to the specific sorption or inner-sphere surface complexation with precipitated Al-oxyhydroxides (1, 43). The specific inner-sphere complexation between uranyl and Al-oxyhydroxides was validated by the EXAFS analysis, in which uranyl appears to be bound directly to aluminate in the sediment (Figure 3) (also see SI Figure S1 and Table S1). The Fourier transform (Figure 3) shows the strong U– O_{ax} , U– O_{eq} , and U–Al₁ signals from the axial oxygen atoms of the uranyl moiety, the equatorial oxygen atom of the uranyl, and the alumina atom of the Al-oxyhydroxide. The model also includes the U– O_{ax} multiple scattering paths and another weaker alumina (U–Al₂) signal. The EXAFS results for the U– O_{ax} , U– O_{eq} , and U–Al distances are consistent with the bonding of the uranyl to alumina in dioxouranium sodium magnesium aluminum

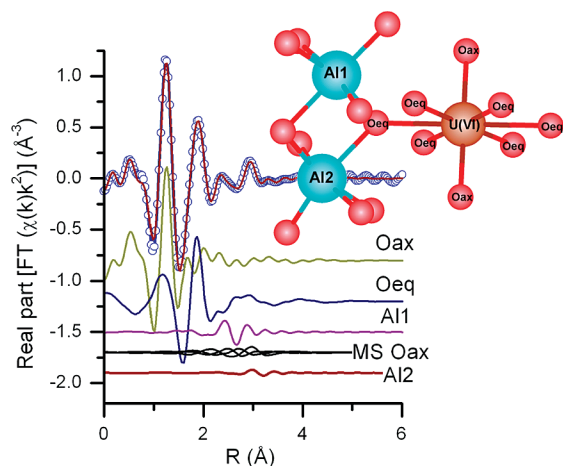


FIGURE 3. Real part of the Fourier transform of EXAFS spectra (symbols) and model (line) of co-precipitated U(VI) with Al-oxyhydroxides in a contaminated acidic sediment, which was titrated to pH 6.7. The components of the model are shown offset beneath. The inset shows the structure of uranyl bound to aluminate. The red, brown, and blue spheres represent O, U(VI), and Al atoms. The atoms that correspond to the components of the model are labeled. The raw data and fitting parameters are available in the Supporting Information.

oxide (ICSD 73443) as shown in the inset of Figure 3. Similarly, in a study of U sorption by amorphous Al-hydroxide by EXAFS, Froideval et al. (30) found that uranyl formed predominant mononuclear and dinuclear inner-sphere surface complexes with Al-hydroxide. The sorption or surface complexation between Tc and aluminate could not be evaluated by EXAFS because of the extremely low concentration of Tc in the sample. However, the fact that little or no desorption of anionic Tc (as TcO_4^-) occurred at pH ~ 10 (Figure 2) provides additional evidence of strong sorption or possible inner-sphere surface complexation between Tc and aluminate because surfaces of aluminate should be negatively charged at pH 10 (1, 44). Previous studies have shown that significant desorption of Tc occurs only when a relatively high concentration of carbonate is added to the system because CO_3^{2-} also forms complexes with Al-oxyhydroxides (1).

Stability of Co-Precipitated U and Tc. Successful remediation of the contaminated site through subsurface pH manipulation depends on the stability of immobilized U and Tc. We subsequently evaluated the stability of precipitated or co-precipitated U and Tc in both pH-adjusted sediment and groundwater samples from the above batch experiments by equilibrating with either $\text{Ca}(\text{NO}_3)_2$ or KHCO_3 at concentrations of either 5 or 50 mM (Figure 4). $\text{Ca}(\text{NO}_3)_2$ was used to determine the exchangeable amounts of U and Tc species by Ca^{2+} or nitrate, whereas KHCO_3 was used to assess the desorption or dissolution of U and Tc through the complexation reactions of carbonates. Results indicate that the immobilized U and Tc was stable in $\text{Ca}(\text{NO}_3)_2$; less than 1% of precipitated U and Tc was released into the solution phase after 7 days of equilibration. These observations again indicate the strong complexation between U or Tc and Al-oxyhydroxides because Ca^{2+} and nitrate ions at 50 mM were incapable of desorbing U and Tc (1, 45). On the other hand, substantially higher amounts of U and Tc were dissolved in KHCO_3 , particularly at a relatively high KHCO_3 concentration (50 mM) (Figure 4a). Less than 10% of U and 15% of Tc were dissolved in 5 mM KHCO_3 , whereas about 20–50% of U and 50–60% of Tc were dissolved in 50 mM KHCO_3 solution. The instability of U at a high carbonate

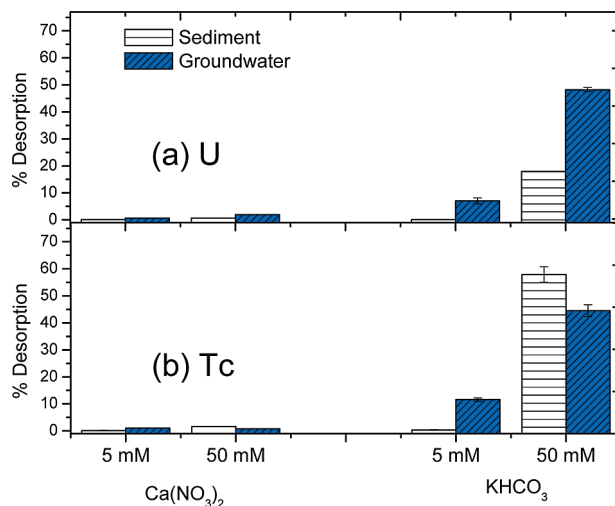


FIGURE 4. Desorption and dissolution of (a) uranium and (b) technetium from sediment minerals and precipitates following the batch titration of a contaminated sediment and groundwater to pH about 6.5. The experiment was performed by equilibrating samples with either 5 or 50 mM of $\text{Ca}(\text{NO}_3)_2$ or KHCO_3 solution in 7 days. The error bars represent one standard deviation of triplicate samples.

concentration is expected because uranyl readily forms stable and soluble complexes with carbonate such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ (5, 46). However, compared with those in the groundwater precipitate, the immobilized U in the sediment appeared to be more stable, especially at the low carbonate concentration (5 mM KHCO_3). This observation can be explained by the buffering capability of the sediment, leading to a lower pH (~ 7.3) in the sediment than in the groundwater precipitate (pH ~ 8.9) by the addition of 5 mM KHCO_3 . Similarly, the immobilized Tc was found to be relatively stable in 5 mM KHCO_3 in the presence of sediments (Figure 4b), but an increased concentration of KHCO_3 (50 mM) led to substantial desorption or dissolution of Tc. Since Tc (as TcO_4^-) itself does not form complexes with carbonates (29, 46), the fact that carbonate is much more effective than nitrate in desorbing anionic TcO_4^- indicates that carbonates were specifically sorbed onto Al-oxyhydroxides and caused a reduction in surface adsorption sites (1, 47), leading to a decreased sorption and/or an increased desorption of Tc in the carbonate solution. This study thus concludes that, as long as a relatively high pH (>5) and a low carbonate concentration are maintained, both U and Tc can be effectively immobilized. It demonstrates the feasibility and effectiveness of controlled pH manipulation for remediation, particularly for the groundwater and sediments that are contaminated with high levels of U, Tc, Al, and toxic metal ions at a low pH.

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Supporting Information Available

Analytical details, one additional table, and five figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Gu, B.; Brooks, S. C.; Roh, Y.; Jardine, P. M. Geochemical reactions and dynamics during titration of a contaminated groundwater with high uranium, aluminum, and calcium. *Geochim. Cosmochim. Acta* **2003**, *67*, 2749–2761.
- (2) Phillips, D. H.; Gu, B.; Watson, D. B.; Roh, Y.; Liang, L.; Lee, S. Y. Performance evaluation of a zero-valent iron reactive barrier: Mineralogical characteristics. *Environ. Sci. Technol.* **2000**, *34*, 4169–4176.
- (3) Istok, J. D.; Senko, J. M.; Krumholz, L. R.; Watson, D.; Bogle, M. A.; Peacock, A.; Chang, Y. J.; White, D. C. In situ bioreduction of technetium and uranium in a nitrate-contaminated aquifer. *Environ. Sci. Technol.* **2004**, *38*, 468–475.
- (4) Couston, L.; Pouyat, D.; Moulin, C.; Decambox, P. Speciation of uranyl species in nitric acid medium by time-resolved laser-induced fluorescence. *Appl. Spectrosc.* **1995**, *49*, 349–353.
- (5) Langmuir, D. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposit. *Geochim. Cosmochim. Acta* **1978**, *42*, 547.
- (6) Moulin, C.; Laszak, I.; Moulin, V.; Tondre, C. Time-resolved laser-induced fluorescence as a unique tool for low-level uranium speciation. *Appl. Spectrosc.* **1998**, *52*, 528–535.
- (7) Zhou, P.; Gu, B. Extraction of oxidized and reduced forms of uranium from contaminated soils: The effects of carbonate concentration and pH. *Environ. Sci. Technol.* **2005**, *39*, 4435–4440.
- (8) Gu, B.; Ku, Y.; Jardine, P. M. Sorption and binary exchange of nitrate, sulfate, and uranium on an anion-exchange resin. *Environ. Sci. Technol.* **2004**, *38*, 3184–3188.
- (9) Wu, W.; Carley, J.; Luo, J.; Ginder-Vogel, M. A.; Cardenas, E.; Leigh, M. B.; Hwang, C.; Kelly, S. D.; Ruan, C.; Wu, L.; Nostrand, J. V.; Gentry, T.; Lowe, K.; Mehlhorn, T. L.; Carroll, S.; Luo, W.; Fields, M. W.; Gu, B.; Watson, D.; Kemner, K.; Marsh, T.; Tiedje, J.; Zhou, J.; Fendorf, S.; Kitanidis, P. K.; Jardine, P. M.; Criddle, C. In situ bioreduction of uranium (VI) to submicromolar levels and reoxidation by dissolved oxygen. *Environ. Sci. Technol.* **2007**, *41*, 5716–5723.
- (10) Phillips, D. H.; Watson, D. B.; Roh, Y.; Mehlhorn, T. L.; Moon, J. W.; Jardine, P. M. Distribution of uranium contamination in weathered fractured saprolite/shale and ground water. *J. Environ. Qual.* **2006**, *35*, 1715–1730.
- (11) Shelobolina, E. S.; O'Neill, K.; Finneran, K. T.; Hayes, L. A.; Lovley, D. R. Potential for in situ bioremediation of a low-pH, high-nitrate uranium-contaminated groundwater. *Soil Sed. Contam.* **2003**, *12*, 865–884.
- (12) Francis, A. J.; Dodge, C. J. Remediation of soils and wastes contaminated with uranium and toxic metals. *Environ. Sci. Technol.* **1998**, *32*, 3993–3998.
- (13) Tokunaga, T. K.; Wan, J. M.; Pena, J.; Brodie, E. L.; Firestone, M. K.; Hazen, T. C.; Sutton, S. R.; Lanzirrotti, A.; Newville, M. Uranium reduction in sediments under diffusion-limited transport of organic carbon. *Environ. Sci. Technol.* **2005**, *39*, 7077–7083.
- (14) Wu, W.; Carley, J.; Gentry, T.; Ginder-Vogel, M. A.; Fienen, M.; Mehlhorn, T. L.; Yan, H.; Carroll, S.; Page, M. N.; Nyman, J.; Luo, J.; Genetile, M.; Fields, M. W.; Hickey, R.; Gu, B.; Watson, D.; Cirpka, O. A.; Zhou, J.; Fendorf, S.; Kitanidis, P. K.; Jardine, P. M.; Criddle, C. Pilot-scale in situ bioremediation of uranium in a highly contaminated aquifer II: Reduction of U(VI) and geochemical control of U(VI) bioavailability. *Environ. Sci. Technol.* **2006**, *40*, 3986–3995.
- (15) Wu, W.; Carley, J.; Fienen, M.; Mehlhorn, T. L.; Lowe, K.; Nyman, J.; Luo, J.; Genetile, M.; Rajan, R.; Wagner, D.; Hickey, R.; Gu, B.; Watson, D.; Cirpka, O. A.; Kitanidis, P. K.; Jardine, P. M.; Criddle, C. Pilot-scale in situ bioremediation of uranium in a highly contaminated aquifer I: Conditioning of a treatment zone. *Environ. Sci. Technol.* **2006**, *40*, 3978–3985.
- (16) Edwards, L.; Kusel, K.; Drake, H.; Kostka, J. E. Electron flow in acidic subsurface sediments co-contaminated with nitrate and uranium. *Geochim. Cosmochim. Acta* **2007**, *71*, 643–654.
- (17) Hendershot, H. W.; Lalande, H.; Duquette, M. Soil reaction and exchangeable acidity. In *Soil Sampling and Methods of Analysis*; Charter, M. R., Ed.; 1993; pp 141–146.
- (18) Gu, B.; Doner, H. E. Adsorption of hydroxy-Al polycations and destabilization of illite and montmorillonite suspensions. *Clays Clay Miner.* **1990**, *38*, 493–500.
- (19) Jardine, P. M.; Zelazny, L. W. Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with ferron. *Soil Sci. Soc. Am. J.* **1986**, *50*, 895–900.
- (20) Luo, W.; Gu, B. Dissolution and mobilization of uranium in a reduced sediment by natural humic substances under anaerobic conditions. *Environ. Sci. Technol.* **2009**, *43*, 152–156.
- (21) Zhou, P.; Yan, H.; Gu, B. Competitive complexation of metal ions with humic substances. *Chemosphere* **2005**, *58*, 1327–1337.
- (22) Segre, C. U.; Leyarovska, N. E.; Chapman, L. D.; Lavender, W. M.; Plag, P. W.; King, A. S.; Kropf, A. J.; Bunker, B. A.; Kemner, K. M.; Dutta, P.; Druan, R. S.; Kaduk, J. *Synchrotron Radiat. Inst.* **2000**, *CP521*, 419–422.
- (23) Kelly, S. D.; Hesterberg, D.; Ravel, B. Analysis of soils and minerals using X-ray absorption spectroscopy. In *Methods of Soil Analysis. Part 5 - Mineralogical Methods*; Ulery, A. L., Drees, L. R., Eds.; Soil Science Society of America: Madison, WI, 2008; pp 367–463.
- (24) Kelly, S. D.; Kemner, K. M.; Carley, J.; Criddle, C.; Jardine, P. M.; Marsh, T. L.; Phillips, D.; Watson, D.; Wu, W. M. Speciation of uranium in sediments before and after in situ biostimulation. *Environ. Sci. Technol.* **2008**, *42*, 1558–1564.
- (25) Zhang, F.; Luo, W.; Parker, J. C.; Spalding, B. P.; Brooks, S. C.; Watson, D. B.; Jardine, P. M.; Gu, B. Geochemical modeling of reactions and partitioning of trace metals and radionuclides during titration of contaminated acidic sediments. *Environ. Sci. Technol.* **2008**, *42*, 8007–8013.
- (26) Phillips, D. H.; Gu, B.; Watson, D. B.; Roh, Y. Mineralogical characteristics and transformations during long-term operation of a zero-valent iron reactive barrier. *J. Environ. Qual.* **2003**, *32*, 2033–2045.
- (27) Chen, J.; Gu, B.; LeBoeuf, E. J.; Pan, H.; Dai, S. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* **2002**, *48*, 59–68.
- (28) Spalding, B. P.; Spalding, I. R. Chemical equilibria model of strontium-90 adsorption and transport in soil in response to dynamic alkaline conditions. *Environ. Sci. Technol.* **2001**, *35*, 365–373.
- (29) Schulte, E. H.; Scoppa, P. Sources and behavior of technetium in the environment. *Sci. Total Environ.* **1987**, *64*, 163–179.
- (30) Froideval, A.; Del Nero, M.; Gaillard, C.; Barillon, R.; Rossini, I.; Hazemann, J. L. Uranyl sorption species at low coverage on Al-hydroxide: TRLFS and XAFS studies. *Geochim. Cosmochim. Acta* **2006**, *70*, 5270–5284.
- (31) Bibak, A.; Moberg, J. P.; Borggaard, O. K. Cobalt retention by Danish spodosol samples in relation to contents of organic-matter and aluminum, iron and manganese oxides. *Acta Agric. Scand. Sect. B* **1995**, *45*, 0153–0158.
- (32) Scheckel, K. G.; Scheinost, A. C.; Ford, R. G.; Sparks, D. L. Stability of layered Ni hydroxide surface precipitates - A dissolution kinetics study. *Geochim. Cosmochim. Acta* **2000**, *64*, 2727–2735.
- (33) Towle, S. N.; Bargar, J. R.; Brown, G. E.; Parks, G. A. Surface precipitation of Co(II)(aq) on Al₂O₃. *J. Colloid Interface Sci.* **1997**, *187*, 0062–0082.
- (34) Sposito, G. *The Chemistry of Soils*; Oxford University Press: New York, 1989.
- (35) Kinjo, T.; Pratt, P. F. Nitrate adsorption. In competition with chloride, sulfate, and phosphate. *Soil Sci. Soc. Amer. Proc.* **1971**, *35*, 725–731.
- (36) Ishiguro, M.; Manabe, Y.; Seo, S.; Akae, T. Effect of sulfate on nitrate transport in volcanic ash soils sampled from the A and the B horizons. *Soil Sci. Plant Nutr.* **2003**, *49*, 249–254.
- (37) Adams, F.; Hajek, B. F. Effects of solution sulfate, hydroxide, and potassium concentrations on the crystallization of alunite, basaluminite, and gibbsite from dilute aluminum sulfate solutions. *Soil Sci.* **1978**, *126*, 169–173.
- (38) Adams, F.; Rawajfeh, Z. Basaluminite and alunite: a possible cause of sulfate retention by acid soils. *Soil Sci. Soc. Am. J.* **1977**, *41*, 686–692.
- (39) Long, D. T.; Fegan, N. E.; McKee, J. D.; Lyons, W. B.; Hines, M. E.; Macumber, P. G. Formation of alunite, jarosite and hydrous iron-oxides in a hypersaline system - Lake Tyrrell, Victoria, Australia. *Chem. Geol.* **1992**, *96*, 183–202.
- (40) Phillips, D. H.; Watson, D. B.; Roh, Y. Uranium deposition in a weathered fractured saprolite/shale. *Environ. Sci. Technol.* **2007**, *41*, 7653–7660.

- (41) Hsi, C. K. D.; Langmuir, D. Adsorption of uranyl onto ferric oxyhydroxides: application of the surface complexation site-binding model. *Geochim. Cosmochim. Acta* **1985**, *49*, 1931–1941.
- (42) Katsoyiannis, I. A. Carbonate effects and pH-dependence of uranium sorption onto bacteriogenic iron oxides: Kinetic and equilibrium studies. *J. Hazard. Mater.* **2007**, *139*, 31–37.
- (43) Barnett, M. O.; Jardine, P. M.; Brooks, S. C. U(VI) adsorption to heterogeneous subsurface media: application of a surface complexation model. *Environ. Sci. Technol.* **2002**, *36*, 937–942.
- (44) Davis, A. J.; Hem, J. D. The surface chemistry of aluminum oxides and hydroxides. In *The Environmental Chemistry of Aluminum*; Sposito, G., Ed.; CRC Press: Boca Raton, FL, 1989; pp 185–219.
- (45) Dong, W. M.; Ball, W. P.; Liu, C. X.; Wang, Z. M.; Stone, A. T.; Bai, J.; Zachara, J. M. Influence of calcite and dissolved calcium on U(VI) sorption to a Hanford subsurface sediment. *Environ. Sci. Technol.* **2005**, *39*, 7949–7955.
- (46) Guillaumont, R. F.; Fanghänel, T.; Fuger, J.; Grenthe, I.; Neck, V.; Palmer, D. A.; Rand, M. H.; Mompean, F. J.; Illemassene, M.; Domenechi-Orti, C. *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium*; Elsevier: Amsterdam, 2003.
- (47) Mukhopadhyay, B.; Walther, J. V. Acid-base chemistry of albite surfaces in aqueous solutions at standard temperature and pressure. *Chem. Geol.* **2001**, *174*, 415–443.

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