

2005

# Oxidative Remobilization of Biogenic Uranium(IV) Precipitates: Effects of Iron(II) and pH

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Zhong, Lirong; Liu, Chongxuan; Zachara, John M.; Kennedy, David; Szecsody, James E.; and Wood, Brian, "Oxidative Remobilization of Biogenic Uranium(IV) Precipitates: Effects of Iron(II) and pH" (2005). *US Department of Energy Publications*. 274.  
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## Oxidative Remobilization of Biogenic Uranium(IV) Precipitates: Effects of Iron(II) and pH

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### ABSTRACT

The oxidative remobilization of uranium from biogenic U(IV) precipitates was investigated in bioreduced sediment suspensions in contact with atmospheric O<sub>2</sub> with an emphasis on the influence of Fe(II) and pH on the rate and extent of U release from the solid to the aqueous phase. The sediment was collected from the U.S. Department of Energy Field Research Center (FRC) site at Oak Ridge, Tennessee. Biogenic U(IV) precipitates and bioreduced sediment were generated through anaerobic incubation with a dissimilatory metal reducing bacterium *Shewanella putrefaciens* strain CN32. The oxidative remobilization of freshly prepared and 1-yr aged biogenic U(IV) was conducted in 0.1 mol/L NaNO<sub>3</sub> electrolyte with variable pH and Fe(II) concentrations. Biogenic U(IV)O<sub>2(s)</sub> was released into the aqueous phase with the highest rate and extent at pH 4 and 9, while the U remobilization was the lowest at circumneutral pH. Increasing Fe(II) significantly decreased U remobilization to the aqueous phase. From 70 to 100% of the U in the sediments used in all the tests was extractable at the experiment termination (41 d) with a bicarbonate solution (0.2 mol/L), indicating that biogenic U(IV) was oxidized regardless of Fe(II) concentration and pH. Sorption experiments and modeling calculations indicated that the inhibitive effect of Fe(II) on U(IV) oxidative remobilization was consistent with the Fe(III) oxide precipitation and U(VI) sorption to this secondary phase.

URANIUM IS A common contaminant in soil and ground water at nuclear material production and U mining sites (Landa and Gray, 1995; Riley and Zachara, 1992). Uranium exists in the environment primarily in the hexavalent U(VI) and tetravalent U(IV) oxidation states. Uranium(IV) generally forms insoluble mineral phases, such as uraninite [UO<sub>2(s)</sub>]. Uranium(VI) exists in the form of potentially soluble precipitates (e.g., Liu et al., 2004) and the uranyl ion, UO<sub>2</sub><sup>2+</sup>, and its aqueous complexes. The mobility of U(VI) is a major concern in subsurface environments as complexation by carbonate reduces adsorption and increases mineral solubility.

Uranium(VI) can be enzymatically reduced to U(IV) by dissimilatory metal reducing bacteria (DMRB) under anoxic conditions in both the laboratory (e.g., Abdelouas et al., 1998; Fredrickson et al., 2000; Gorby and Lovley, 1992; Lovley et al., 1991) and the field (Senko et al., 2002). This process yields an insoluble precipitate [U(IV)O<sub>2(s)</sub>] that immobilizes U from ground water. The stimulation of metal reducing bacteria and consequent microbial immobilization has been proposed as a remediation

technology (www.lbl.gov/NABIR; verified 15 June 2005). A key to the success of such containment technology is the long-term maintenance of U in solid phase when reduced ground water-aquifer regions return to normal oxic conditions. The oxidative remobilization of U(IV) needs not to be avoided completely, but must be slow enough to maintain a uranium concentration below the ground water protection standard of 30 µg/L (USEPA, 2000).

Although the oxidative remobilization of biogenic UO<sub>2(s)</sub> in bioreduced sediments has not been widely investigated, the oxidation of UO<sub>2(s)</sub> as spent nuclear fuels has been extensively studied (e.g., De Pablo et al., 1999; Hiskey, 1979, 1980; Nicol and Needes, 1977; Sharma et al., 1996; Shoesmith et al., 1989, 1996a, 1996b, 1998; Sunder et al., 1997). Uranite in nuclear fuel is rapidly oxidized by O<sub>2</sub> and other oxidants in aqueous solution. Limited studies indicate that biogenic UO<sub>2(s)</sub> can be oxidized and remobilized by O<sub>2</sub> (Abdelouas et al., 1999; Zheng et al., 2002), manganese oxides (Fredrickson et al., 2002; Liu et al., 2002), and nitrate reduction intermediates including NO<sub>2</sub><sup>-</sup>, N<sub>2</sub>O, and NO (Senko et al., 2002). The factors controlling the remobilization rate of biogenic UO<sub>2(s)</sub> are poorly understood, but the mineral association of UO<sub>2(s)</sub> appears important. The presence of mackinawite (FeS) that was precipitated during microbial reduction of U(VI) by sulfate reducing bacteria, for example, can protect biogenic UO<sub>2(s)</sub> from oxidative remobilization (Abdelouas et al., 1999). Coprecipitation of U(IV) with Fe(III) oxides and other mineral forms (Ménager et al., 1994; Payne et al., 1994) may provide a significant diffusional barrier to U(IV) oxidation.

In this communication, we investigated the oxidative remobilization of biogenic U(IV)O<sub>2(s)</sub> in a bioreduced sediment and evaluated the influence of Fe(II) and pH on the rate and extent of U release from the solid to the aqueous phase. Ferrous iron is a typical product of dissimilatory metal reducing bacterium activity under anoxic conditions as they utilize Fe(III) oxides as electron acceptors (Abdelouas et al., 1999; Bennett et al., 1993, 2000; Fredrickson et al., 2000; Senko et al., 2002; Wielinga et al., 2000). Laboratory experiments were performed to assess whether Fe(II) would function as an antioxidant for U(IV). Moreover, we speculated that Fe(III) oxides resulting from Fe(II) oxidation might veneer biogenic UO<sub>2</sub> particles and prevent their remobilization, or function as an adsorbent for U(VI) retarding its post-oxidative release to the aqueous phase. The results of this study contribute to the understanding of the stability and remobilization of biogenic UO<sub>2(s)</sub> when subsurface

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Published in J. Environ. Qual. 34:1763–1771 (2005).  
Technical Reports: Bioremediation and Biodegradation  
doi:10.2134/jeq2005.0057

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**Abbreviations:** DCB, dithionite–citrate–bicarbonate; FRC, Field Research Center; HFO, hydro ferric oxide; UO<sub>2(s)</sub>, uraninite.

environments that have been stimulated by electron donor additions return to normal oxic conditions.

## MATERIALS AND METHODS

### Materials

The sediment was obtained from the background site at the U.S. Department of Energy Office of Biological and Environmental Research Natural and Accelerated Bioremediation Research (NABIR) Field Research Center (FRC) in West Bear Creek Valley at the Oak Ridge site in eastern Tennessee. A nearby U(VI) plume exists in these same sediment types and pilot experiments are being implemented in the field at this location to investigate the microbial immobilization of ground water U(VI). The sediment was composited from several distinct strata of a shale-limestone saprolite. The mineralogical properties of the composite sediment have been reported elsewhere (Fredrickson et al., 2004; Kukkadapu et al., 2005) and are selectively listed in Table 1.

A dissimilatory metal reducing bacterium, *S. putrefaciens* strain CN32, was used to reduce the sediment and to generate biogenic  $UO_{2(s)}$ . The cell culturing, harvesting, and washing processes were described elsewhere (Fredrickson et al., 1998). Briefly, CN32 was cultured aerobically in tryptic soy broth (TSB), harvested from TSB cultures at mid to late log phase by centrifugation, and washed twice with 30 mM PIPES pH buffer and once with pH 7 bicarbonate buffer to remove residual media. The cells were suspended in bicarbonate buffer (20 mM  $HCO_3^-$ ) and purged with  $O_2$ -free  $N_2$  for reduction experiments.

### Sediment Reduction

The bioreduced sediment was generated by incubating 1 g of sediment in 10 mL of 20 mmol/L bicarbonate buffer at pH 7 with  $7$  to  $9 \times 10^7$  cells/mL of *S. putrefaciens* CN32, 10 mmol/L sodium lactate as electron donor, and a headspace of  $N_2$  and  $CO_2$  (80:20). The incubation was performed at 30°C on an orbital shaker (25 rpm). After 60 d of incubation, the sediment was pasteurized by heating at 80°C for 1 h and then frozen at -20°C until use. Viable cells of CN32 in the reduced sediment were not detected by growth on TSB agar plates following pasteurization.

A sediment that was chemically treated to remove iron oxides was also prepared to evaluate the importance of the phyllosilicate fraction of the sediment and Fe(III) oxide resulting from Fe(II) oxidation on U(IV) oxidative remobiliza-

tion. The chemical treatment of the sediment was described in detail elsewhere (Liu et al., 2005). Briefly, the FRC sediment was reacted with a reductant solution (dithionite-citrate-bicarbonate, DCB: 0.1 mol/L  $Na_2S_2O_4$ , 0.3 mol/L Na-citrate, and 0.1 mol/L  $NaHCO_3$ ) for 24 h on an orbital shaker (25 rpm) at room temperature. After phase separation by centrifugation ( $5000 \times g$  for 20 min) and removal of supernatants, the treated sediment was reacted with the reductant solution for another 24 h under the same conditions. The sediment was collected after the second reaction by centrifugation and washed four times with 0.1 mmol/L  $NaHCO_3$  solution to remove residual DCB.

### Biogenic Uraninite

Biogenic  $UO_{2(s)}$  was generated according to a method described by Fredrickson et al. (2002). It was produced by microbial reduction of uranyl acetate in a bicarbonate buffer with *Shewanella putrefaciens*, strain CN32 and  $H_2$  as the electron donor. After microbial reduction, the  $UO_{2(s)}$  solids were treated with 10% NaOH to remove cells and organic debris. They were then washed three times in 0.1 M Na perchlorate and two times in anaerobic deionized  $H_2O$ . X-ray diffraction analysis indicated that the resulting solid was uraninite and the diffraction pattern was identical to that previously reported for biogenic uraninite (Fredrickson et al., 2000). Washed biogenic  $UO_{2(s)}$  was used freshly in the experiments, or was stored under strict anaerobic conditions for 12 mo until use.

### Uranium(IV) Oxidative Remobilization

The remobilization of biogenic  $UO_{2(s)}$  was studied as a function of pH and Fe(II) concentration in bioreduced sediment suspensions at a solid to solution ratio of 25 g/L. The bioreduced sediment and biogenic  $UO_{2(s)}$  were generated separately as described above and mixed to simulate a scenario that U(VI) in the FRC sediment was completely reduced and  $UO_{2(s)}$  was homogeneously distributed. The bioreduced sediment was weighted into a Nalgene bottle (Nalge Nunc, Rochester, NY) (125 mL) in an anaerobic chamber and mixed with a solution (100 mL) containing 0.1 mol/L  $NaNO_3$ , 10 to 16  $\mu$ mol/L bioreduced U(IV), and variable Fe(II) (as  $FeCl_2$ ) concentrations (0, 0.5, and 5 mmol/L, or 0, 0.02, and 0.2 mmol/g of sediment). After pH adjustments to desired values from 4 to 9 with  $HNO_3$  or NaOH, the suspensions were moved out of the anaerobic chamber for oxidation on a shaker in contact with the atmosphere through the holes in the bottle caps. The pH in the suspensions was monitored and adjusted using  $HNO_3$  or NaOH if it deviated by more than 0.2 unit from the desired values. At selected times, the bottles were opened and suspension aliquots (0.5 mL) were collected into 10 mL centrifuge tubes and centrifuged ( $5000 \times g$  for 20 min) for phase separation. Pretesting using the pristine sediment spiked with U(VI) indicated that the phase separation scheme used above provided aqueous samples with U(VI) composition equivalent to filtration through a 0.1- $\mu$ m filter. After phase separation, the aqueous U(VI) was analyzed with a Kinetic Phosphorescence Analyzer (KPA) (Chemchek Instrument, Richland, WA). The detection limit of U(VI) with the KPA was 1 ng/L. All samples were diluted between 5 and 1200 times and analyzed in 0.1 mol/L  $HNO_3$  to provide a consistent sample matrix.

### Uranium(VI) Extraction

The total U(VI) concentration in the suspensions was extracted to determine the extent of biogenic U(IV) oxidation. The suspensions at the end of the remobilization experiments were spiked with a concentrated (1 mol/L)  $NaHCO_3$  solution to attain a final carbonate concentration of 0.2 mol/L. Pre-

**Table 1. Field Research Center (FRC) saprolite sediment properties.**

Property	Value
DCB <sup>†</sup> -extractable, $\mu$ mol/g	
Mn	35.7
Fe	269
Al	58.5
Total, $\mu$ mol/g	
Mn	41.7
Fe	820
CEC <sup>‡</sup> , cmol/kg	11.6
Surface area, $m^2/g$	32.2
Oxide Fe(III), %	32
Silicate Fe, %	68
CEC of phyllosilicate fraction, cmol/kg	55.1
Dominant mineral components	quartz, illite, mica, vermiculite, and goethite

<sup>†</sup> Dithionite-citrate-bicarbonate.

<sup>‡</sup> Cation exchange capacity.

testing using the pristine sediments indicated that the U(VI) extraction efficiency increased with increasing bicarbonate concentration and became constant above 0.1 mol/L. The bicarbonate-spiked suspensions were centrifuged after 30 h of extraction at pH 9.5, and the supernatants were sampled for U(VI) measurements as described previously.

### Uranium(VI) Sorption

Uranium(VI) sorption to the bioreduced FRC sediment with and without Fe(II) additions was performed to evaluate the potential influence of U(VI) sorption on U(IV) oxidative remobilization. The bioreduced sediments (0.25 g) were weighted into 15-mL falcon centrifuge tubes in an anaerobic chamber and mixed with NaNO<sub>3</sub> (10 mL) to yield a final electrolyte concentration of 0.1 mol/L. These were spiked with variable concentrations of Fe(II). The suspensions were adjusted to desired pH values with HNO<sub>3</sub> or NaOH, moved out of the anaerobic chamber, and mixed on an orbital shaker for 1 wk in contact with atmosphere. The suspensions were then spiked with uranyl nitrate to yield a final uranium concentration of 10 μmol/L. After equilibration for 24 h, the suspensions were centrifuged (5000 × g, 20 min) and the centrifugates sampled for measurements of pH and U(VI) concentration. Previous kinetic experiments using the pristine, bioreduced, and bioreduced-reoxidized FRC sediments (Liu et al., 2005) indicated that U(VI) sorption reached steady state within 24 h. The final measured pH is reported as the equilibrium pH. The sorbed U(VI) concentration was calculated as the difference between total added and final aqueous U(VI) concentrations.

### Modeling

FITEQL (Herbelin and Westall, 1999) was used to calculate U(VI) aqueous speciation and adsorption, and to evaluate the amount of U(VI) sorption to the sediments after U(IV) oxidation. The aqueous speciation reactions and constants used in the calculations are from Guillaumont et al. (2003). The Davies equation was used for activity calculation. A ferrihydrite surface complexation model (Waite et al., 1994) was used to calculate U(VI) adsorption. The model was further described in the modeling section.

## RESULTS AND DISCUSSION

### Sediment Properties

The FRC sediment was a clay-rich saprolite consisting of sand- and silt-sized aggregates of finer grained materials including quartz, mica, vermiculite, and illite (Table 1). The sediment contained a significant amount of crystalline Fe(III) oxides that were extractable by dithionite–citrate–bicarbonate (DCB) solution and silicate Fe(III)–Fe(II). The predominant form of Fe in the FRC sediment was silicate Fe (68%), while the crystalline Fe(III) oxides existed primarily as goethite (Table 1).

Microbial reduction of the sediment generated 0.14 mmol/g of Fe(II), defined as the biogenic Fe(II), which was determined with 0.5 M HCl extraction for 24 h. The Fe(II) was sorbed to the bioreduced sediment above pH 6 and desorbed below that (Liu et al., 2005). The DCB treatment removed 32% of Fe (0.27 mmol/g) from the sediment (Table 1). Mössbauer analysis indicated that the DCB treatment completely removed crystalline Fe(III) oxides from the sediment.

### Uranium(IV) Oxidative Remobilization

Biogenic U(IV) was oxidized to U(VI) in contact with atmospheric O<sub>2</sub>. Uranium(VI) was released to the aqueous phase in spite of the presence of biogenic and/or added Fe(II) in the bioreduced sediments (Fig. 1). The rate and extent of U(IV) oxidation and consequent release to aqueous phase was a function of pH and Fe(II) concentration. The rate was faster initially and decreased with time in all cases. At pH 7 (Fig. 1b) and pH 4 (Fig. 1a), aqueous U(VI) concentrations increased initially, reached a peak, and then decreased and stabilized. The aqueous U(VI) concentration stabilized after 15 d at and below pH 7 (Fig. 1a and 1b), but continuously increased with increasing time at pH 9 (Fig. 1c). The

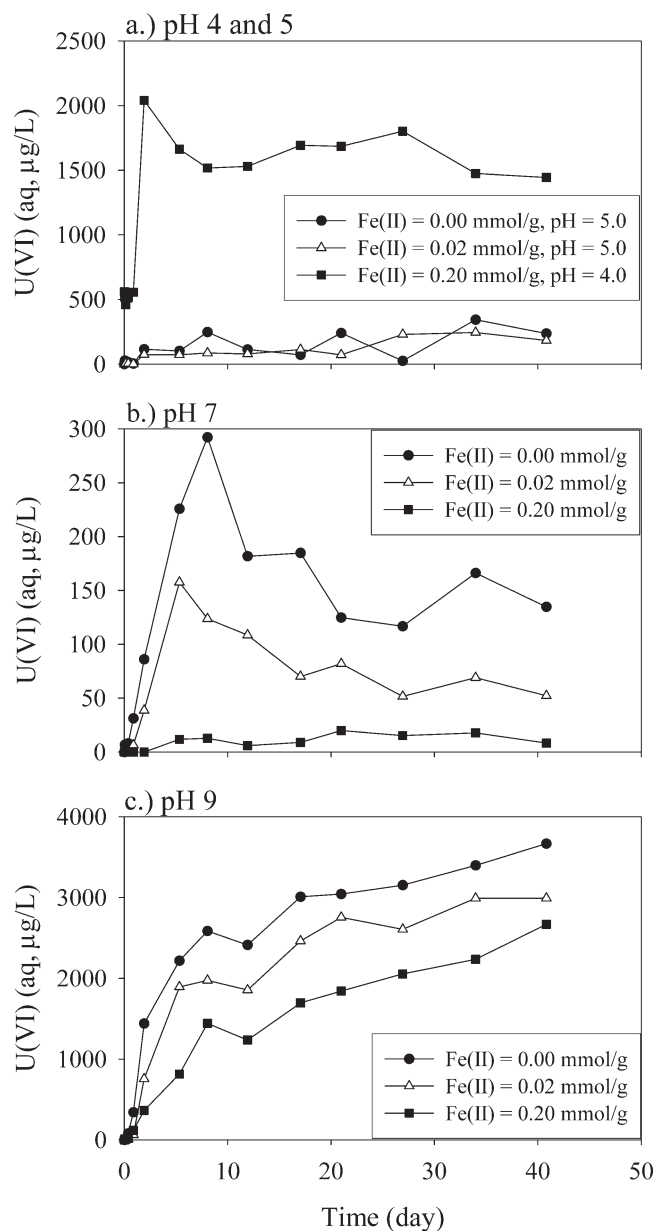


Fig. 1. Oxidative remobilization of biogenic uraninite [UO<sub>2(s)</sub>] in bio-reduced sediment suspensions with variable concentrations of Fe(II) addition at pH 4 or 5 (a), 7 (b), and 9 (c). The initial UO<sub>2(s)</sub> in the system was 16 μmol/L (3808 μg/L).

aqueous U(VI) concentration was consistently the lowest at pH 7, slightly higher at pH 5, and much higher at pH 4 and pH 9 regardless of Fe(II) addition. Increasing concentrations of added Fe(II) at a certain pH consistently decreased the rate and extent of U release to the aqueous phase, with the greatest relative effect noted at pH 7 (Fig. 1b). The bioreduced sediment itself contained 0.14 mmol/g of sorbed, biogenic Fe(II). The results of the Fe(II) addition experiments indicated that small increase in Fe(II) concentration (e.g., 0.02 mmol/g) can have significant impact on U(IV) oxidative remobilization rate.

The aging of biogenic  $\text{UO}_{2(s)}$  did not affect its reoxidation rate (data not shown). Figure 1 presents results for biogenic  $\text{UO}_{2(s)}$  that was aged for 1 yr. The release rate and extent of U(VI) from freshly prepared biogenic  $\text{UO}_{2(s)}$  were almost identical to those in Fig. 1. The result was expected given that the freshly prepared and aged  $\text{UO}_{2(s)}$  exhibited the same crystallite size and diffraction pattern (Fredrickson et al., 2000) and were prepared independently from the bioreduced sediment. In natural environments, however, biogenic U(IV) may oxidize more slowly if it is incorporated into other mineral phases or associated with mineral antioxidants such as FeS (Abdelouas et al., 1999).

Biogenic U(IV) was also oxidized and released to the aqueous phase in the DCB-treated sediment suspensions (Fig. 2) in a similar manner as in the bioreduced sediment (Fig. 1). The U(VI) concentration peaks that were observed in the bioreduced sediment at pH 4 and 7 (Fig. 1) were not observed in the DCB-treated sediment. The aqueous U(VI) concentrations were higher in the DCB-treated sediment at pH 4, 5, and 9 than those in the bioreduced ones under the same Fe(II) concentration. The higher aqueous U(VI) concentration in the DCB-treated cases suggested either that the biogenic Fe(II) in the bioreduced sediments inhibited U(IV) oxidation or that oxidized U(VI) adsorbed to the residual Fe(III) oxides in the bioreduced sediment.

However, both these explanations appeared inconsistent with the observations at pH 7 (Fig. 1b and 2b), where similar release profiles were observed for the bioreduced and DCB-treated sediments. In a recent study (Liu et al., 2005) we demonstrated that U(VI) adsorption at pH 7 was identical on bioreduced and DCB-treated FRC sediment when U(VI) was below  $1 \times 10^{-6}$  mol/g, in spite of the absence of strongly sorbing Fe(III) oxides in the latter sediment. Here, a concentration of  $6.5 \times 10^{-7}$  mol/g was used in the remobilization experiments, indicating that under the conditions of study both sediments should sorb U(VI) to a comparable degree. The adsorptivity of the DCB-treated sediment may be attributed to phyllosilicates which are abundant in the sediment (Kukkadapu et al., 2005) and are known to sorb U(VI) to edge and fixed charged sites (McKinley et al., 1995; Pabalan and Turner, 1997; Turner et al., 1996; Zachara and McKinley, 1993). We speculate that adsorption of U(VI) retards the overall release of U from these two sediments at pH 7 to comparable degree.

The aqueous U(VI) concentration in the DCB-treated sediment also decreased with increasing added Fe(II)

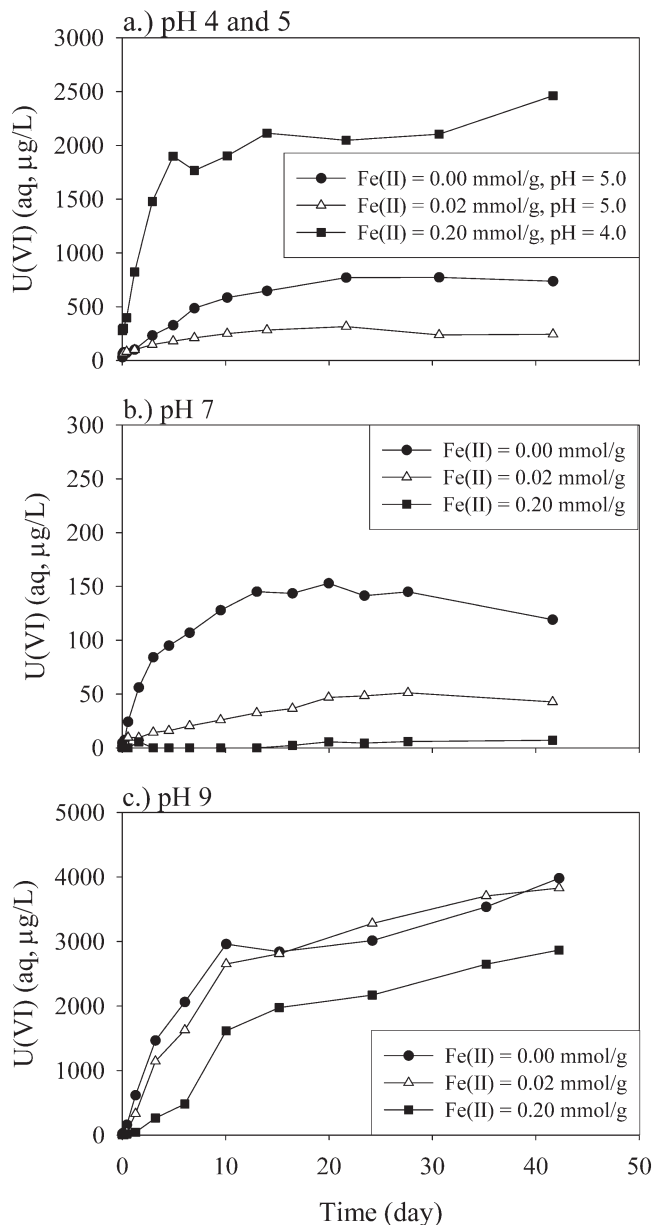


Fig. 2. Oxidative remobilization of biogenic uraninite [ $\text{UO}_{2(s)}$ ] in the dithionite–citrate–bicarbonate (DCB)-treated sediment suspensions with variable concentrations of Fe(II) addition at pH 4 or 5 (a), 7 (b), and 9 (c). The total  $\text{UO}_{2(s)}$  in the system was  $16 \mu\text{mol/L}$  ( $3808 \mu\text{g/L}$ ).

concentration at all pH values (Fig. 2), with the greatest relative decrease at pH 7. Iron(II) was therefore effective in decreasing the extent of U(IV) oxidative remobilization in the FRC sediments when Fe(III) oxides were and were not present.

### Uranium(IV) Oxidation and Uranium(VI) Sorption

We speculated that the inhibitory effect of Fe(II) addition on the rate and extent of U(IV) oxidative remobilization might be due to an antioxidant effect of Fe(II) by competitively consuming  $\text{O}_2$  and/or U(VI) adsorption to iron oxides resulting from Fe(II) oxidation. Iron(II)

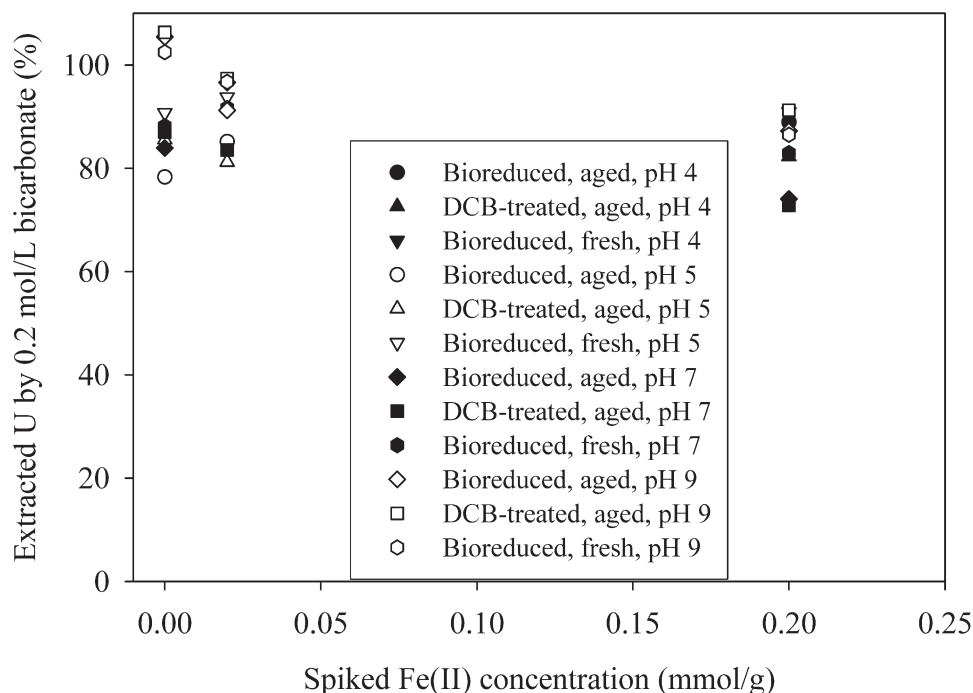


Fig. 3. Bicarbonate extractable U(VI) at the termination of the biogenic uraninite [UO<sub>2(s)</sub>] oxidative remobilization experiments. DCB, dithionite-citrate-bicarbonate.

has a chemical potential to reduce U(VI) when Fe(II) is sorbed on mineral surfaces (Liger et al., 1999), and thus, it may preferentially be oxidized by O<sub>2</sub> over U(IV). The initial oxidation product of Fe(II) in the FRC sediment is likely to be high surface area and poorly crystallized hydro ferric oxide (HFO) (Kukkadapu et al., 2005), which has high adsorptive potential for U(VI) at circumneutral pH (e.g., Hsi and Langmuir, 1985; Waite et al., 1994). The fine-grained precipitates with brown and yellowish color were visually observed in the Fe(II)-spiked sediment suspensions after the suspensions were contacted with air. Adsorption of U(VI) to HFO may strongly retard its post-oxidative release to the aqueous phase.

Uranium(VI) extraction with bicarbonate (0.2 mol/L) was performed to evaluate the extent of U(IV) oxidation in the sediment suspensions. Bicarbonate extraction is an operational approach to quantify the desorbable concentration of sorbed U(VI) (Duff et al., 1998, 2000, 2002; Kohler et al., 2004; Mason et al., 1997). This approach does not extract U(IV) (Buck et al., 1996) and was used here to quantify the extent of U(IV) oxidation. From 70 to 100% of the U (with an average of 89 ± 8%) was extracted with bicarbonate at the end of the oxidation experiments (Fig. 3). Generally, the U extractability was different only slightly at different pH values and Fe(II) concentrations in either the bioreduced or DCB-treated sediments. The results indicated that most of biogenic U(IV) was oxidized to U(VI) by experiment termination (41 d) and the effect of pH and Fe(II) on the oxidation extent was minimal. The nature (valence, mineral environment) of the residual or nonextractable U was not determined.

Uranium(VI) sorption showed strong pH dependence

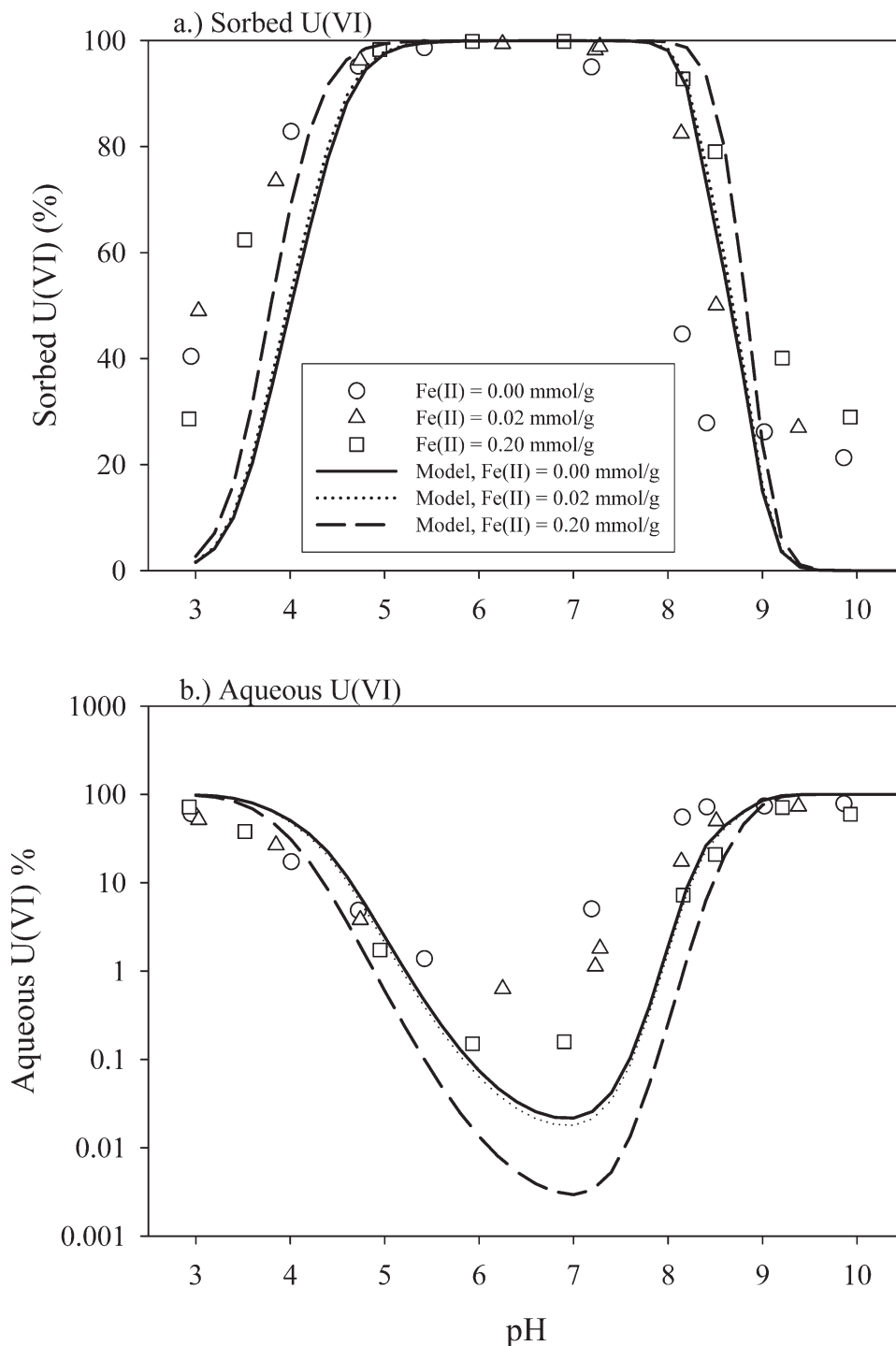
for all the treatments (shown only for the bioreduced, reoxidized sediment in Fig. 4a). Uranium(VI) was strongly adsorbed in a pH range from 5 to 8 and decreased with increasing pH distance from this range. The changes in U(VI) adsorption as a function of pH reflected the known competition between aqueous and sorbed U(VI) species as a function of carbonate concentration and pH (e.g., Waite et al., 1994). Uranium(VI) sorption at lower pH was unaffected by Fe(II) addition. Above pH 8, U(VI) sorption increased with added Fe(II) concentration. The aqueous U(VI) concentration decreased expectedly with increasing Fe(II) addition between pH 5.5 and 7.5 (Fig. 4b) because Fe(II) oxidative precipitation provided additional U(VI) adsorption sites. The Fe(II) effect was not observable in Fig. 4a due to the plot scale.

The trends in aqueous U(VI) concentration in the adsorption experiments with respect to pH and added Fe(II), as well as their magnitude (Fig. 4b) were similar to those noted in the remobilization experiments (Fig. 1). This similarity and the high bicarbonate extractability of U in the remobilization experiments (Fig. 3) allowed us to conclude that U(VI) adsorption to the sediment was a primary reaction controlling oxidative U release to the aqueous phase in Fig. 1 and 2. The surface complexation of U(VI) to residual crystalline Fe(III) oxides, and to HFO may all contribute to U(VI) adsorption after U(IV) oxidation. The results from the DCB-treated cases (Fig. 2) indicated that the secondary HFO was a more effective sorbent for U(VI) than were the residual crystalline Fe(III) oxides. The high degree adsorption at pH 7 (Fig. 4) led to lower aqueous U(VI) concentrations than at other pH values (Fig. 1 and 2).

### Calculation of Uranium Mobilization Extent

A model based on U(VI) adsorption to ferrihydrite (Davis, 2001; Waite et al., 2000) was used to calculate the influence of U(VI) adsorption on oxidative remobilization. A recent study indicated that the ferrihydrite-based model reasonably well described U(VI) adsorption to the pristine, bioreduced, and bioreduced-reoxidized FRC sediments without parameterization despite the

fact that goethite is the dominant Fe(III) oxide phase in the pristine sediment (Liu et al., 2005). We first tested the ferrihydrite model using U(VI) adsorption data (Fig. 4), and then used the model to predict the aqueous U(VI) concentration in the oxidative dissolution experiments in Fig. 1 by assuming that (i) all U(IV) was oxidized to U(VI) and (ii) U(VI) was complexed to Fe(III) oxide surfaces in the sediments.



**Fig. 4.** Uranium(VI) adsorption to the bioreduced-reoxidized sediment with variable concentrations of Fe(II) addition. The sediment was oxidized after Fe(II) addition and before uranyl addition for sorption experiments. The total U(VI) concentration was 10  $\mu\text{mol/L}$ . (a) U(VI) adsorption edges, (b) aqueous U(VI) concentration. The lines were generated from a ferrihydrite adsorption model (see text).



The total adsorbent Fe(III) was assumed to equal the sum of the residual crystalline Fe(III) oxides in the sediment [i.e., 16% of total Fe(III), Table 1] plus precipitated HFO resulting from Fe(II) oxidation. The dissolved CO<sub>2</sub> activity (as H<sub>2</sub>CO<sub>3</sub>) was fixed by equilibrium with the atmosphere (10<sup>-3.5</sup> atm CO<sub>2</sub>). The ferrihydrite model allows U(VI) complexation to two surface sites with different reaction constants (e.g., weak and strong), while surface acidity and carbonate surface complexation constants are the same for both sites. The reactions and constants that were used in the calculation were listed in Table 2. The total surface site concentration was calculated by assuming a site density of 0.875 sites/mol Fe, among which 0.21% were strong U adsorption sites (Waite et al., 1994).

The calculated aqueous U(VI) concentration from the surface complexation model matched well with the experimental adsorption data in the lower and higher pH regions (Fig. 4b). The calculated values from pH 5.5 to 7.5 were lower by one order of magnitude than the measured ones, indicating that the sediments sorbed less U than the ferrihydrite at circumneutral pH. This disparity resulted from our assumption that the residual crystalline Fe(III) oxides exhibit a site density and surface complexation reaction constants equivalent to ferrihydrite.

The U(VI) adsorption model simulated the trends of aqueous U(VI) concentration in the biogenic U(IV) oxidation experiments (Fig. 5). Each experimental point in Fig. 5 was averaged from the last four measured aqueous U(VI) concentrations on the corresponding U(VI) profile as a function of time (Fig. 1). The calculated values matched the data best at pH 4, 5, and 9,

**Table 2. Surface complexation reactions for U(VI) adsorption.†**

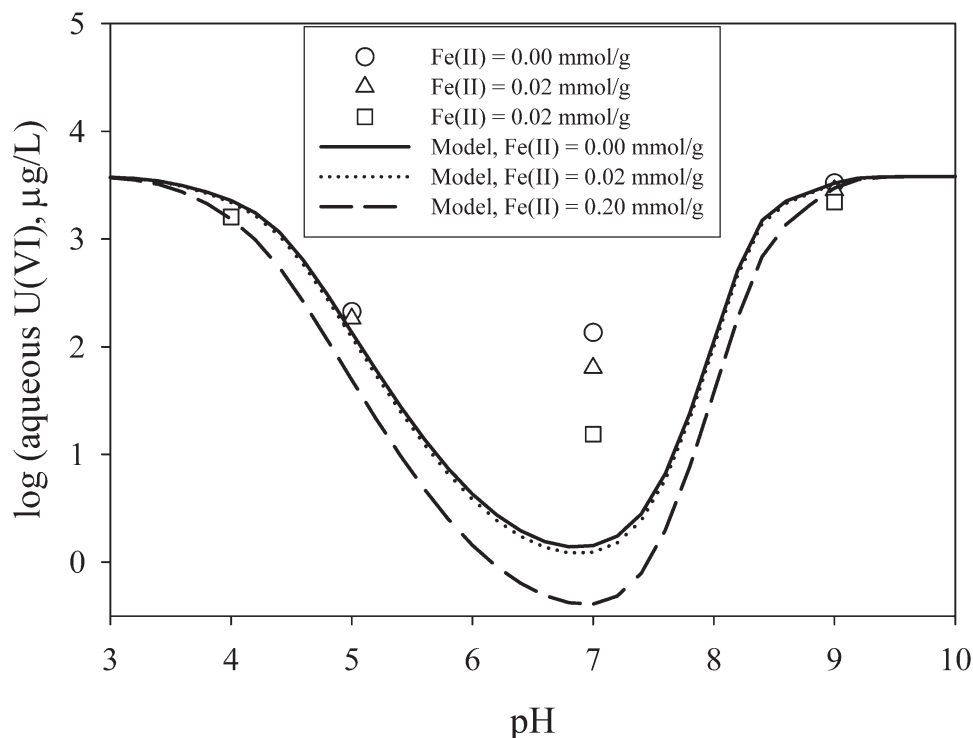
Surface reactions	log <i>K</i> ( <i>I</i> = 0.0)
$>Fe_{(s,w)}OH = >Fe_{(s,w)}O^- + H^+$	-9.13
$>Fe_{(s,w)}OH + H^+ = >Fe_{(s,w)}OH_2^+$	6.51
$>Fe_{(s,w)}OH + H_2CO_3 = >Fe_{(s,w)}CO_3H^0 + H_2O$	2.90
$>Fe_{(s,w)}OH + H_2CO_3 = >Fe_{(s,w)}CO_3^- + H_2O + H^+$	-5.09
$>Fe_{(s)}(OH)_2 + UO_2^{2+} = (>Fe_{(s)}O_2)UO_2^0 + 2H^+$	-2.34
$>Fe_{(s)}(OH)_2 + UO_2^{2+} = (>Fe_{(s)}O_2)UO_2^0 + 2H^+$	-6.14
$>Fe_{(s)}(OH)_2 + UO_2^{2+} + H_2CO_3 = (>Fe_{(s)}O_2)UO_2CO_3^- + 4H^+$	-12.31
$>Fe_{(w)}(OH)_2 + UO_2^{2+} + H_2CO_3 = (>Fe_{(w)}O_2)UO_2CO_3^- + 4H^+$	-17.24

† Total and strong site densities and reaction constants from Waite et al. (1994) and modified in Davis (2001). Total site density = 0.875 mol/mol Fe and strong site density = 0.0018 mol/mol Fe were from Waite et al. (1994); solid/solution ratio = 25 g/L.

but underestimated the U(VI) concentration at pH 7. The discrepancy at pH 7 was similar to that observed in modeling the sorption experiments (Fig. 4b). An alternative modeling approach to the data in Fig. 4 would have been to use FITEQL to fit a ferrihydrite site concentration that provided the best match to the adsorption data. This site concentration would have been lower than the one used, and it would have provided better predictions of U(VI) aqueous concentration in the oxidation experiments (Fig. 5). However, the qualitative agreement between the model predictions and experimental data for oxidative solubilization in Fig. 5 indicated the adsorption was the primary reaction controlling solid-liquid U distribution under oxidizing conditions.

## CONCLUSIONS

This study demonstrated that biogenic UO<sub>2(s)</sub> is readily oxidized by atmospheric O<sub>2</sub>. Clearly it will be a challenge



**Fig. 5. Prediction of U(IV) oxidative remobilization with the ferrihydrite adsorption model. The experimental data were calculated from the average of the last four data points in each kinetic profile of the remobilization experiments in Fig. 1.**

to prevent the oxidative dissolution of biogenic  $UO_{2(s)}$  in subsurface sediments after metal reducing bacteria cease action and if flowing ground water carries sufficient  $O_2$ . Although the presence of antioxidants such as Fe(II) (this study) and Fe(II) containing minerals (Abdelouas et al., 1999) may delay U(IV) oxidative remobilization, eventually oxidative remobilization will occur after facile oxygen reductants are depleted.

The rate and extent of  $UO_{2(s)}$  oxidative remobilization varied with pH and decreased with increasing Fe(II) concentration. At circumneutral pH with 0.02 or 0.20 mmol/g Fe(II) (Fig. 1), aqueous U(VI) concentrations were stabilized near or below the ground water protection standard of 30  $\mu\text{g/L}$ . It is therefore possible that the rate and extent of biogenic U(IV) oxidative remobilization may be controlled by manipulating subsurface biogeochemical conditions such as pH and Fe(II) concentration. The similar results observed in the DCB-treated and bioreduced sediments at circumneutral pH conditions (Fig. 1 and 2) implied that Fe(II) may be generally effective in inhibiting U(IV) oxidative remobilization in subsurface sediments with variable pristine iron oxide contents. The key appears to optimize biogeochemical conditions that will facilitate formation of HFO or iron oxides that strongly adsorb U(VI). This study further implied that a ferrihydrite-based U(VI) adsorption model may be used as a first approximation to estimate the extent of U(IV) oxidative remobilization if sediment U(VI) adsorption properties were unavailable.

#### ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy through the Natural and Accelerated Biological Remediation (NABIR) program. Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. We thank Steve Smith at Pacific Northwest National Laboratory for help in preparing DCB-treated sediment and its characterization.

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