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Remediation and Recovery of Uranium from Contaminated Subsurface Environments with Electrodes

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Previous studies have demonstrated that *Geobacter* species can effectively remove uranium from contaminated groundwater by reducing soluble U(VI) to the relatively insoluble U(IV) with organic compounds serving as the electron donor. Studies were conducted to determine whether electrodes might serve as an alternative electron donor for U(VI) reduction by a pure culture of *Geobacter sulfurreducens* and microorganisms in uranium-contaminated sediments. Electrodes poised at −500 mV (vs a Ag/AgCl reference) rapidly removed U(VI) from solution in the absence of cells. However, when the poise at the electrode was removed, all of the U(VI) returned to solution, demonstrating that the electrode did not reduce U(VI). If *G. sulfurreducens* was present on the electrode, U(VI) did not return to solution until the electrode was exposed to dissolved oxygen. This suggests that *G. sulfurreducens* on the electrode reduced U(VI) to U(IV) which was stably precipitated until reoxidized in the presence of oxygen. When an electrode was placed in uranium-contaminated subsurface sediments, U(VI) was removed and recovered from groundwater using poised electrodes. Electrodes emplaced in flow-through columns of uranium-contaminated sediments readily removed U(VI) from the groundwater, and 87% of the uranium that had been removed was recovered from the electrode surface after the electrode was pulled from the sediments. These results suggest that microorganisms can use electrons derived from electrodes to reduce U(VI) and that it may be possible to remove and recover uranium from contaminated groundwater with poised electrodes.

Introduction

Uranium contamination of groundwater is a widespread environmental problem (*1*). The volume and areal extent of uranium contamination often precludes pump and treat remediation strategies. An alternative approach is to reduce the soluble, and thus mobile, U(VI) to relatively insoluble U(IV), which precipitates (*2*−*4*). This prevents further migration of the contamination. Laboratory and field studies have demonstrated that adding electron donors, such as acetate, to uranium-contaminated aquifers stimulates the activity of dissimilatory metal-reducing microorganisms and promotes U(VI) reduction (*2*−*6*). In this manner, soluble uranium contamination can be concentrated as a solid phase in a discrete zone within the aquifer.

Although in situ uranium bioremediation with dissimilatory metal-reducing microorganisms has significant potential as a bioremediation tool, it also has some possible limitations. For example, it is necessary to carefully maintain conditions to promote the activity of the appropriate dissimilatory metal-reducing microorganisms. In field studies, U(VI) was actively reduced as long as a community with a high proportion of U(VI)-reducing *Geobacter* species was maintained (*4*). However, as Fe(III), the primary electron acceptor supporting the growth of the *Geobacter* species (*7*), was depleted from the sediments near the site of acetate injection, *Geobacter* species declined and sulfate-reducing microorganisms, which did not reduce U(VI), became the primary acetate-consuming organisms. Thus, additional environmental manipulations to sustain the *Geobacteraceae* for long periods of time are required.

Another potential limitation of this approach is that although U(VI) reduction prevents the further mobility of the uranium, uranium remains in the environment in the form of the precipitated U(IV). Studies to date have indicated that the U(IV) precipitates generated during in situ uranium bioremediation can be stable in the environment (*8*). However, it may still be desirous to remove the concentrated U(IV) precipitates after a site is remediated. This could be accomplished with microbial (*7*) or chemical (*9*) extraction methods or, in the case of relatively shallow sites, excavation. These extraction methods may cost as much or more as the U(VI) reduction step. Therefore, a method for uranium remediation which would permit a simpler method of removing the precipitated uranium would be beneficial.

Although organic acids and hydrogen are the common electron donors for *Geobacter* species (*10*), these organisms can also accept electrons from electrodes (*11*). For example, with a properly poised electrode as the sole electron donor, *Geobacter metallireducens* reduced nitrate to nitrite and *Geobacter sulfurreducens* reduced fumarate to succinate. This raised the possibility that *Geobacter* species might also be able to reduce U(VI) with electrodes serving as the electron donor and that this could be an alternative strategy for promoting reduction of U(VI) in contaminated subsurface environments.

Entrapment of ions at the electric double layers of carbon electrodes can extract various ions from water (*12*−*15*) and is collectively known as capacitive deionization. Capacitive deionization technology has been applied to remove heavy metals from a variety of waste streams (*16*−*21*). Furthermore, electric potential at a cathode may reduce target contaminants such as pertechnetate (*22*), cadmium (*23*), and chromate (*24*). During electrokinetic remediation of contaminated soil and groundwater, current is applied to electrodes which are inserted into the ground and contaminants are actively transported to the anode or cathode via electro-osmosis, electromigration, diffusion, and/or electrophoresis (*25*−*28*). However, the presence of natural electrolytes and humic substances often confounds this strategy (*27*, *29*). Furthermore, little is known about the effect of microorganisms on the electrodes or how these organisms may affect contaminant removal. A recent study of the effect of electrokinetic remediation on soil microbial communities found little change in microbial or fungal diversity after treatment (*30*); however, it is known that members of *Geobacteraceae* may be enriched from sediment on cathodically poised electrodes for nitrate respiration (*11*).

Here we report that electrodes can serve as an electron donor for U(VI) reduction by *Geobacter sulfurreducens* and that providing an electrode as a potential electron donor can

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promote the removal of uranium from contaminated groundwater. This represents a novel approach to in situ remediation of uranium groundwater contamination, which may have several advantages over previously described approaches.

Experimental Procedures

Biotic and Abiotic Defined Reactors. The glass, dual-chambered fuel cell and graphite electrodes were constructed and prepared as described previously (*11*, *31*). After assembly, the reactors were autoclaved, then flushed with sterile, anaerobic gas (80:20 N_2/CO_2). Both the working and counter electrode chambers were filled with anaerobic, sterile media containing the following in g/L: $NaH_2PO_4 \cdot 6H_2O$, 0.6; NH_4Cl, 0.25; KCl, 0.1; and $NaHCO_3$, 2.0. The pH of the medium was 6.9. The chambers were placed on a multiposition stir plate, and the working chamber was stirred with a magnetic stir bar at 180 rpm. The counter chamber was not stirred but was continuously bubbled with anaerobic gas. The chambers were allowed to equilibrate at −500 mV (vs a Ag/AgCl reference electrode) for 24 h before inoculating with cultures or adding soil or uranium. The control chambers were treated in an identical fashion but were not connected to a potentiostat. Current measurements and electron recovery conversions were performed as described previously (*11*). U(VI) was added from an aqueous UO_2Cl_2 stock solution which was equilibrated with anaerobic gas (80:20 N_2/CO_2). Attempts to anaerobically recover U(VI) from the electrodes was achieved while bubbling both the working and counter chambers with anaerobic N_2/CO_2 to prevent oxygen intrusion. Aerobic recovery of U(VI) was performed by bubbling air through the working and counter chambers.

Geobacter sulfurreducens strain PCA (ATCC no. 51573) was obtained from our culture collection and grown in the previously described medium (*32*) at 30 °C. Acetate served as the electron donor. Cells were maintained on 100 mmol/L poorly crystalline Fe(III) oxide as the electron acceptor and were transferred 3 times into medium with 40 mM fumarate as the electron acceptor prior to inoculation into the electrode chamber. A 10% inoculum of fumarate-grown cells was added to the working chamber containing a poised electrode. Fumarate respiration and current consumption served as evidence that *G. sulfurreducens* was respiring on the surface of the electrode (*11*). Respiration of fumarate and current consumption was observed within 48 h of inoculating the working chamber with *G. sulfurreducens*. Before addition of uranium, the medium was exchanged to remove any remaining planktonic cells and the fumarate.

Batch Soil Experiments. Contaminated soil and groundwater was collected from a former uranium ore processing facility in Rifle, CO (*4*). Chambers were constructed from 60 mm i.d. borosilicate glass (see the Supporting Information, Figure S1). The reactors were 20 cm tall and included 20 mm access ports at 4.5 and 12.5 cm from the bottom. A graphite electrode (working electrode) grade G-10 7.62 × 1.27 × 2.54 cm^3 (Graphite Engineering; Greenville, MI) was placed at the bottom of the reactor. The chamber was filled with enough contaminated soil to cover the electrode. The depth of soil was approximately 10 cm. An identical electrode (counter electrode) was suspended above the working electrode. The remaining volume was filled with contaminated groundwater from the Rifle site. A Ag/AgCl reference electrode (World Precision Instruments; Sarasota, FL) was placed in a sampling port near the working electrode. The top of the chamber was closed with a rubber stopper, and the water above the sediment was bubbled with N_2 gas. Uranium was added to provide 10 μM U(VI), and the chamber was shaken periodically to mix the soil and water. After a period of 96 h, power was supplied to the electrodes and poise at the working electrode was established, initially at −500 mV (vs Ag/AgCl) and decreased stepwise to −700 mV. Samples for U(VI) determinations were removed from the overlying water after shaking and filtered through a syringe filter (0.2 μm pore diameter).

Column Experiments. Columns were constructed of borosilicate glass (23 cm long 5 cm i.d. with 20 mm sampling ports at 1, 6, 11, 15, and 22 cm) (see the Supporting Information, Figure S2). With the exception of electrodes placed at 6 and 15 cm, the column was completely filled with contaminated soil from Rifle, CO. The working electrode, 6 cm from the inlet, was a porous, cylindrical (4.75 cm o.d. 1.27 cm thick), grade G-10 graphite (Graphite engineering; Greenville, MI). A Ag/AgCl reference electrode was fixed into the 6 cm sampling port within 1 cm of the working electrode. The counter electrode, at 15 cm, was identical to the working electrode. Contaminated groundwater from Rifle, CO was fed via syringe pumps (Harvard Apparatus; Holliston, MA). The uranium concentration in the groundwater was amended with UO_2Cl_2 to provide a concentration of 80 μM. The flow rate to the column was 1.0 mL/min. Water samples were collected from the 11 cm port with a syringe.

Analytical Methods. Uranium was measured by kinetic phosphorescence analysis as described previously (*3*). Sulfate was analyzed with ion chromatography using a Dionex DX-100 as described elsewhere (*33*).

The microbial community was assessed as previously described (*11*, *34*). Electrodes were rinsed with sterile medium and scraped with a sterile razor blade into 1.5 mL of TE buffer (pH 8) to produce a slurry of graphite and cells. DNA was extracted from the graphite with a modified version of the miniprep of bacterial genomic DNA protocol (*35*). 16S rRNA genes were amplified with the primer 8 forward (*36*) with 519 reverse (*36*) or 338 forward (*37*) and 907 reverse (*38*) and Archaeal primers 344 forward (*39*) and 915 reverse (*40*). PCR mixtures and conditions were followed as detailed elsewhere (*34*). Clone libraries were constructed from the 16S rRNA genes using the TOPO TA cloning kit version R (Invitrogen; Carlsbad, CA) according to the manufacturer's instructions.

A total of 144 clones under each condition (with and without current) were selected for sequencing. The 16S rRNA genes were amplified from each clone using M13 forward and reverse primers (Invitrogen) using whole-colony PCR. PCR products were purified using the QIAquick PCR purification kit (Quiagen; Valencia, CA). Inserts were sequenced at the UMASS Environmental Biotechnology Center's sequencing facility. Sequences were compared to the GenBank database with the BLASTN (*41*) algorithm.

Results and Discussion

Defined System. A graphite electrode poised at −500 mV (vs Ag/AgCl) removed U(VI) in sterile medium from solution (Figure 1, inset). An amount of 80 μM U(VI) was removed from solution in 24 h, at which time U(VI) was added to give a concentration of 120 μM. The second addition of U(VI) was removed within 48 h. No U(VI) was lost from solution under any of the conditions evaluated if the electrode was not poised (data not shown). When *G. sulfurreducens* was present on the electrode, U(VI) was removed, but at an initial rate which was ca. 6 times slower than that when cells were not present (Figure 1, inset).

When poise was removed from the working electrode in the cell-free system U(VI) was released back into solution with nearly complete recovery of the added U(VI) in solution (Figure 1). Identical U(VI) recovery results were obtained when the chambers were immediately placed in an anaerobic glovebox (data not shown), as opposed to bubbling with anaerobic gas. In contrast, no U(VI) returned to solution for more than 600 h when *G. sulfurreducens* was present on the working electrode. However, addition of air into the working chamber resulted in rapid and complete recovery of U(VI) (Figure 1). These results suggest that the uranium on the

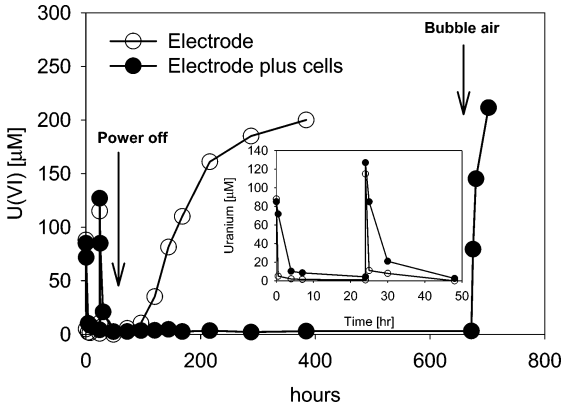

FIGURE 1. Uranium removal and recovery in the presence of a potentiostat-poised graphite electrode in the presence and absence of *G. sulfurreducens*. The potentiostat was poised at −500 mV (vs a Ag/AgCl reference). The inset figure shows a shortened time axis for the same data set which better illustrates the addition and removal of U(VI). Uranium was added at $t = 0$ h (80 μM) and $t =$ 24 h (120 μM).

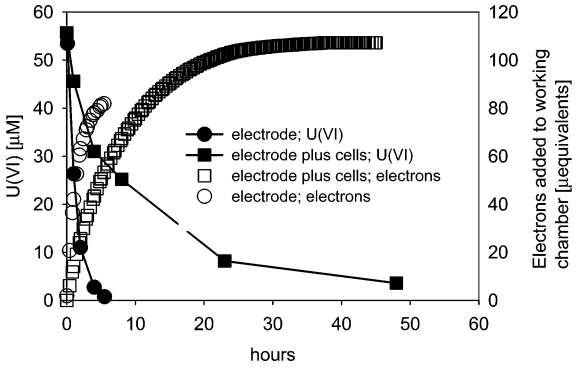

FIGURE 2. Uranium removal and corresponding electron balance using a poised graphite electrode (−500 mV) with and without *G. sulfurreducens*. Filled and open data markers correspond to the uranium concentration and the cumulative electrons added to the working chamber, respectively, under each condition.

electrodes was in a different form in the presence of *G. sulfurreducens* than in its absence.

The recovery of U(VI) under anaerobic conditions in the systems in which *G. sulfurreducens* was absent suggests that the uranium was in the U(VI) state. Although U(V) is a potential reduction product, it rapidly disproportionates to the (VI) and (IV) valence states (*42*). Furthermore, previous studies have shown that U(VI) reduction at a carbon-fiber electrode is negligible at poised potentials down to −900 mV (vs Ag/AgCl) (*43*). Thus, in the absence of cells, U(VI) removal was most likely due to adsorption of U(VI) onto the electrode surface.

In contrast, the requirement for oxygen in order recover U(VI) from the systems that contained *G. sulfurreducens* suggests that, prior to the addition of the oxygen, the uranium was in the form of U(IV). The most likely explanation for this is that *G. sulfurreducens* is able to use the electrode as an electron donor for U(VI) reduction in a manner similar to the previously described (*11*) reduction of fumarate or nitrate with the electrode serving as an electron donor for *Geobacter* species.

To further evaluate U(VI) removal at the electrode surface, electron consumption associated with U(VI) removal was monitored (Figure 2). In the presence of cells the removal of 55 μM U(VI) consumed 107 μequiv of electrons, or 97% of the amount expected for reduction of U(VI) to U(IV). Although the results summarized above suggested that U(VI) was not reduced in the absence of cells, the removal of 53 μM of

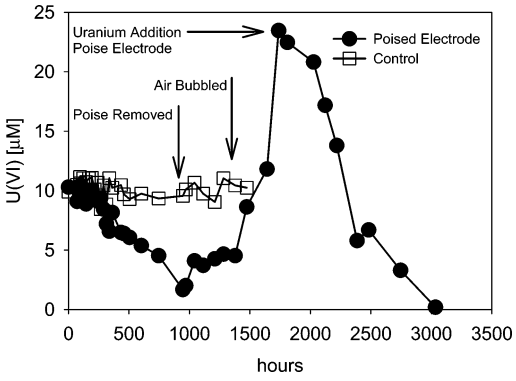

FIGURE 3. Removal and recovery of U(VI) in batch incubations of uranium-contaminated soil and groundwater from Rifle, CO. After 96 h, the initial poise was set at −500 mV (vs Ag/AgCl). It was adjusted to −600 mV at 170 h and −700 mV at 314 h. Power was turned off at 970 h, and air was bubbled into the system at 1474 h. At 1738 h, more U(VI) was added and power was reapplied at a potential of −700 mV.

U(VI) was associated with the input of 82 μequiv of electrons into the working chamber. Since U(VI) did not appear to be reduced to U(V) or U(IV), the observed current flow may have been associated with maintaining the poised reducing potential at the working electrode and the associated electrical double layer in the presence of oxidized ions, rather than a transfer of electrons from the electrode to U(VI). Current consumption in the absence of reduction of the target ions is commonly observed during capacitive deionization (*13*, *18*, *44*). Nonfaradaic current is observed when the voltage at the working electrode, electrode surface area, or solution composition is changed. Adsorption at the graphite surface changes the electrode−solution interface, charging potential, and solution composition. The process of adsorption is nonfaradaic and is known to be accompanied by current flow (*45*).

Batch Reactors with Contaminated Sediment. To determine whether poised electrodes would remove U(VI) from contaminated groundwater associated with sediments, electrodes were placed in subsurface sediments and associated groundwater from a uranium-contaminated subsurface site in Rifle, CO. The working electrodes were buried in contaminated sediment and water, and the counter electrodes were suspended in the overlying contaminated water.

Initially, no poise was placed on the working electrode and U(VI) concentrations remained stable for 96 h (Figure 3). After 96 h, the poise of the buried, working electrode was set at −500 mV. U(VI) concentrations had decreased, from 10.4 to 8.8 μM at 146 h. At 170 h, the working electrode potential was reduced to −600 mV, but at 314 h, U(VI) concentrations had only deceased to 8.3 μM. The poise at the working electrode was then decreased to −700 mV. At 946 h later, U(VI) concentrations had decreased to 1.7 μM. Uranium concentrations in the control reactor without poise remained steady for 1474 h (Figure 3).

Poise to the working electrode was removed after 970 h. Within 72 h, approximately 30% of the U(VI) removed had returned to solution. U(VI) concentrations then remained stable for the next 300 h (Figure 3). At 1378 h, air was bubbled into the system. At 96 h after the introduction of air, 83% of the U(VI) that had been removed had appeared in solution, and all of the U(VI) was recovered in solution within 260 h. The finding that recovery of U(VI) required the presence of oxygen indicates that most of the U(VI) removed from solution was in the form of U(IV). Nitrate (NO_3^-) and sulfate (SO_4^{2-}) were initially present in the groundwater at 0.1 mM and 9.5 mM, respectively. At the end of the experiment, the SO_4^{2-} concentration had decreased to 4 mM and NO_3^- was

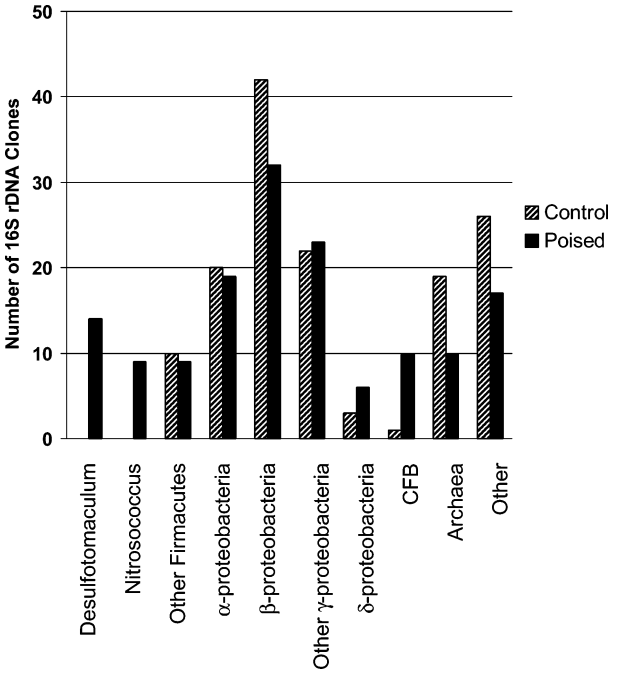

FIGURE 4. Comparison of 16S rRNA clones found on poised and unpoised (control) electrodes during remediation of uranium contamination of soil and groundwater. A total of 144 clones from each sample were analyzed. Clones were placed into groups based on the closest percent similarity in the database as determined by the BLASTN algorithm (*41*).

no longer detectable (<0.005 mM). The initial concentration of soluble Fe(II) was 14 μM and increased to 34 μM at the end of the experiment. It is likely that the electrodes had stimulated microbial reduction of SO_4^{2-}, NO_3^-, and possibly Fe(III), in addition to stimulating U(VI) reduction.

To evaluate what microorganisms might be involved in U(VI) reduction at the electrode surface, the sediment system was returned to anaerobic conditions, U(VI) was added to provide a concentration of 23.5 μM, and current was reapplied to the working electrode to maintain the poise at −700 mV (Figure 3). U(VI) concentrations steadily decreased until the reactor was sacrificed for analysis of the microbial community on the electrode.

Comparison of the 16S rRNA gene sequences recovered from the surface of the electrodes serving as electron donors in sediments with sequences recovered from the surface of control electrodes not connected to a potentiostat indicated that there was a slight enrichment of sequences which were most closely related to *Desulfotomaculum* and *Nitrosococcus* species (Figure 4). These sequences were not detected on the control electrodes. There was also an increase in the percentage of sequences most closely related to δ-proteobacteria and bacteria in the *Chlorobium*/*Flavobacterium*/*Bacteroidetes* (CFB) classification; however, genus-specific enrichment from these families was not observed. Several sequences decreased on the connected electrode.

Although poised electrodes serving as an electron donor for nitrate reduction were enriched with *Geobacter* species in a previous study (*11*), it is not surprising that the electrodes emplaced in the Rifle sediments were not. Nitrate is an electron acceptor for several *Geobacter* species (*10*), and nitrate concentrations in that previous study were at millimolar concentrations. However in the Rifle sediments nitrate, as well as U(VI), the other potential soluble electron acceptor for *Geobacter* species in this environment, were in micromolar concentrations. In contrast, as noted above millimolar concentrations of sulfate were available and were being reduced in the sediments with poised electrodes.

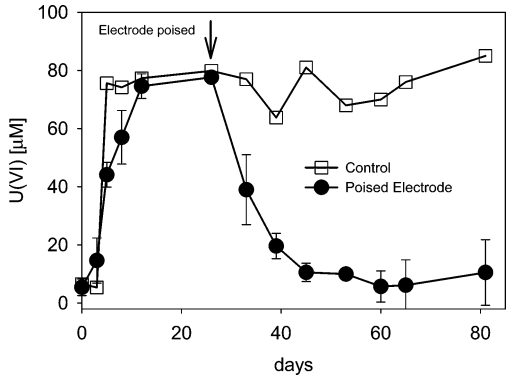

FIGURE 5. Uranium removal by graphite electrodes in flow-through columns packed with uranium-contaminated soil from Rifle, CO. Columns were fed with uranium-containing groundwater from Rifle, CO. The working electrodes in the control column were not given a poised potential. Samples were removed from the 11 cm sampling port. The results represent the mean and range of the results from two columns.

Therefore, it might be expected that sulfate-reducing microorganisms, such as *Desulfotomaculum* species, would be enriched on the electrode. *Nitrosococcus* are ammonia- and methane-oxidizing chemolithotrophs. Potential methane- and ammonium-oxidizing microorganisms were enriched on cathodes harvesting electricity from marine sediments (*34*).

Column Experiments with Contaminated Sediment. To evaluate the potential for U(VI) removal under the more dynamic groundwater flow conditions found in contaminated aquifers, studies were next conducted with flow-through columns packed with sediments from the Rifle site (Figure 5). U(VI) concentrations in groundwater from the site were increased to 80 μM. Slow removal of U(VI) in batch experiments at −500 mV indicated that greater reducing potential should be applied to the electrode in subsequent experiments with sediment. After achieving a steady effluent of uranium from the columns, the electrodes in the experimental columns were poised at −600 mV (vs Ag/AgCl). U(VI) removal began immediately and was sustained for over 40 days. The control column, which contained nonpoised graphite electrodes, did not remove uranium. At the end of the experiment, a column was sacrificed and the working electrode was quickly removed from the column, detached from the potentiostat, and immediately submerged in aerobic, 50 mM bicarbonate buffer for oxidation and extraction of uranium. An amount of 89 μmol of U(VI) was recovered from the oxidation and extraction, which represented 87% of the total U(VI) removed in the column over the duration of the experiment.

In summary, the results suggest that U(VI) can be effectively removed from groundwater with graphite electrodes poised at ca. −600 mV (vs Ag/CgCl). Whereas U(VI) may only be adsorbed to the electrode in the absence of the microorganisms, it appears to be reduced to U(IV) when microorganisms are present. The U(IV) remains as a stable precipitate on the electrode in the absence of oxygen. This offers the possibility that once uranium is precipitated from contaminated groundwater onto electrodes, the electrodes can then be removed from the groundwater, extracting the precipitated uranium from the subsurface. This contrasts with delivering electrons to the subsurface in the form of an organic electron donor in which the U(VI) can effectively be removed from the groundwater, but the precipitated U(IV) remains in the subsurface. Field studies to evaluate the possibility of remediation and recovery of uranium from groundwater contamination on a large scale with electrodes are warranted.

Acknowledgments

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Supporting Information Available

Additional information which diagrams the apparatuses used in the batch and column studies with contaminated sediment and groundwater from Rifle, CO. This material is available free of charge via the Internet at http://pubs.acs.org.

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