

Extraction of Oxidized and Reduced Forms of Uranium from Contaminated Soils: Effects of Carbonate Concentration and pH

PING ZHOU AND BAOHUA GU*

Environmental Sciences Division, Oak Ridge
National Laboratory, MS 6036, P.O. Box 2008,
Oak Ridge, Tennessee 37831

Uranium may present in soil as precipitated, sorbed, complexed, and reduced forms, which impact its mobility and fate in the subsurface soil environment. In this study, a uranium-contaminated soil was extracted with carbonate/bicarbonate at varying concentrations (0–1 M), pHs, and redox conditions in an attempt to evaluate their effects on the extraction efficiency and selectivity for various forms of uranium in the soil. Results indicate that at least three different forms of uranium existed in the contaminated soil: uranium(VI) phosphate minerals, reduced U(IV) phases, and U(VI) complexed with soil organic matter. A small fraction of U(VI) could be sorbed onto soil minerals. The mechanism involved in the leaching of U(VI) by carbonates appears to involve three processes which may act concurrently or independently: the dissolution of uranium-(VI) phosphate and other mineral phases, the oxidation–complexation of U(IV) under oxic conditions, and the desorption of U(VI)–organic matter complexes at elevated pH conditions. This study suggests that, depending on site-specific geochemical conditions, the presence of small quantities of carbonate/bicarbonate could result in a rapid and greatly increased leaching and the mobilization of U(VI) from the contaminated soil. Even the reduced U(IV) phases (only sparingly soluble in water) are subjected to rapid oxidation and therefore potential leaching into the environment.

Introduction

Uranium is a common contaminant at waste disposal sites in the U.S. Department of Energy (DOE) complex as a result of nuclear energy utilization and weapons production over the past few decades (1). Through accidental spills and/or improper waste management and disposal, significant amounts of uranium have been released to the environment, leading to the contamination of soil and groundwater resources. Uranium commonly exists in the environment in either the U(VI) or U(IV) oxidation state. The oxidation state can affect the rate of migration of the species through soil and porous geologic media (2, 3). The most stable chemical species of uranium in aqueous solution under oxic/suboxic conditions is the uranyl ion (UO_2^{2+}). However, since most groundwater contains carbonate and bicarbonate anions, uranyl forms stable complexes with carbonates such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ or $\text{UO}_2(\text{CO}_3)_3^{4-}$ which are poorly retained by soil sediments and thus highly mobile in soil and ground-

water. On the other hand, the reduced U(IV) species are only sparingly soluble and relatively immobile in soil (4). Additionally, the mobility and fate of uranium in soil are affected by complex geochemical processes such as precipitation/dissolution, sorption/desorption, and complexation with soil organic matter and other chemical species (5–7). For example, uranium may exist in soil as sorbed, precipitated, coprecipitated, or complexed forms such as uranyl hydroxide, uranyl phosphate, or calcium uranyl phosphate minerals at about neutral pH conditions. Uranyl has also been reported to combine with organic ligands such as soil humic substances, acetate, malonate, oxalate, and citrate (5, 6, 8). It is therefore important to understand these various chemical species of uranium to determine the long-term stability and potential leaching behavior of uranium in complex natural geochemical environments.

A method for extracting U(VI) in soil is to complex it with either organic or inorganic ligands, thus making it soluble (9). Of the various ligands, bicarbonate and carbonate have been reported to be highly effective and selective in leaching uranium from soil sediments and minerals (10–12), although relatively few studies have evaluated the effects of carbonate/bicarbonate concentrations and pH on the extraction efficiency (the amount of uranium extracted) and selectivity for U(VI) and U(IV) in soil. The reported extraction efficiency ranged from tens of percent to nearly 100% because extraction efficiency and kinetics are largely dependent on different forms of uranium in addition to site-specific geochemical conditions in soil (10–12). The present study was therefore aimed to (1) evaluate the influence of bicarbonate/carbonate concentration and pH on the extraction efficiency and kinetics of uranium in a contaminated soil, (2) determine the extraction selectivity of both reduced U(IV) and oxidized U(VI) species under anaerobic and oxic conditions, and (3) investigate the fraction of uranium that is complexed with soil organic matter.

Experimental Section

Soil Sample and Its Characterization. The contaminated soil samples were collected from the field research center (FRC) of the Natural and Accelerated Bioremediation Research Program (NABIR) at the DOE Y-12 National Security Complex in Oak Ridge, TN. A 2 in. diameter core (FW065) was taken from the site at a depth of 18–21 ft. The soil sample was sealed in the plastic container, which was double-sealed in a glass bottle to prevent the loss of moisture and to minimize its exposure to air.

An aliquot of this soil sample was used for the determination of its elemental composition after digestion of the soil in acid (13). Briefly, ~0.2 g of the contaminated soil was digested in a mixture of 9 mL of 70% HNO_3 and 3 mL of 37% HCl for 10 min on a hot plate, as outlined in U.S. EPA SW-846 Method 3015. Once cooled, the samples were diluted to 100 mL with deionized water, and a 10 mL aliquot was withdrawn and analyzed for total uranium and other metal ions by means of inductively coupled plasma mass spectrometry (ICP-MS; ELAN 6000). The major elemental compositions are listed in Table 1 along with soil pH and organic matter content. Soil pH was determined in water (1:1), whereas total soil organic matter was determined by the combustion technique (13).

The mineralogical compositions of both the bulk soil and the clay fraction were determined by means of X-ray diffraction (XRD) (14). The clay fraction of the contaminated soil was collected by sedimentation techniques using a centrifuge at 12000 rpm (15). After the supernatant was decanted, clay samples were smeared on glass slides, and the XRD

* Corresponding author phone: (865) 574-7286; fax: (865) 576-8543; e-mail: gub1@ornl.gov.

TABLE 1. Chemical Composition and Characteristics of the Contaminated FRC Soil^a

[Fe]	59.7	[U]	0.27
[Al]	109.2	[Ca]	0.78
[Si]	251.7	[P]	0.77
[K]	44.7	soil organic C	7.5
[Mg]	10.4	pH	4.0
[Mn]	2.1		

^a Elemental composition was determined after acid digestion of the soil in duplicate, and the total organic carbon concentration was determined by soil combustion. All units except for pH are grams per kilogram.

patterns of the air-dried, oriented samples were recorded using a Scintag XDS 2000 diffractometer (Scintag, Sunnyvale, CA), operated at a scan rate of 2 deg/min ($2\theta = 2^\circ$).

Extraction of Soil Uranium by Bicarbonate Solution. The contaminated soil was extracted using a modified method described by Phillips et al. (12) and Senko et al. (16). The solid-to-bicarbonate extractant ratio was kept constant throughout the experiment using ~1.7 g of soil (with 22% moisture content) in 20 mL of degassed NaHCO_3 solutions at varying concentrations (0.03–1 M). The pH of the final equilibrium soil suspension ranged from ~8.2 to 8.6, depending on the bicarbonate concentration. The extraction was performed under both anaerobic and oxic conditions by vigorously stirring the soil suspension using a magnetic stirrer. For the anaerobic extraction, the samples were placed in serum bottles sealed with thick butyl rubber stoppers and aluminum caps in a glovebox under a N_2/H_2 atmosphere. However, during the oxic extraction, the serum bottles were open to the air, allowing the oxidation of U(IV) by atmospheric oxygen. Extraction using deionized water was also performed as a control (no carbonates), and the pH of these samples was adjusted to ~8.0 using dilute NaOH rather than NaHCO_3 . At varying time intervals, an aliquot of the soil suspension was filtered through a 0.2 μm syringe filter (National Scientific Co.), and the filtrate was analyzed for the dissolved U(VI) concentration. All experiments were performed in duplicate or triplicate for some selected samples. The experimental error was typically less than 10%.

To study the effect of pH on the U(VI) extraction efficiency of carbonates, the leaching experiments were also performed using a combination of NaHCO_3 and Na_2CO_3 solutions at varying ratios while keeping the total molar concentration at 0.03 M. The solid:liquid ratio was again kept at ~1.7 g of soil in 20 mL of degassed $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solution, and the pH of the final extractant solution ranged from ~8.2 to 10.4. Deionized water was used as a control by adjusting its pH with dilute NaOH to delineate the effects of pH and carbonates on extraction efficiency and selectivity. These experiments were performed in an anaerobic glovebox in the absence of CO_2 . Additionally, all filtrate samples from this experiment were analyzed for total organic carbon (TOC) contents as described in the Standard Methods for the Examination of Water and Wastewater (17) using a TOC analyzer (Shimadzu TOC-5000A, Shimadzu Corp.).

Extraction of Bioreduced Uranium. To validate whether bicarbonate would extract the reduced U(IV), bioreduced U(IV) precipitates were equilibrated with the bicarbonate solution in a manner similar to that of the soil samples under both oxic and anaerobic conditions. The bioreduced U(IV) was obtained by following the procedure described previously by Gu and Chen (18) and Brooks et al. (19). The bioreduction of U(VI) has been studied extensively, and this process results in the formation of insoluble uraninite (UO_2) solid phases (20, 21). To separate the biogenic U(IV) from the solution, the U(IV) precipitates were allowed to settle for ~5 days in the anaerobic glovebox, and the supernatant was removed carefully using a pipet. The amount of U(IV) solids was

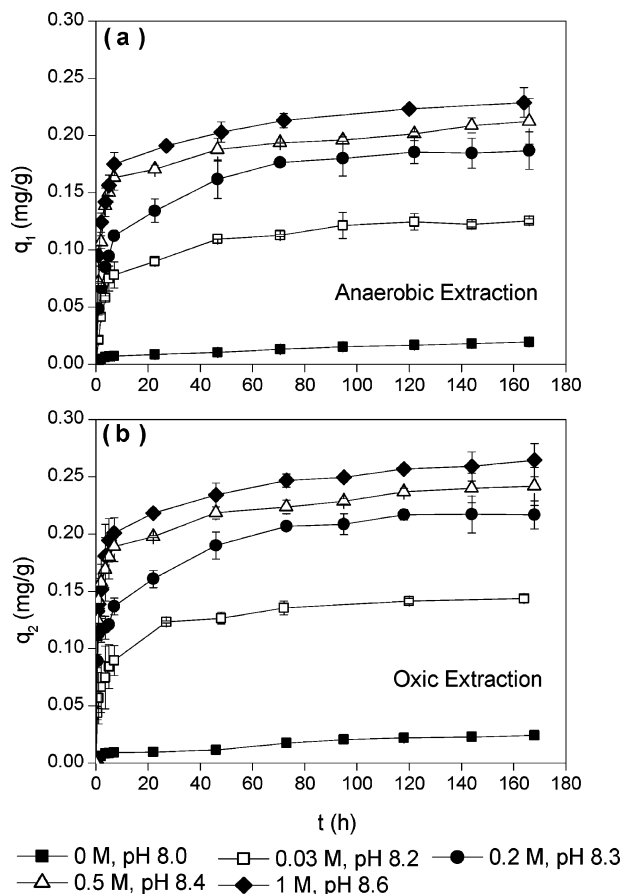


FIGURE 1. Effect of bicarbonate concentration on the extraction of uranium under (a) anaerobic and (b) oxic conditions. Deionized water (pH adjusted to 8 by NaOH) was used as a control.

estimated by the mass balance analysis of the initial and residual uranium in the supernatant solution. The extraction was then commenced first under anaerobic conditions: ~2 mg of U(IV) solids was equilibrated in 1 M NaHCO_3 solution for ~8 days, and no significant amounts of U(VI) were extracted. Samples were then transferred out of the glovebox and extracted under oxic conditions by vigorous stirring in an open beaker. At different time intervals, aliquots of supernatant solutions were taken and analyzed for solubilized U(VI) concentrations.

U(VI) Analysis. Extracted samples were analyzed for U(VI) concentrations by the steady-state phosphorescence technique using a fluorescence spectrometer (Jobin-Yvon-SPEX Instruments, Inc.) (18). Filtrate samples (0.1 mL) were diluted with a dilution factor of 50 using 10% deoxygenated H_3PO_4 . The H_3PO_4 solution was purged with N_2 for 1 h and kept under a N_2/H_2 atmosphere for 2 days in a glovebox before use. The uranium(VI) phosphate complex gives off strong phosphorescence with an intensity that is directly proportional to the amount of hexavalent U(VI) in the solution. The reduced forms of U(VI) do not interfere with the analysis (18). The detection limit is around 10^{-7} M. The instrument was operated in the emission acquisition mode at an emission wavelength of 515.4 nm and an excitation wavelength of 280 nm.

Results and Discussion

Uranium Extraction by Bicarbonate. The amount of U(VI) extracted under both anaerobic and oxic conditions as a function of time, with varying concentrations of bicarbonate solutions used for the extraction, is shown in Figure 1. Deionized water adjusted at a similar pH using dilute NaOH

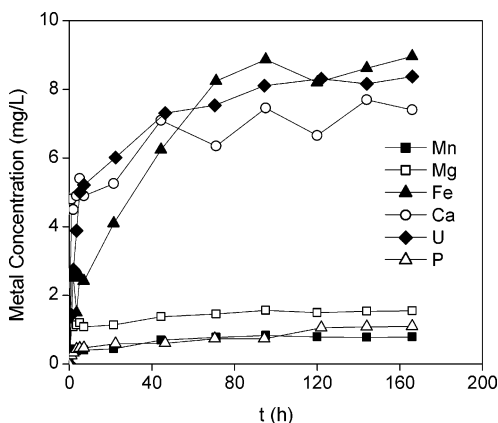
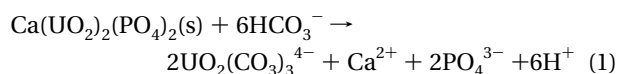


FIGURE 2. Leaching of metal ions and phosphate by 0.03 M bicarbonate under anaerobic conditions. The equilibrium pH of the soil suspension was 8.2.

was used as a control. Results indicate that U(VI) leaching was fast initially, but several days were required for the maximum fraction of U(VI) to be extracted. Typically, most of the U(VI) was released within the first 20 h of the extraction. For example, about 68% of U(VI) was extracted by 1 M NaHCO₃ within the first 5 h and an additional 14% over the next 15 h (Figure 1a). Extraction of U(VI) became very slow thereafter and appeared to reach equilibrium in about a week. These observations are consistent with the results obtained by Kohler et al. (22), who reported that a steady-state concentration of dissolved U(VI) was achieved after ~120 h of extraction using bicarbonate.

Bicarbonate extraction of U(VI) may be partially explained by the desorption of U(VI) from the binding sites of soil minerals and the dissolution of the U(VI)-bearing mineral phases (23). However, in a study using uranyl hydroxide and uranyl phosphate-amended soils, Elias et al. (9) reported that 90.5–97.6% of the spiked uranyl hydroxide and 94.3% of uranyl phosphate could be extracted by 1 M NaHCO₃. They concluded that the primary mechanism of extraction of U(VI) from the contaminated soil was the dissolution of the uranium-bearing particulate materials rather than desorption of uranium from the exchange sites of clay minerals (9). Using energy-dispersive X-ray (EDX) analysis, Buck et al. (7) found that calcium uranyl phosphates [Ca(UO₂)₂(PO₄)₂·xH₂O] were the major mineral phases found in the Fernald soil. Likewise, we expect that uranyl phosphate or calcium uranyl phosphate could be the dominant U(VI) mineral phase in this contaminated soil, given the fact that the soil contains a relatively high amount of calcium and phosphate (Table 1). Indeed, the presence of uranyl phosphate minerals in this soil was verified using extended X-ray absorption fine-structure spectroscopic analysis (24).

The dissolution of calcium uranyl phosphate minerals by carbonates may be written as



Accordingly, the reaction should be accompanied by the release of phosphate, calcium, and U(VI). Indeed, we observed that the extraction of U(VI) coincided with the release of phosphate and other metal ions (Figure 2). By converting to the molar concentration, the extracted uranium and phosphate increased concurrently at a molar ratio of ~1.22:1. Given the experimental error, this U(VI):P molar ratio roughly followed the stoichiometrical coefficient expressed in eq 1. However, a much higher amount of calcium was extracted than predicted by eq 1, suggesting the dissolution of calcium-containing minerals other than cal-

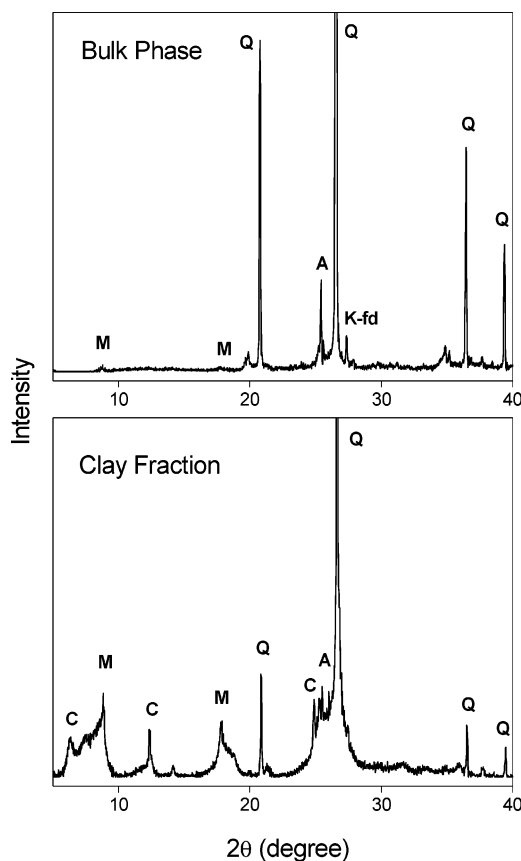


FIGURE 3. X-ray diffraction analysis of the bulk and clay fractions of the contaminated FRC soil (air-dried). Dominant mineral phases include quartz (Q), muscovite (M), potassium feldspar (K-fd), anhydrite (A), and chamosite (C).

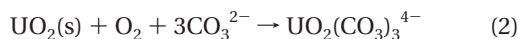
cium uranyl phosphate mineral phases. Indeed, XRD analysis revealed an abundance of the mineral anhydrite (CaSO₄) (Figure 3). The presence of calcium uranyl phosphate could not be detected by the XRD analysis because uranium is only a minor component (or contaminant) in this soil. XRD analysis of the clay fraction of the soil also revealed the presence of abundant chamosite, [Fe^{II},Mg,Fe^{III}]₅Al(Si₃Al)O₁₀(OH,O)₈, an iron aluminum silicate hydroxide mineral of the chlorite group (Figure 3). This observation is not surprising because the soil had a low pH and contained relatively high concentrations of iron and aluminum (Table 1).

The amount of U(VI) extracted also depended on the bicarbonate concentration and increased with an increase of the bicarbonate concentration (Figure 1). The amounts of U(VI) extracted at concentrations of 0.03, 0.2, and 0.5 M reached a plateau of about 54.7%, 81.6%, and 92.5%, respectively, of the amount extracted by 1 M NaHCO₃ under anaerobic conditions. Given that an excess amount of carbonate was used for the complexation of U(VI) (eq 1), these observations could be partially attributed to a relatively slow dissolution or desorption kinetics of the complexed uranium-(VI) phosphate solids or sorbed U(VI) species, particularly at a low bicarbonate concentration (0.03 M). One possible explanation is that there is a large reservoir of precipitated phosphate in the soil, making these phosphate minerals available to react with bicarbonate. For example, sorbed or complexed orthophosphates could be replaced by bicarbonate and thus be extracted from the soil (25). The relatively low amount of U(VI) extracted by the 0.03 M NaHCO₃ solution may also be partially attributed to its lower pH (~8.2) in comparison with the amount of that extracted at higher bicarbonate concentrations with higher pH values (up to ~8.6), as will be discussed below.

The acid digestion of the soil indicates that the total uranium content in the soil is ~ 0.27 mg/g (Table 1). Therefore, bicarbonate extraction using 1 M NaHCO_3 under oxic conditions was effective: ~ 83.5 and 96.5% of the total uranium in the contaminated soil was extracted in a single anaerobic and oxic extraction, respectively. By contrast, Phillips et al. (12) reported that the effectiveness of 0.01 M bicarbonate extraction ranged from 20% to 90% of the extraction achieved with 1 M nitric acid extraction. The variation in extraction efficiency depended on the different types of soils used. Similarly, Gabelle et al. (1) found that about 65% of the sorbed or spiked U(VI) could be extracted from the soil using 0.06 M NaHCO_3 . Mason et al. (26) found that 75–90% of the uranium could be removed using a 0.5 M Na_2CO_3 solution in a column leaching experiment.

Oxidation and Extraction of U(IV). Results of U(VI) extraction under both oxic and anaerobic conditions also suggest that more U(VI) was extracted from soil under oxic than under anaerobic extraction (Figure 1). Figure 4 shows the difference between the amount of uranium extracted under oxic and anaerobic conditions as a function of time. For example, the average amounts of U(VI) extracted using a 1 M NaHCO_3 solution under anaerobic and oxic conditions were 0.229 and 0.264 mg/g of soil, respectively. These observations indicate that a small fraction of uranium in soil was present in the reduced U(IV) forms because of the relatively low solubility of these forms and their nonreactivity with carbonates (26). Specifically, $\sim 15\%$ of the uranium may exist as U(IV) species and $\sim 85\%$ in the form of U(VI) in this contaminated soil.

This observation is supported by Kohler's study, which reported that reduced U(IV) was highly insoluble when extracted under a nitrogen atmosphere, even in the presence of high carbonate concentrations (22). Buck et al. (7) obtained direct evidence of the reduced U(IV) as UO_2 in the contaminated soil by means of a transmission electron microscope and found that most of the UO_2 particles were 50–200 nm in diameter. These reduced U(IV) particles were found to be susceptible to carbonate leaching in the presence of oxygen. In other words, the reduced U(IV) is readily oxidized and thus can be extracted by bicarbonates. The overall oxidation reaction in the presence of carbonates may be written as (27)



Results presented in Figure 4 also indicate that the leaching of U(IV) became relatively stabilized after a ~ 40 h extraction period, which was significantly shorter than the leaching of oxidized U(VI) phases. These observations are attributed to relatively fast oxidation kinetics of the reduced U(IV) species in soil and are supported by the extraction experiments of the bioreduced U(IV) in 1 M NaHCO_3 under both anaerobic and oxic conditions (Figure 5). Results clearly indicate that the reduced U(IV) could not be extracted by the carbonate solution under anaerobic conditions even after an extended period of reaction (8 days). On the other hand, when the sample was exposed to the air (or oxygen), a rapid oxidation of U(IV) and dissolution of U(VI) occurred. Nearly 100% of the bioreduced U(IV) solids were reoxidized in less than 10 h. The estimated half-life for the oxidation of biogenic U(IV) was ~ 1 h.

Influence of pH on U(VI) Extraction. In addition to carbonate concentration, pH is an important geochemical parameter and is anticipated to have a significant impact on uranium leaching, precipitation, and/or mobilization. To delineate the effects of both carbonates and pH on U(VI) leaching, additional extraction experiments were performed using the bicarbonate/carbonate solution at various ratios (1:0, 1:1, and 0:1) while keeping the total carbonate con-

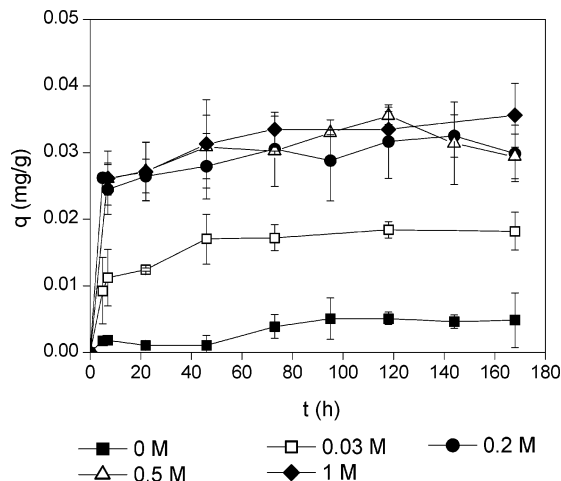


FIGURE 4. Difference between the amounts of uranium extracted by bicarbonate at varying concentrations under oxic and anaerobic conditions. This difference is attributed to the oxidation of U(IV) in the soil under oxic conditions.

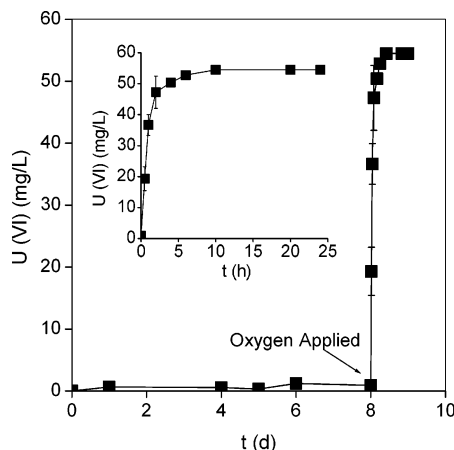


FIGURE 5. Extraction of bioreduced U(IV) using 1 M NaHCO_3 under anaerobic and oxic conditions.

centration constant (0.03 M) in the absence of CO_2 . These extractant solutions resulted in an equilibrium pH of the soil suspension at about 8.2, 9.4, and 10.4, respectively. Furthermore, parallel experiments were conducted using extractant solutions at about the same pH values adjusted solely by NaOH solution (or in the absence of CO_2 , bicarbonate, or carbonate). Results indicate that a much larger amount of U(VI) was extracted by the carbonate solution at pH 10.4 than by the bicarbonate solution at $\text{pH} \approx 8.2$ (Figure 6a), even though total bicarbonate or carbonate concentrations were kept the same, at 0.03 M. The higher the pH, the greater the amount of uranium extracted by the carbonate solution. However, a much smaller amount of U(VI) was extracted when no bicarbonate/carbonate was added even though the pH of the extract solution was kept comparable with those used in the carbonate extractions (e.g., $\text{pH} 9.4$ vs 9.45 and 10.4 vs 10.1) (Figure 6b).

This difference between the amounts of U(VI) extracted by the carbonate and the hydroxide solutions under similar pH conditions may thus be attributed exclusively to the effect of carbonates, and the results are presented in Figure 6c. Data suggest that the amount of U(VI) extracted by carbonates accounted for ~ 50 – 60% of U(VI) extracted by 0.03 M carbonates. The fact that extraction reached a plateau quickly after ~ 10 h implies that the dissolution or desorption of U(VI) by carbonates in soil is a relatively fast process. It has been speculated that, during the process of dissolution, only simple

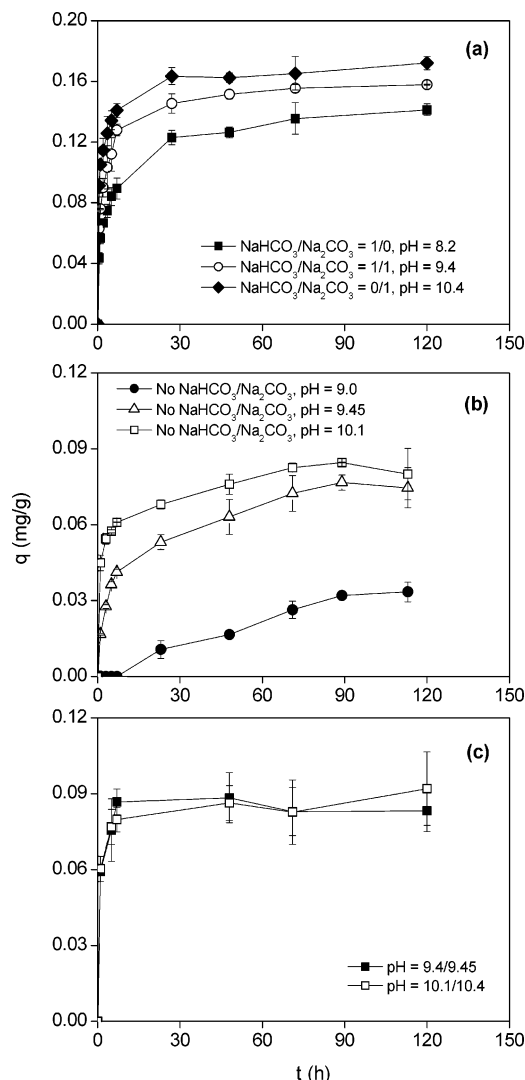


FIGURE 6. Influences of pH on the extraction of U(VI) from the contaminated soil. (a) The pH was varied by changing the ratio of the carbonate to bicarbonate while the total carbonate concentration was kept at 0.03 M. (b) The pH was adjusted using NaOH only (no carbonate, bicarbonate, or CO_2). (c) Difference between the amount of U(VI) extracted by the carbonate/bicarbonate and NaOH solutions at about the same pH conditions.

detachments of U(VI)-bearing coatings on soil aggregates or surface dissolution of uranium(VI) phosphate precipitates and subsequent complexation by bicarbonate/carbonate are needed to solubilize U(VI) from the soil (28). On the other hand, extraction by NaOH at comparable pH conditions accounted for only ~40–50% of U(VI) extracted and took a much longer time to equilibrate (Figure 6b). This fraction of extracted U(VI) may be partially desorbed from soil minerals, but a careful examination of the data (Figure 6b) suggests that this pool of sorbed U(VI) could not account for the amount of U(VI) extracted from the soil on the basis of the U(VI) sorption and desorption edges (1, 22, 29, 30). Although U(VI) is known to be strongly sorbed onto oxide minerals such as aluminum, iron, or manganese oxides, its sorption usually exhibits an adsorption edge at pH 4–5 (30–32), and almost 100% of U(VI) could be sorbed at pH 6–7. The typical U(VI) desorption edge is observed at pH 8–9 when the soil suspension is in equilibrium with atmospheric CO_2 , and desorption usually occurs within a few hours (1, 30). In other words, an increase of pH from 8 to 9 would be expected to rapidly release most of the sorbed U(VI) into the soil. Our data (Figure 6b) indicate, however, that only ~0.01 mg/g

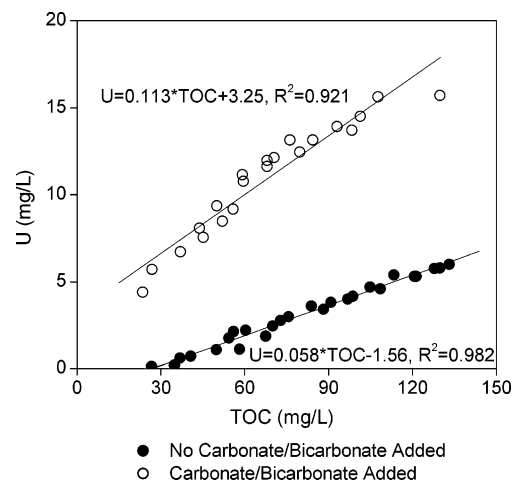


FIGURE 7. Relationships between the amounts of uranium and TOC extracted at about the same pH conditions but in the presence or absence of carbonates (also see Figure 6).

U(VI) was extracted after 24 h at pH 9, and ~0.03 mg/g after ~5 days of equilibration. Therefore, the adsorbed U(VI) may account for only a relatively small fraction (<10%) of the total U(VI) in this contaminated soil.

However, the amount of U(VI) extracted by hydroxide (Figure 6b) may be attributable to the complexation of U(VI) with soil organic matter, and this conclusion is supported by the fact that the leaching of U(VI) coincided with the release of TOC and that a strong linear relationship was found between U(VI) and TOC released from the soil (Figure 7). In particular, the total amounts of soil organic carbon extracted were similar (ranging from ~30 to 130 mg/L) in either the presence or absence of carbonates, but the amounts of U(VI) extracted varied significantly. The extract solutions turned a brown color both in the presence and in the absence of carbonates. This color change is due primarily to desorbed soil humic substances at an elevated pH, which causes the deprotonation of the surface functional groups and therefore the desorption of soil humics (26, 33). It could thus be expected that a similar amount of soil organic matter was found in the leaching solution when soil pH was kept the same (Figure 7). The presence of humic substances could also have enhanced the leaching of U(VI) as a result of its complexation reactions with humics, although a large percentage of U(VI) in soil may exist in the form of uranium(VI) phosphate phases (7), as discussed earlier. For example, Crancon and Lee (34) reported that a large fraction of U(VI) was associated with humic materials in various soils they studied.

The association of U(VI) with humic materials may also partially explain the relatively slower release of U(VI) when extracted by the hydroxide (Figure 6b) than by the carbonates (Figure 6c). The slow release of the U(VI)–organic matter complexes could be caused by the slower diffusion and desorption rates of the U(VI)–organic matter complexes. Similarly, in a study of U(VI) leaching by carbonates and anionic surfactants, Gadelle et al. (1) reported a greatly reduced extraction efficiency when using the surfactants as compared with that of carbonates. They attributed this phenomenon to a slower diffusion caused by the much larger size of the surfactant molecules.

Results of this study suggest that at least three different forms of uranium exist in this contaminated FRC soil: calcium uranium(VI) phosphate, reduced U(IV) phases, and U(VI) complexed with soil organic matter. A small fraction of U(VI) could also be desorbed from soil minerals such as chamocite, an iron- and aluminum-rich silicate mineral. The processes involved in the leaching of U(VI) by carbonates appear to involve three mechanisms that operate concur-

rently or independently: (1) the dissolution of uranium(VI) phosphate or other mineral phases, (2) the oxidation of U(IV) and complexation of U(VI) under oxic conditions, and (3) the desorption of U(VI)-organic matter complexes at elevated pH conditions. These processes could have profound influences on the mobilization and fate of U(VI) in the subsurface soil environment because of the ubiquitous presence of carbonates and organic matter in soil. Although carbonate-free water is inefficient for extracting U(VI) from the soil at a relatively low pH, the presence of small quantities of carbonate/bicarbonate could result in rapid and greatly increased leaching and therefore cause mobilization of U(VI) from the contaminated soil. As shown in Figures 1 and 6, >50% of the total U(VI) could be extracted when the bicarbonate concentration was increased to ~30 mM. Even the reduced U(IV) species, which are sparingly soluble in water, are subjected to rapid reoxidation (Figure 5) and potential leaching into the environment. The sorbed, complexed, or precipitated U(VI) in soil could be solubilized or mobilized as a result of the perturbation of groundwater chemistry, such as changes in dissolved oxygen, pH, and carbonate/bicarbonate concentrations, resulting in dramatic changes in solubilized U(VI) concentrations and therefore in the transport and fate of uranium in the subsurface soil environment.

Acknowledgments

We thank H. Yan for providing the bioreduced U(IV), X. Yin for assisting in the ICP-MS analysis, J. W. Moon and E. Specht for conducting XRD, and D. Watson for providing FRC soil samples. This research was supported by the NABIR Program, Office of Biological and Environmental Research, U.S. Department of Energy (DOE), under Contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, which is managed by UT-Battelle LLC.

Literature Cited

- Gadelle, F.; Wan, J.; Tokunaga, T. K. Removal of uranium(VI) from contaminated sediments by surfactants. *J. Environ. Qual.* **2001**, *30*, 470–478.
- Langmuir, D. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposit. *Geochim. Cosmochim. Acta* **1978**, *42*, 547.
- Gu, B.; Watson, D. B.; Phillips, D. H.; Liang, L. In *Handbook of groundwater remediation using permeable reactive barriers: Applications to radionuclides, trace metals, and nutrients*; Naftz, D. L., Morrison, S. J., Davis, J. A., Fuller, C. C., Eds.; Academic Press: Boston, 2002; pp 305–342.
- Finneran, K. T.; Housewright, M. E.; Lovley, D. R. Multiple influences of nitrate on uranium solubility during bioremediation of uranium-contaminated subsurface sediments. *Environ. Microbiol.* **2002**, *4*, 510–516.
- Huang, F. Y.; Brady, P. V.; Lindgren, E. R.; Guerra, P. Biodegradation of uranium-citrate complexes: Implications for extraction of uranium from soils. *Environ. Sci. Technol.* **1998**, *32*, 379–382.
- Ganesh, R.; Robinson, K. G.; Reed, G. D.; Sayler, G. Reduction of hexavalent uranium from organic complexes by sulfate- and iron-reducing bacteria. *Appl. Environ. Microbiol.* **1997**, *63*, 4385–4391.
- Buck, E. C.; Brown, N. R.; Dietz, M. L. Contaminant uranium phases and leaching at the Fernald site in Ohio. *Environ. Sci. Technol.* **1996**, *30*, 81–88.
- Artinger, R. R.; Kim, J. I.; Sachs, S.; Schmeide, K.; Heise, K. H.; Bernhard, G.; Nitsche, H. Humic colloid-borne migration of uranium in sand columns. *J. Contam. Hydrol.* **2002**, *58*, 1–12.
- Elias, D. A.; Senko, J. M.; Krumholz, L. R. A procedure for quantitation of total oxidized uranium for bioremediation studies. *J. Microbiol. Methods* **2003**, *53*, 343–353.
- Sheppard, S. C.; Evenden, W. G. Bioavailability indexes for uranium-effect of concentration in 11 soils. *Arch. Environ. Contam. Toxicol.* **1992**, *23*, 117–124.
- Osiensky, J. L.; Williams, R. E. Factors affecting efficient aquifer restoration at insitu uranium-mine sites. *Ground Water Monit. Rev.* **1990**, *10*, 107–112.
- Phillips, E. J. P.; Landa, E.; Lovley, D. R. Remediation of uranium contaminated soils with bicarbonate extraction and microbial U(VI) reduction. *J. Ind. Microbiol.* **1995**, *14*, 203–207.
- McLean, E. O. In *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*; Page, A. L., Miller, R. H., Keeney, D. R., Eds.; American Society of Agronomy: Madison, WI, 1982; pp 199–223.
- 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.
- Aparicio, P.; Ferrell, R. E. An application of profile fitting and clay++ for the quantities representation (QR) of mixed-layer clay minerals. *Clay Miner.* **2001**, *36*, 501–514.
- Senko, J. M.; Istok, J. D.; Suflita, J. M.; Krumholz, L. R. In-situ evidence for uranium immobilization and remobilization. *Environ. Sci. Technol.* **2002**, *36*, 1491–1496.
- Rand, M. C.; Greenberg, A. E.; Taras, M. J. *Standard Methods for the Examination of Water and Wastewater*; American Public Health Association: Washington, DC, 1975.
- Gu, B.; Chen, J. Enhanced microbial reduction of Cr(VI) and U(VI) by different natural organic matter fractions. *Geochim. Cosmochim. Acta* **2003**, *67*, 3575–3582.
- Brooks, S. C.; Fredrickson, J. K.; Carroll, S. L.; Kennedy, D. W.; Zachara, J. M.; Plymale, A. E.; Kelly, S. D.; Kemner, K. M.; Fendorf, S. Inhibition of bacterial U(VI) reduction by calcium. *Environ. Sci. Technol.* **2003**, *37*, 1850–1858.
- Gorby, Y. A.; Lovley, D. Enzymatic uranium precipitation. *Environ. Sci. Technol.* **1992**, *26*, 205–207.
- Lovley, D. R.; Phillips, E. J. P.; Gorby, Y. A.; Landa, E. R. Microbial reduction of uranium. *Nature* **1991**, *350*, 413–416.
- Kohler, M.; Curtis, G. P.; Meece, D. E.; Davis, J. A. Methods for estimating adsorbed uranium(VI) and distribution coefficients of contaminated sediments. *Environ. Sci. Technol.* **2004**, *38*, 240–247.
- Giammar, D. E.; Hering, J. G. Time scales for sorption-desorption and surface precipitation of uranyl on goethite. *Environ. Sci. Technol.* **2001**, *35*, 3332–3337.
- Kelly, S. D.; Kemner, K. M.; O'Loughlin, E. J.; Boyanov, M. I.; Watson, D.; Jardine, P. M.; Phillips, D. H. U L3-Edge EXAFS Measurements of Sediment Samples from Oak Ridge National Laboratory, Tennessee, U.S.A. *Advanced Photon Source Activity Report*; ANL-04/16; Argonne National Laboratory: Argonne, IL, 2004; <http://www.aps.anl.gov/News/Reports/index.html>.
- Watanabe, F. S.; Olsen, S. R. Test of an ascobic acid method for determining phosphorous in water and NaHCO₃ extracts from soils. *Soil Sci. Soc. Am. Proc.* **1965**, *29*, 677–678.
- Mason, C. F. V.; Turney, W. R. J. R.; Thomson, B. M.; Lu, N.; Longmire, P. A.; Chisholm-Brause, C. J. Carbonate leaching of uranium from contaminated soils. *Environ. Sci. Technol.* **1997**, *31*, 2707–2711.
- Harrington, C. D.; Ruehle, A. E. *Uranium Production Technology*; Van Nostrand Co.: Princeton, NJ, 1958.
- Elless, M. P.; Lee, S. Y. Uranium solubility of carbonate-rich uranium-contaminated soils. *Water, Air, Soil Pollut.* **1998**, *107*, 147–162.
- Villalobos, M.; Trotz, M. A.; Leckie, J. O. Surface complexation modeling of carbonate effects on the adsorption of Cr(VI), Pb(II), and U(VI) on goethite. *Environ. Sci. Technol.* **2001**, *35*, 3849–3856.
- 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.
- Waite, T. D.; Davis, J. A.; Xu, N. Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. *Geochim. Cosmochim. Acta* **1994**, *58*, 5465.
- 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.
- Stevenson, F. J. *Humus chemistry*; John Wiley & Sons: New York, 1982.
- Crancon, P.; van der Lee, J. Speciation and mobility of uranium-(VI) in humic-containing soils. *Radiochim. Acta* **2003**, *91*, 673–679.

Received for review October 25, 2004. Revised manuscript received April 1, 2005. Accepted April 1, 2005.

ES0483443