# Reductive Precipitation of Uranium(VI) by Zero-Valent Iron

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This study was undertaken to determine the effectiveness of zero-valent iron ($Fe^0$) and several adsorbent materials in removing uranium (U) from contaminated groundwater and to investigate the rates and mechanisms that are involved in the reactions. $Fe^0$ filings were used as reductants, and the adsorbents included peat materials, iron oxides, and a carbon-based sorbent (Cercona Bone-Char). Results indicate that $Fe^0$ filings are much more effective than the adsorbents in removing uranyl ($UO_2^{2+}$) from the aqueous solution. Nearly 100% of U was removed through reactions with $Fe^0$ at an initial concentration up to 76 mM (or 18 000 mg of U/L). Results from the batch adsorption and desorption and from spectroscopic studies indicate that reductive precipitation of U on $Fe^0$ is the major reaction pathway. Only a small percentage (<4%) of $UO_2^{2+}$ appeared to be adsorbed on the corrosion products of $Fe^0$ and could be desorbed by leaching with a carbonate solution. The study also showed that the reduced U(IV) species on $Fe^0$ surfaces could be reoxidized and potentially remobilized when the reduced system becomes more oxidized. Results of this research support the application of the permeable reactive barrier technology using $Fe^0$ as a reactive media to intercept U and other groundwater contaminants migrating to the tributaries of Bear Creek at the U.S. Department of Energy's Y-12 Plant located in Oak Ridge, TN.

## Introduction

Zero-valent iron ($Fe^0$) has been extensively studied in recent years for use in degrading or removing both organic and inorganic environmental contaminants (*1−10*). Because $Fe^0$ filings are inexpensive and readily available, they have been considered one of the most promising permeable barrier materials for treating contaminated groundwater plumes (*2, 11*). To date, about a dozen full-scale and pilot-scale in-situ permeable reactive barriers have been installed (*12*), with most of the installations targeting chlorinated organic hydrocarbons in groundwater (*11, 12*). At the Elizabeth City site, in North Carolina, a barrier wall has been installed to remove both chromate ($CrO_4^{2-}$) and trichloroethylene from the contaminated groundwater (*3, 13*).

While numerous laboratory and field studies have focused on the reaction kinetics and mechanisms between $Fe^0$ and

chlorinated organic contaminants, relatively few studies have examined the potential for using $Fe^0$ to reduce or remove radionuclides and heavy metals in contaminated groundwater (*3, 14, 15*). In particular, it is still unclear whether the removal of uranyl ($UO_2^{2+}$) results from reductive precipitation or from adsorption onto the corrosion products of $Fe^0$ (*15−18*). It is important to know which of these two mechanisms dominates the reaction because it largely determines the mobility and fate of uranium (U) under a given geochemical environment. For example, if $UO_2^{2+}$ is predominately adsorbed onto the hydrous iron oxides or the corrosion products of $Fe^0$, the adsorbed U would be readily desorbed by the presence of competing ions and complexing agents such as carbonate ($CO_3^{2-}$) and dissolved organic matter in groundwater. Furthermore, a change in the groundwater pH would profoundly influence the adsorption and desorption behavior of U on iron oxide surfaces. Alternatively, if U is primarily removed by reductive precipitation, the precipitated U would not be remobilized unless the groundwater redox conditions are changed and the reduced U(IV) species are reoxidized, forming more soluble U(VI) species.

From a thermodynamic perspective, $Fe^0$ is able to reduce a number of redox-sensitive radionuclide and metal species such as $UO_2^{2+}$, $CrO_4^{2-}$, and pertechnetate ($TcO^{4-}$), thereby resulting in lower solubility species of uranium(IV) oxyhydroxides, $Cr(OH)_3$, and $TcO_2$ (*14, 15, 19−21*). Studies (*3, 19*) have shown that $CrO_4^{2-}$ and $TcO_4^-$ can be rapidly and effectively removed by $Fe^0$. A reductive precipitation is suggested to be the major reaction mechanism for the removal of these two contaminants by $Fe^0$. In addition to removing $CrO_4^{2-}$ and $TcO_4^-$, according to a recent study related to groundwater remediation (*15*), $Fe^0$ is able to effectively remove $UO_2^{2+}$ and $MoO_4^{2-}$ from aqueous solutions, and the reductive precipitation for the removal of these contaminants has also been suggested as a possible mechanism. However, because $UO_2^{2+}$ can also be adsorbed onto the iron corrosion products, these authors concluded that the exact mechanism of $UO_2^{2+}$ removal is not yet clear and could be due to any of the following: (1) reduction of uranyl by $Fe^0$ to form U(IV) species; (2) adsorption of $UO_2^{2+}$ to iron oxyhydroxide corrosion products; and (3) a combination of reductive precipitation and adsorption. Fiedor et al. (*18*) reported that $UO_2^{2+}$ is only slowly and incompletely reduced to U(IV) species under anoxic conditions by using a piece of $Fe^0$ coupon in a relatively large volume of $UO_2^{2+}$ solution.

The adsorption of $UO_2^{2+}$ on iron oxyhydroxides is known to take place, particularly at a relatively high pH, under which the oxide surface becomes negatively charged (*22−25*). Hsi and Langmuir (*23*) indicated that all iron oxide materials strongly adsorb dissolved uranyl species at about pH 5−10 and that the amount of adsorption is greatest on amorphous ferric oxyhydroxide and least on well-crystallized hematite. The adsorption mechanism was attributed to a surface complexation between $UO_2^{2+}$ and iron oxyhydroxides (*23, 25*). The removal of U(VI) by iron corrosion products consisting of over 97% hydrous iron(II) oxide under saline conditions (34.3% salts) was recently reported by Grambow et al. (*16*). They found that a large percentage of U was rapidly adsorbed onto the iron corrosion products and U(VI) species were only partially reduced. These observations are expected because a reduction of U(VI) to U(IV) by Fe(II) species is thermodynamically unfavorable except under strong acidic conditions (reactions 1 and 2). $Fe^0$ is much stronger a reductant than $Fe^{2+}$ ($E^0$ in reactions 1 and 3), and $UO_2^{2+}$ reduction by direct electron transfer at the $Fe^0$ surface would be favorable following electrochemical corrosion, as

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**TABLE 1. Properties of Reactive Media and Experimental Conditions for Rate Reactions between Uranyl (at an Initial Concentration of 1000 mg of U/L) and $Fe^0$ Filings and Iron Oxide**

| media | surface area $(m^2/g)$ | size | solid/solution ratio (w/v) | volume (mL) | note |
|---|---|---|---|---|---|
| Master-Builder iron | 0.98 | 0.5−1 mm | 1:5 | 10 | sieved |
| Peerless iron, medium | 0.10 | 0.5−1 mm | 1:5 | 10 | sieved |
| Peerless iron, course | 0.08 | 3−12 mm | 1:5 | 10 | as received |
| Cercona cast iron | 0.02 | 0.2−3 mm | 1:5 | 10 | as received |
| Cercona iron-palladized | ND[a] | 0.2−3 mm | 1:5 | 10 | Pd-coated (0.05%) |
| iron oxide | 10.1 | 0.2−0.25 $\mu$m | 1:20 | 10 | as received |
| control blank | | | | 10 | no solids |

[a] ND, not determined.

illustrated by Powell et al. (*14*):

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^0 = +0.771\ V \qquad (1)$$

$$UO_2^{2+} + 4H^+ + 2e^- \rightarrow U(IV) + 2H_2O$$
$$E^0 = +0.327\ V \qquad (2)$$

$$Fe^{2+} + 2e^- \rightarrow Fe^0 \qquad E^0 = -0.440\ V \qquad (3)$$
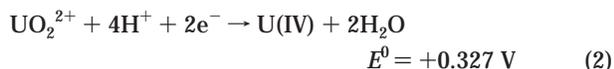
Thus, both reduction of U(VI) by $Fe^0$ and adsorption of U(VI) by iron oxyhydroxides can result in a removal of U from aqueous solution; a better understanding of these two reaction mechanisms is of practical importance because the reaction pathways largely determine the fate and long-term consequences of U retained within the $Fe^0$ media under specific geochemical environments.

The objectives of this study were to determine the effectiveness of $Fe^0$ and several adsorbent materials in removing U from contaminated groundwater and to investigate the rates and mechanisms that are involved in the reactions. The work was part of remedial actions using permeable reactive barrier technology to intercept and treat U, nitrate, chlorinated organic compounds, and other contaminants migrating to the tributaries of Bear Creek at the U.S. Department of Energy's Y-12 Plant located in Oak Ridge, TN. This paper focuses on the U removal from the groundwater because it is a major contributor to health and environmental risks downgradient of the Bear Creek (*26*).

## Materials and Methods

**Determining Reaction Rates.** The reaction kinetics between $Fe^0$ and $UO_2^{2+}$ were studied in batch experiments by mixing 2 g of iron filings with 10 mL of uranyl nitrate $[UO_2(NO_3)_2]$ solution at an initial concentration of 4.2 mM (1000 mg of U/L) in a glass vial (~12.5 mL in capacity). Stock $UO_2(NO_3)_2$ solution was made in Milli-Q water, and the initial pH of the reactant solution was 5 with an ionic strength of ~12.5 mM. Four sources of iron filings were evaluated: (1) medium-size Master-Builder iron (0.5−1 mm) (Master-Builders, OH), (2) Cercona cast iron (Cercona of America, OH), (3) medium-size Peerless iron (0.5−1 mm) (Peerless Metal Powers and Abrasives, MI), and (4) coarse Peerless iron filings (3−12 mm). The general properties of these iron filings and the experimental conditions are listed in Table 1. In each of the reaction vials, a small headspace (~2 mL) was present, and the aqueous solutions were not subject to any degassing. After the $UO_2^{2+}$ solution and $Fe^0$ were combined, the mixture was agitated on a rotator at ~10 rpm. At various time intervals, a reaction vial was sacrificially sampled. The supernatant solution was withdrawn and filtered immediately with a 5-$\mu$m Gelman Acrodisc syringe filter. The filtered solution (8 mL) was transferred to a 20-mL scintillation vial and mixed with 8 mL of Ultima-Gold scintillation cocktail; U activity in the mixture was then analyzed by means of a Packard liquid scintillation analyzer (model 2700TR) equipped with an

automatic $\alpha$- and $\beta$-discriminator (*27*). The detection limit is approximately 0.5 mg/L for $^{238}U$. A phosphorescence lifetime analyzer (ChemChek, KPA-11) was also used for U analysis in selected batch studies in which the aqueous solution was filtered through a 0.2-$\mu$m Gelman PTFE syringe filter. This analytical technique allowed a very low detection limit for U (on the order of 1 ng/L), thus enabling an assessment of the completeness of the reductive precipitation of U in solution.

Additionally, the reaction rates between $UO_2^{2+}$ and an iron oxide powder (~200−250 nm in size) and a palladium-coated Cercona cast iron were determined and compared with that of the four $Fe^0$ metals. The experimental conditions are also listed in Table 1. The iron oxide was expected to mimic the reactions between $UO_2^{2+}$ and the $Fe^0$ corrosion products; a palladium-coated Cercona iron was used to study the reductive precipitation of $UO_2^{2+}$ under an enhanced $Fe^0$ corrosion rate (induced by the Pd coating on the $Fe^0$ surface) (*5, 28*).

**Adsorption Capacity and Removal Efficiency.** A second set of experiments was performed to determine the U adsorption or removal capacity of the reductive or adsorbent materials, including $Fe^0$ filings, iron oxide powder, a carbon-based adsorbent [Cercona Bone-Char, containing ~25% carbon with calcium and aluminum phosphate as a binder (Cercona of America)], and Ward's natural peat (Ward's Natural Science Establishment, NY). The peat is a coal-like, fully decomposed organic material. The experimental procedures are similar to what has been described above except that varying amounts of $UO_2^{2+}$ were added into a series of reactant solutions (Table 2). The solids and solutions were allowed to equilibrate overnight before filtration and analysis. A low solid-to-solution ratio was used in these experiments because of the relatively large surface area and the low bulk density of the adsorbent materials. In the case of iron oxide powder, 0.1 g was used in 10 mL of solution, and samples were filtered with 0.2-$\mu$m syringe filters for the iron oxide samples because the average particle size of iron oxide was ~200−250 nm (*29, 30*). In the case of Cercona Bone-Char, 0.5 g was used in 10 mL of solution, and after reaching equilibrium, samples were filtered with 5-$\mu$m syringe filters. To determine the amount of U adsorption on peat, 0.3 g of the solid was added to 15 mL of uranium solution with an initial U concentration up to ~50 mM (12 000 mg/L).

**U Partitioning on $Fe^0$ and its Corrosion Products.** Because $Fe^0$ corrodes in water, uranyl species are expected to adsorb onto $Fe^0$ corrosion products such as iron oxyhydroxides. To evaluate the mechanisms and partitioning of U on $Fe^0$ and its corrosion products, the following experiments were performed. A 10-mL $UO_2(NO_3)_2$ solution of 42 mM (10 000 mg of U/L) was equilibrated with 2 g of $Fe^0$ for approximately 3 weeks on a shaker. The solid and solution mixture was then removed from the shaker, and the supernatant was immediately decanted. The iron filings were thus separated from the $Fe^0$ corrosion products (i.e., par-

**TABLE 2. Properties of Fe⁰ Filings and Adsorbents and Experimental Conditions for Their Reactions with Uranyl**

| media | surface area $(m^2/g)$ | size | solid/solution ratio (w/v) | initial U (mg/L) | solution volume (mL) | note |
|---|---|---|---|---|---|---|
| Master-Builder iron | 0.98 | 0.5−1 mm | 1:5 | 0−18 000 | 10 | sieved |
| Peerless iron, coarse | 0.08 | 3−12 mm | 1:5 | 0−18 000 | 10 | as received |
| Wards peat | ND[a] | 2 mm | 1:50 | 0−12 000 | 15 | crushed and sieved |
| iron oxide | 10.1 | 0.2−0.25 $\mu$m | 1:100 | 0−12 000 | 10 | as received |
| Cercona Bone-Char | ND | 1−5 mm | 1:20 | 0−12 000 | 10 | as received |
| Cercona Fe-Bone-Char | ND | 1−5 mm | 1:20 | 0−12 000 | 10 | as received, 10% Fe⁰ |

[a] ND, not determined.

ticulates) in the supernatant. Note that the iron residue was not washed, because of concern that additional iron oxyhydroxide corrosion products would possibly be generated by repeated washing processes. The amount of U associated with the filterable particles was estimated by analyzing U concentrations in solution before and after samples were filtered through a 5-$\mu$m filter. If U was sorbed or coprecipitated with Fe⁰ corrosion products, U activity would be higher in the unfiltered samples than in the filtered samples. To further evaluate whether U was reductively precipitated or adsorbed on the iron corrosion products, 4 mL of the suspension was extracted with 4 mL of 0.2 M Na₂CO₃ solution (to give a final Na₂CO₃ concentration of 0.1 M). After equilibration for 30 min, the carbonate solution was filtered, and its U concentration was analyzed. Extraction of U in the remaining iron filings was performed in a similar manner by adding 10 mL of 0.1 M Na₂CO₃ solution and equilibrating the solution for 30 min. After equilibrium was reached, the Na₂CO₃ solution was filtered, and its U content was analyzed.

**X-ray Diffraction and SEM Analyses.** The corrosion products of Fe⁰ were identified by X-ray diffraction (XRD) analysis. Samples were prepared by filtering the suspended particles from the mixture of Fe⁰ and UO₂²⁺ solution under vacuum. The filtered disks were immediately mounted on a Scintag XDS-2000 diffractometer for mineralogical analysis. This process took <10 min. The preparation time was kept to a minimum because oxidation and crystallization of the corrosion products might have occurred if they were allowed to sit for an extended period (*31*).

The particle size and the size distribution of Fe⁰ corrosion products and U coatings on Fe⁰ were examined by means of a scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) diffraction analysis (JEOL JSM-35CF scanning microscope). All samples were placed on aluminum stubs and sputtered with gold to prevent electrical charging during the SEM and EDX analyses.

**Fluorescence Spectroscopy.** U reductive precipitation on Fe⁰ was further evaluated by fluorescence spectroscopy, with the understanding that only oxidized U(VI) species would yield strong fluorescence (*32*). Two series of fluorescence experiments were performed. In the first series, Fe⁰ filings (5 g) and iron oxide powders (0.5 g) were mixed separately with 50 mg of U in an aqueous solution of UO₂(NO₃)₂. Samples were equilibrated for 1 week, and their steady-state luminescence spectra were measured by means of a fiber-optic probe inserted directly in Fe⁰ or iron oxide suspension (*33*). The 337-nm line of a pulsed nitrogen laser (pulse duration = 5 ns) was used as the excitation source in these studies. A fiber-optic superhead probe (Dillor) was used in both the excitation and the collection of signals from the samples. The emission was collected at 180° with respect to the excitation direction and dispersed with a Spex 500M monochromator with a 150-nm groove/mm grating blazed at 655 nm. The dispersed radiation was detected by means of a CCD detector (Spex System One) with an entrance slit width of less than 0.8 nm and a resolution of 0.2 nm.

The second series of fluorescence experiments was designed to evaluate the possible reoxidation of the pre-

cipitated U(IV) on Fe⁰ surfaces when exposed to air and to provide additional evidence of U reduction in Fe⁰. Three samples were prepared as follows. The first was an Fe⁰-rusted sample, which was created by immersing Fe⁰ filings in water for 24 h and then drying them in air. The sample was then reacted with UO₂²⁺ for 10 min, after which the supernatant solution was decanted. The U-loaded rusted iron sample was air-dried for ∼2 days before analysis. The second sample was prepared by reacting the Fe⁰ filings (without any treatment) with the U solution for 2 h and then drying the sample with a Speed-Vac for 4 h before analysis. In this case, the air was not excluded, but the exposure period was shorter than that of the first sample. The third sample was prepared in a similar manner as the second except it was not dried (to exclude air contact); the supernatant was decanted, and the moist Fe⁰ residue (with U) was immediately analyzed. The fluorescence spectra were acquired by directly inserting a fiber-optic probe into the Fe⁰ filings after they were cooled by liquid N₂ to minimize the quenching effects of Fe⁰.

## Results and Discussion

**Uranium Reaction Rates.** The rates of removal of UO₂²⁺ by various Fe⁰ filings are presented in Figure 1. Because no strong buffers were added to counteract the electrolysis of water by Fe⁰, the solution pH increased from 5 to approximately 10 in less than 30 min (data not shown). Results indicate that all iron filings studied are effective in removing UO₂²⁺ from the aqueous solution. Over 97% of U was removed within 30 min by all the Fe⁰ media, and no detectable amount of U was left in the aqueous phase after about 1 h of reaction. The logarithmic decay of the UO₂²⁺ concentration during the initial stage of the reaction (Figure 1B) indicates an apparent pseudo-first-order removal of UO₂²⁺ by Fe⁰. On the basis of the first-order reaction rate law, the apparent initial reaction rate constants and the half-lives for U removal were tabulated in Table 3. For the commercial iron filings obtained from Master-Builders and Peerless, a general trend of increase in reaction rates was observed with the increase of surface areas (Table 3). A range of reaction half-lives (1.8−5.7 min) has been derived for these media (with a range of surface area of 0.08−0.98 m²/g). The reaction rate constants for the Cercona cast iron media did not follow the trend of the other commercial iron filings, possibly because it was a direct machine product without heat treatment (to remove residual oil) that is common to other commercial iron filings. However, the Pd-coated Cercona cast Fe⁰ exhibited a faster initial removal rate (half-life = 2.2 min) than the uncoated Fe⁰ (half-life = 3.6 min).

In contrast to Fe⁰, iron oxide was not as effective in removing UO₂²⁺ in solution; only 15% of UO₂²⁺ was removed by the oxide. The rate of removal of UO₂²⁺ by the iron oxide appears to be fast; the solution U concentration fell within 5% of the steady-state value over a period of less than 1 min. These observations indicate that the U was removed by iron oxide largely through the surface adsorption or complexation processes, which often exhibit relatively fast reaction kinetics.

**TABLE 3. Initial Reaction Rate Constants and Half-Lives Based on a Pseudo-First Order Rate Law[a]**

| media | surface area (m²/g) | size (nm) | rate constant (min⁻¹) | half-lives (min) | $R^2$ of the linear fit |
|---|---|---|---|---|---|
| Master-Builder iron | 0.98 | 0.5−1 | 0.39 | 1.79 | 0.96 |
| Peerless iron, medium | 0.10 | 0.5−1 | 0.29 | 2.41 | 1 |
| Peerless iron, course | 0.08 | 3−12 | 0.12 | 5.68 | 1 |
| Cercona cast iron | 0.02 | 0.2−3 | 0.19 | 3.61 | 0.99 |
| Cercona iron-palladized | ND[b] | 0.2−3 | 0.31 | 2.22 | 0.99 |

[a] The weight-based solid solution ratios are 1:5. The initial concentration is 4.2 mM (1000 mg of U/L) in 10 mL of aqueous solution. [b] ND, not determined.
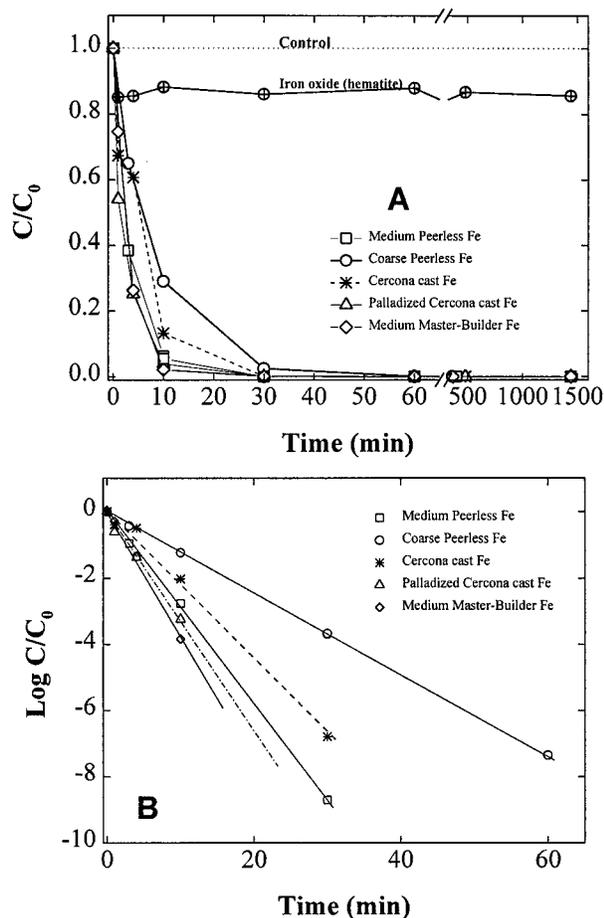


FIGURE 1. (A) Time-dependent reactions between uranyl and zerovalent iron (Fe⁰) filings or iron oxide powder in aqueous solution and (B) the logarithmic plot of the initial reaction rates. The initial concentration ($C_0$) was 4.2 mM (1000 mg of U/L).

The incomplete removal of U by the iron oxide could be attributed to the limited availability of surface sites; the adsorption reached its maximum because more $UO_2^{2+}$ was present in the solution than could be adsorbed.

On the other hand, the reductive precipitation process usually takes longer than the adsorption process because it involves the corrosion of Fe⁰ and an electron transfer from Fe⁰ to $UO_2^{2+}$. Because the U solution was not deoxygenated before the experiment, a further time-lag was required to establish a low redox potential for both iron surface and solution. The near complete removal of U by Fe⁰ filings shows that the reductants have a much higher capacity than the iron oxide despite the fact that the Fe⁰ filings have a lower specific surface area (0.02−1 m²/g) than the iron oxide powder (10.1 m²/g). The apparent "high capacity" for U removal by Fe⁰ suggests that electrochemical corrosion of iron is the main driving force, producing electrons for U(VI) reduction
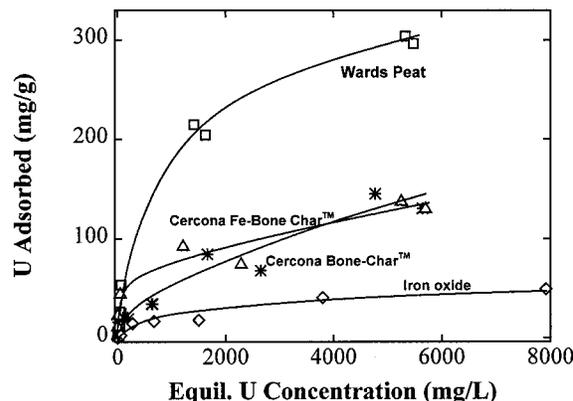


FIGURE 2. Uranyl adsorption by adsorbent materials. The solution-to-solid ratios were 20, 50, and 100 for Cercona Bone-Char, Wards peat, and iron oxide, respectively. The initial uranyl concentration ranged from 0 to 50 mM (12 000 mg of U/L).

and removal from the aqueous phase. So long as the corrosion proceeds, the U(VI) will be reduced and removed from water, giving apparent "infinite" capacity.

Another line of evidence suggesting the reductive precipitation of $UO_2^{2+}$ by Fe⁰ filings is from a study in which palladized-Cercona iron filings were used and accelerated U removal was observed (Figure 1). The corrosion rate of the base metal (Fe⁰) is expected to increase by the coated palladium as a result of galvanic reaction, in which iron is sacrificed (5, 28). The increased corrosion would produce electrons for U(VI) reduction, accounting for the observed higher reaction rate.

It is known that the reactions between Fe⁰ and chlorinated organic compounds are strongly correlated to the specific surface area of Fe⁰ (2, 6, 34, 35). Unfortunately, the surface area of coarser iron (0.08 m²/g) used in the study did not differ much from the finer iron filings (0.1 m²/g). Nevertheless, reaction rates of the commercial iron filings showed a general trend, i.e., a slower rate with the smaller surface area (coarser Peerless iron filings) than with the larger surface area iron (Master-Builder iron filings). Therefore, the surface-dependent U(VI) removal is consistent with the previous observation of $CrO_4^{2-}$ reduction by Fe⁰ (3), indicating that $UO_2^{2+}$ reduction by direct electron transfer at the Fe⁰ surface is a favorable reaction following the electrochemical corrosion of Fe⁰ as illustrated previously (14).

**U Removal Efficiency and Capacity.** The efficiency and capacity of U removal through reductive precipitation and adsorption by Fe⁰ and several adsorbent materials (iron oxide, peat, and Cercona bone-char) were further evaluated in batch studies. These studies used a relatively high U concentration for estimating the capacity of U retention or reduction by these adsorbent or reductive materials. Figure 2 shows the typical adsorption isotherms of $UO_2^{2+}$ on adsorbent materials. These adsorption isotherms indicated a relatively rapid increase in adsorption initially but a decrease as solution concentration increased. The adsorption can be described

**TABLE 4. U Partitioning in the $Fe^0$ and the Suspended Particles (i.e., the Corrosion Products of $Fe^0$) before and after Washing with 0.1 M $Na_2CO_3$**

| | Peerless iron filings | | | Master-Builder iron filings | | |
|---|---|---|---|---|---|---|
| | before wash (mg) | after wash (mg) | U desorbed (%) | before wash (mg) | after wash (mg) | U desorbed (%) |
| U in $Fe^0$ | 96.09 | 95.89 | 0.21 | 97.23 | 97.16 | 0.07 |
| U in suspended particles | 3.91 | 1.39 | 64.5 | 2.77 | 0.18 | 93.6 |
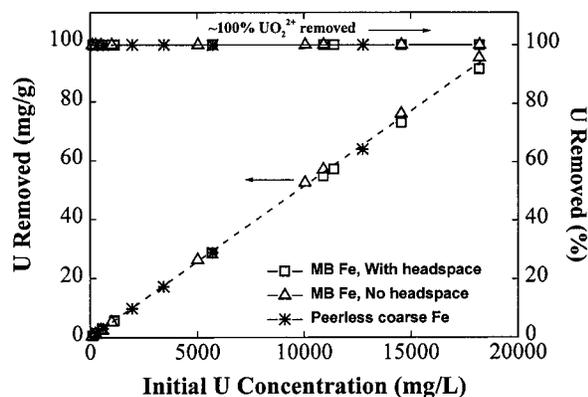


**FIGURE 3.** Effect of initial U concentration on U removal efficiency by medium-sized Master-Builder (with headspace or without headspace) and Peerless coarse iron filings (2 g in 10 mL of solution). The initial uranyl concentration ranged from 0 to 76 mM (18 000 mg of U/L).

by the Langmuir adsorption equation (*29, 36*):

$$q = \frac{Kq_{max}C}{KC + 1}$$

where $q$ is the amount of U adsorbed in mg/g, $K$ is the adsorption affinity of U on the adsorbent and related to the initial slope of the adsorption isotherm, $q_{max}$ is the maximum quantity or capacity of U adsorbed, and $C$ is the solution U concentration in mg/L. Results indicted that all of the adsorbent materials were quite effective in removing U at a relatively low solution concentration (<50 mg of U/L). The initial slopes ranged from about 40 to > 10 000 mL/g, with the Cercona Fe Bone-Char being the most effective at a low initial concentration. However, the Wards peat exhibited an adsorption capacity that was 2−3 times higher than that of Cercona Bone-Char and about 5−6 times higher than that of the ferric iron oxides on a weight basis. As the solution U concentration increased, a relatively large percentage of U was left in the solution phase because of the limited sorption capacity of the solid materials.

In contrast, reactions between $UO_2^{2+}$ and $Fe^0$ resulted in almost 100% removal of U in solution, as shown in Figure 3. Regardless of the initial U concentration in solution (up to 76 mM or 18 000 mg/L), no detectable amounts of U were found in solution after reaction with $Fe^0$. Note that the *x*-axis is expressed as the equilibrium concentration of $UO_2^{2+}$ in solution in Figure 2 whereas in Figure 3 it is expressed as the initial U concentration because U concentration in the equilibrium solution was under the detection limit of the analytical instruments. Analysis by a phosphorescence lifetime instrument revealed not only an extremely high sensitivity for U(VI) detection (on the order of parts per trillion) but also the valence state of U because U(IV) does not phosphoresce (*32, 33*). To determine if the reduced U(IV) species were present in the equilibrium solution phase, some selected aqueous samples were exposed to the air, treated with hydrogen peroxide ($H_2O_2$) and $HNO_3$, and reanalyzed by the phosphorescence lifetime analyzer. Again, no detect-

able amount of U was found in the solution after the treatment. These results were therefore indicative of a reductive precipitation of U by $Fe^0$ rather than an adsorption process. Adsorption would have resulted in a partitioning of U in the solution phase, which would increase with an increase of U addition, as shown in Figure 2. No maximum loading capacity may be defined for U removal as long as sufficient amounts of $Fe^0$ are present in the system to maintain an electron flow and a favorable reducing environment. The adsorption process may dominate only when $Fe^0$ is consumed and the corrosion products of iron (iron oxyhydroxides) are formed in the system.

We further evaluated the percentage distribution of U in the $Fe^0$ and its corrosion products in suspension because, if U is largely adsorbed on the corrosion products of $Fe^0$, the adsorbed U could be desorbed from those suspended colloidal particles or co-transported with these particles in water. This would reduce the effectiveness of an in-situ iron reactive barrier for retaining contaminants. Results (Table 4) indicated that only a small percentage of U was associated with the suspended particles (or the corrosion products) after agitating for ~3 weeks in the batch experiments. The majority of added $UO_2^{2+}$ precipitated on the $Fe^0$. Additionally, a desorption experiment with 0.1 M $Na_2CO_3$ indicated that U associated with suspended particles (i.e., the corrosion products) was readily desorbed (>64%). However, only small amounts of U (<0.21%) in $Fe^0$ could be washed out with the carbonate solution (Table 4). It is known that $CO_3^{2-}$ complexes with $UO_2^{2+}$ to form negatively charged U species such as $UO_2(CO_3)_2^{2-}$. The adsorption of $UO_2(CO_3)_2^{2-}$ is expected to be negligible on negatively charged iron oxyhydroxide surfaces at the given pH condition (pH > 10) because the zero point of charge of common iron oxyhydroxides is in the range of 6−8.5 (*23, 37*). Therefore, these results suggest that $UO_2^{2+}$, which was in the initial solution, was converted to less soluble U(IV) species by the $Fe^0$. The large percentage of extracted U from suspended particulates implies that U was primarily adsorbed in its oxidation state of (VI) by the corrosion products, although these corrosion products only constituted a small percentage of the $Fe^0$ mass. These observations are consistent with that of Grambow et al. (*16*), who found that a large percentage of $UO_2^{2+}$ was adsorbed on the corrosion products of $Fe^0$ and that $UO_2^{2+}$ was only partially reduced to U(IV) species. It is important to note, however, that the suspended particles of iron corrosion products were obtained by rigorously shaking the $Fe^0$ filings in solution, after which the suspension was decanted immediately. Under static flow-through conditions, the effluent is generally clear, and no suspended particles could be observed by means of turbidity measurements (data not shown); this suggests that iron corrosion products may be attached to the $Fe^0$ filings or precipitated downgradient in the iron media.

**Identification of Reaction Byproducts.** The reductive precipitation and coating of U on $Fe^0$ surfaces was also studied by SEM, EDX, and fluorescence spectroscopic analyses. Figure 4 shows two SEM images: one is a grain of $Fe^0$ filing, and the other is a grain of $Fe^0$ after being immersed in a U solution (the U loading was about 50 mg of U/g of $Fe^0$). A uniform thin layer of U coating on the U-treated iron is apparent in
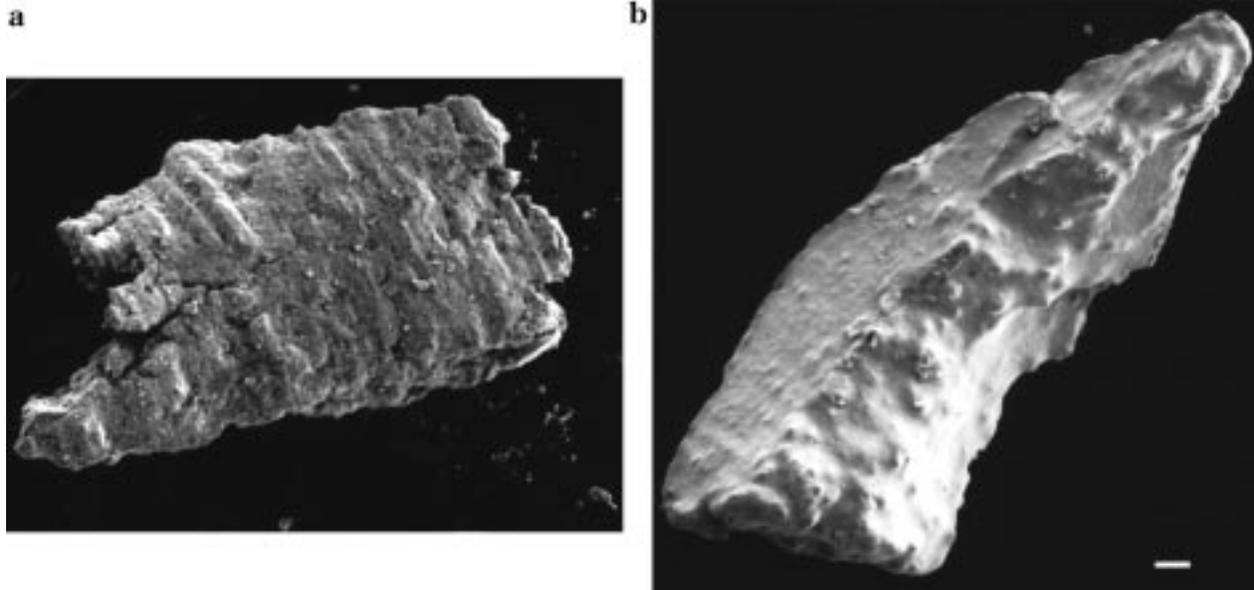
**FIGURE 4.** Scanning electron microscopy of the iron particles (Master-Builder) (a) without any treatment and (b) coated with ~5% U by reacting 10 mL of uranyl solution at concentration of 42 mM (10 000 mg of U/L) with 2 g of iron.
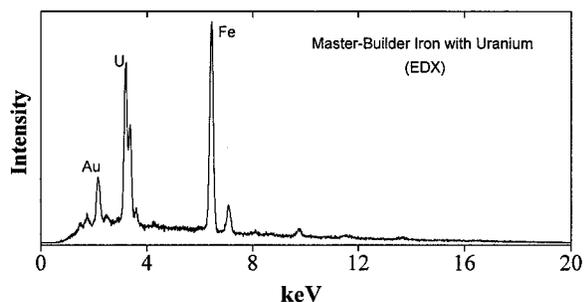


**FIGURE 5.** Energy-dispersive X-ray (EDX) analysis indicating the presence of precipitated U on zero-valent iron surfaces (as shown in Figure 4b). Both U and Fe showed strong signals. Au signal is an artifact from sample preparation.



**FIGURE 6.** Fluorescence spectra of uranyl in (a) initial solution, (b) after reactions with ferric iron oxide (hematite) in suspension, and (c) after reactions with zero-valent iron ($Fe^0$) filings. The initial U concentration was 12.6 mM (3000 mg/L). The adsorption of uranyl by hematite reduced the fluorescence intensity of U(VI), whereas the fluorescence signal was not observed after its reaction with $Fe^0$.

comparison with the untreated $Fe^0$ grain in the SEM images. The EDX spectrum of the U-treated grain showed both iron and uranium peaks (Figure 5). Note that the appearance of gold (Au) in the EDX spectra was due to specimen preparation by gold-sputtering for SEM and EDX analyses. Similar EDX spectra were obtained for U adsorbed on the iron corrosion products although the uranium peak was relatively weak because of a low adsorption of uranyl on the surfaces of the iron oxide particles (data not shown). XRD analysis identified these iron corrosion products as primarily partially oxidized magnetite (or maghemite). The mixed ferrous and ferric oxides are expected because only a limited amount of oxygen was present in the initial aqueous solution.

Reductive precipitation of $UO_2^{2+}$ to U(IV) by $Fe^0$ is thermodynamically favorable according to reactions 2 and 3 (*38*). The reduced U(IV) readily forms oxyhydroxide precipitates in solution (*39, 40*) or precipitates on $Fe^0$ surfaces, as shown in Figure 4. We further employed the fluorescence spectroscopic technique in an attempt to identify the valence state of U on $Fe^0$ surfaces and in solution. The analytical technique was also employed to evaluate the possible reoxidation processes of the reduced U(IV) on $Fe^0$ surfaces. It is known that only the oxidized U(VI) gives strong fluorescence whereas the reduced U(IV) does not (*32*). In Figure 6, the fluorescence spectra is plotted for (a) a $UO_2^{2+}$ aqueous solution, (b) a $UO_2^{2+}$ suspension containing iron oxide powder (hematite), (c) a $UO_2^{2+}$ solution in the presence

of $Fe^0$, and (d) a background aqueous solution without $UO_2^{2+}$. The $UO_2^{2+}$ aqueous solution itself showed strong intensity in fluorescence (*41*). In the presence of hematite, the $UO_2^{2+}$ spectra remained with a slightly reduced intensity because hematite particles could cause a quenching of fluorescence. In contrast, no fluorescence spectra were observed after $UO_2^{2+}$ reacted with $Fe^0$. These results are consistent with the batch kinetic and equilibrium studies, which suggest that $UO_2^{2+}$ is reduced to U(IV) by $Fe^0$. Because $UO_2^{2+}$ is only adsorbed onto iron oxide, but not reduced, a strong fluorescence spectra could be observed in the iron oxide systems as a result of the adsorbed uranyl species and the $UO_2^{2+}$ remaining in solution.

The evidence presented above further demonstrates that, in the presence of $Fe^0$, $UO_2^{2+}$ is primarily reduced to U(IV) and precipitated on the iron surface. However, it is unknown if the reduced U(IV) species on iron surfaces are reoxidized to U(VI) species over time or upon exposure to atmospheric oxygen. Figure 7 shows the fluorescence spectra of three
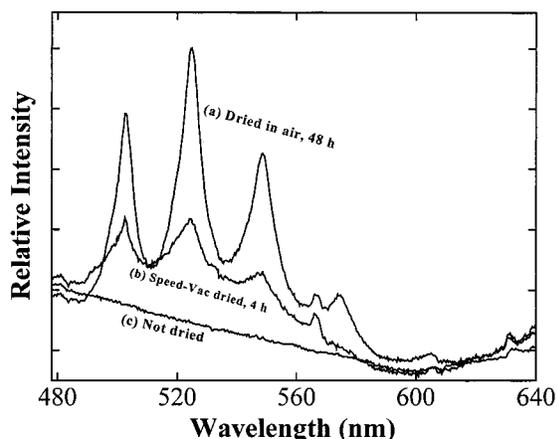
**FIGURE 7.** Fluorescence spectra of uranium on (a) air-dried rusty iron surfaces (exposed to oxygen for 48 h), (b) Speed-Vac-dried iron surfaces (exposed to oxygen for 4 h), and (c) zero-valent iron (Fe$^0$) filings not exposed to oxygen. No U(VI) signal was detected from Fe$^0$ that was not subjected to oxidation. However, U(VI) was detected, and the intensity was proportional to the exposure time when Fe$^0$ was exposed to atmospheric oxygen.

solid Fe$^0$ samples that were exposed to air for varying lengths of time after reacting with $UO_2^{2+}$ solutions. A strong fluorescence spectrum was observed after $UO_2^{2+}$ was reacted with a rusted Fe$^0$ and then dried in the air for 2 days. By comparison, a much weaker fluorescence spectrum was observed when reoxidation was allowed to occur in a short period (4 h drying by Speed-Vac) after the $UO_2^{2+}$ reacted with Fe$^0$. No fluorescence spectra could be identified for the freshly prepared U−Fe$^0$ specimen. These results indicate that the reduced U(IV) species on Fe$^0$ surfaces could be reoxidized. Furthermore, the reoxidation rate appeared to be relatively slow (on the order of hours or more) in comparison with its reduction process (on the order of minutes, Table 3).

**Implications for Groundwater Remediation.** Both batch experiments and spectroscopic studies showed that Fe$^0$ is effective in removing U from water under reducing conditions. The major reaction pathway is reduction of $UO_2^{2+}$ by Fe$^0$ to form insoluble U(IV) species on iron surfaces. Adsorption of $UO_2^{2+}$ by corrosion products accounts for a small percentage of total $UO_2^{2+}$ removal. The overall removal rates are fast, and the half-lives of the reactions are between 2 and 6 min based on a pseudo-first-order rate law.

This study implies that using iron in a permeable reactive barrier to remove U is feasible for groundwater remediation. However, the precipitated U(IV) on Fe$^0$ surfaces may be reoxidized when it is exposed to oxygen. The oxidized U(VI) species may potentially be desorbed or mobilized. The effect of dissolved oxygen in groundwater on the rate of reoxidation has not been determined in this study but would be an important subject of future study. As long as a reducing condition is maintained by Fe$^0$ in the permeable reactive barrier, it is likely that the reduced U(IV) will be retained in the Fe$^0$ media by either coprecipitation or cementation with iron oxyhydroxides. Both laboratory and field-scale experiments are under way to determine the removal efficiency in situ and to assess the geochemical influence to the iron barrier technology. Detailed discussion of these aspects is beyond the scope of this paper and will be published elsewhere. The long-term performance of Fe$^0$ reactive barriers is still open to debate with respect to their efficiency, byproducts formation, and clogging (*2, 12, 42*). Nevertheless, results of this work indicate that Fe$^0$ is an inexpensive yet very effective media that can be used to remove certain redox-sensitive radionuclides and metals in addition to its ability to degrade many chlorinated organic compounds.

## Literature Cited

(1) Gillham, R. W.; Blowes, D. W.; Ptacek, C. J.; O'Hannesin, S. F. In *In Situ Remediation: Scientific Basis for Current and Future Technologies*; Gee, G. W., Wing, N. R., Eds.; Battelle Press: Columbus, OH, 1994; Chapter 2, pp 913−929.

(2) Gillham, R. W.; O'Hannesin, S. F. Metal-catalysed abiotic degradation of halogenated organic compounds. Presented at the IAH Conference Modern trends in hydrogeology; Hamilton Ontario, Canada, 1992.

(3) Blowes, D. W.; Ptacek, C. J.; Jambor, J. L. *Environ. Sci. Technol.* **1997**, *31*, 3348−3357.

(4) Benner, S. G.; Blowes, D. W.; Ptacek, C. J. *Ground Water Monit. Rem.* **1997**, *17*, 99−107.

(5) Liang, L.; Korte, N.; Goodlaxson, J. D.; Clausen, J.; Fernando, Q.; Muftikian, R. *Ground Water Monit. Rem.* **1997**, *17*, 122−127.

(6) Matheson, L. J.; Tratnyek, P. G. *Environ. Sci. Technol.* **1994**, *28*, 2045−2053.

(7) Tratnyek, P. G. *Chem. Ind.* **1996**, *13*, 481−520.

(8) Korte, N. E.; Muftikian, R.; Grittini, C.; Fernando, Q.; Clausen, J. L.; Liang, L. *Abstr. Pap.—Am. Chem. Soc.* **1995**, *35*, 752.

(9) Sivavec, T. M.; Horney, D. P. *Abstr. Pap.—Am. Chem. Soc.* **1995**, *35*, 695.

(10) Gu, B.; Liang, L.; Cameron, P.; West, O. R.; Korte, N. *Proceedings of the 1997 International Containment Technology Conference and Exhibition*, St. Petersburg, FL, **1997**; pp 760−766.

(11) Vogan, J. RTDF Permeable Reactive Barriers Action Team Meeting, Virginia Beach, VA, September 18−19, **1997**.

(12) Liang, L.; Jacobs, G. K.; Gu, B. *Ground Water Monit. Rem.* Submitted for publication.

(13) Puls, R. RTDF Permeable Reactive Barriers Action Team Meeting, Virginia Beach, VA, September 18−19, **1997**.

(14) Powell, R. M.; Puls, R. W.; Hightower, S. K.; Sabatini, D. A. *Environ. Sci. Technol.* **1995**, *29*, 1913.

(15) Cantrell, K. J.; Kaplan, D. I.; Wietsma, T. W. *J. Hazard Mater.* **1995**, *42*, 201−212.

(16) Grambow, B.; Smailos, E.; Greckeis, H.; Muller, R.; Hentschel, H. *Radiochim. Acta* **1996**, *74*, 149−154.

(17) Wersin, P.; Hochella, M. F., Jr.; Persson, P.; Redden, G.; Leckie, J. O.; Harris, D. W. *Geochim. Cosmochim. Acta* **1994**, *58*, 2829−2843.

(18) Fiedor, J. N.; Bostick, W. D.; Jarabek, R. J.; Farrell, J. *Environ. Sci. Technol.* **1998**, *32*, 1466−1473.

(19) Korte, N. E.; Liang, L.; Gu, B.; Muck, M. T.; Zutman, J. L.; Schlosser, R. M.; Siegrist, R. L.; Houk, T. C.; Fernando, Q. *In Situ Treatment of Mixed Contaminants in Groundwater: Application of Zero-Valence Iron and Palladized Iron for Treatment of Groundwater Contaminated With Trichloroethylene and Technetium-99*; ORNL/TM-13530; Oak Ridge National Laboratory: Oak Ridge, TN, 1997.

(20) Sedlak, D. L.; Chan, P. G. *Geochim. Cosmochim. Acta* **1997**, *61*, 2185−2192.

(21) Pratt, A. R.; Blowes, D. W.; Ptacek, C. J. *Environ. Sci. Technol.* **1997**, *31*, 2492−2498.

(22) Langmuir, D. *Geochim. Cosmochim. Acta* **1978**, *42*, 547.

(23) Hsi, C. K. D.; Langmuir, D. *Geochim. Cosmochim. Acta* **1985**, *49*, 1931−1941.

(24) Ho, C. H.; Miller, N. H. *J. Colloid Interface Sci.* **1986**, *110*, 165.

(25) Payne, T. E.; Waite, T. D. *Radiochim. Acta* **1991**, *52/53*, 487−493.

(26) Morse, J. W.; Choppin, G. R. *Rev. Aquat. Sci.* **1991**, *4*, 1−22.

(27) SAIC Report. *SY/EN-5479*; Science Applications International Corporation: Oak Ridge, TN, 1996.

(28) Gu, B.; Dowlen, K. E.; Liang, L.; Clausen, J. L. *Sep. Technol.* **1996**, *6*, 123−132.

(29) Mallat, T.; Bodnar, Z.; Petro, J. *Tetrahedron* **1991**, *47*, 441−446.

(30) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. *Environ. Sci. Technol.* **1994**, *28*, 38−46.

(31) Gu, B.; Mehlhorn, T. L.; Liang, L.; McCarthy, J. F. *Geochim. Cosmochim. Acta* **1996**, *60*, 1943−1950.

(32) Dixon, J. B.; Weed, S. B. *Minerals in Soil Environment*, 2nd ed.; Soil Science Society of America: Madison, WI, 1989.

(33) Dai, S.; Metcalf, D. H.; Del Cul, G. D.; Toth, L. M. *Inorg. Chem.* **1996**, *35*, 7786−7790.

(34) Dai, S.; Del Cul, G. D.; Metcalf, D.; Toth, L. M. *Spectrosc. Lett.* **1994**, *27*, 687.

(35) Campbell, T. J.; Burris, D. R. *Abstr. Pap.—Am. Chem. Soc.* **1995**, *35*, 775.

(36) Roberts, A. L.; Totten, L. A.; Arnold W. A.; Burris, D. R.; Campbell, T. J. *Environ. Sci. Technol.* **1996**, *30*, 2654−2659.

(37) Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361−1403.

(38) Sposito, G. *The surface chemistry of soils*; Oxford University Press: New York, 1984.

(39) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1976.

(40) Dai, S.; Toth, L. M.; Del Cul, G. D.; Metcalf, D. H. *J. Phys. Chem.* **1996**, *100*, 220.

(41) Rabinowitch, E.; Belford, R. L. *Spectroscopy and Photochemistry of Uranyl Compounds*; MacMillan: New York, 1964.

(42) Puls, R. RTDF Permeable Reactive Barriers Action Team Meeting, Beaverton, OR, April 15−16, 1998.