Understanding the Mechanism of Uranium Removal from Groundwater by Zero-Valent Iron Using X-ray Photoelectron Spectroscopy

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The contaminant of most concern in groundwater at the Oak Ridge Y-12 Plant’s Bear Creek Valley Characterization Area is soluble uranium. The removal mechanism of soluble uranium from groundwater by zero-valent iron (ZVI, Fe⁰) was investigated. X-ray photoelectron spectroscopy (XPS, ESCA) was used to determine the uranium oxidation state at the Fe⁰ or iron oxide surface. Product speciation and relative reaction kinetics for the removal of soluble uranium under aerobic and anaerobic conditions with ZVI are presented. Under aerobic conditions, U⁶⁺ is rapidly and strongly sorbed to hydrous ferric oxide particulates (“rust”), whereas U⁴⁺ is slowly and incompletely reduced to U⁴⁺ under anaerobic conditions.

Introduction

A concerted effort is under way to remediate groundwater contaminated with radionuclides (e.g., ⁹⁹Tc,U), other regulated metals (e.g., Hg²⁺, Cr⁶⁺), and volatile organic compounds (VOCs) at the Oak Ridge Y-12 Plant’s Bear Creek Valley Characterization Area. Zero-valent iron (ZVI, Fe⁰) has been identified as a leading potential technology for use in this remediation effort. Previous works have demonstrated that ZVI can effectively remove Cr⁶⁺, Hg²⁺, Ag¹⁺, Tc⁷⁺, and U⁵⁺ from solution (1).

Soluble uranium (UO₂²⁻) is the contaminant of most concern in the Bear Creek Valley watershed. Soluble uranium is associated with both toxicity and cancer risks for the potential human receptors in the surrounding areas. Studies have shown that iron based minerals, such as pyrite or magnetite, can effectively adsorb U from groundwater under favorable conditions (i.e., E₀, pH, dissolved O₂, etc.). Recently, Cantrell et al. (2) were able to show that ZVI particles can be used to rapidly remove UO₂²⁻ (i.e., U⁵⁺) from a surrogate groundwater stream. They proposed that UO₂²⁻ may be removed from solution by any of three mechanisms: (a) reduction of U⁵⁺ by ZVI to form the less soluble U⁴⁺ (i.e., UO₂-xH₂O) phase, (b) sorption onto iron oxide corrosion products by ion exchange with hydroxyl sites, or (c) a combination of reduction/precipitation. However, the mechanism by which ZVI facilitates the removal of U⁵⁺ from solution is still not well understood.

The goal of this study is to gain a better understanding of the mechanistic aspects (e.g., chemisorption, redox and/or coprecipitation) of U⁵⁺ removal by ZVI from a synthetic surrogate of Bear Creek Valley groundwater. Sorption, as a removal mechanism, is not preferred because soluble uranium will remain in its more soluble oxidation state (i.e., U⁶⁺), thereby lending itself to be easily transported by the colloidal iron corrosion products. Due to the reversible nature of the sorption mechanism, another concern is the potential release of soluble uranium back into the groundwater. Reduction of U⁶⁺ to U⁴⁺ is the preferred removal mechanism since the resulting U⁴⁺ species is less soluble and thus less mobile in groundwater, assuming that the U⁴⁺ species is not colloidal. Therefore, the solubility of uranium in groundwater plays an important role when considering effective strategies for its remediation.

Thermodynamically reduction to U⁴⁺ is slightly favorable in strongly acidic media as indicated by the modest positive value for the standard cell potential, E° in eq 1:

\[ \text{Fe}^0 + 1.5 \text{UO}_2^{2-} + 6 \text{H}^+ = \text{Fe}^{3+} + 1.5 \text{U}^{4+} + 3 \text{H}_2\text{O} \]

\[ E° = +0.17 \text{V} \]  

However, reports by Wersin et al. (3) indicate that reduction to the less soluble U⁴⁺ (e.g., UO₂-xH₂O) is controlled kinetically and not thermodynamically. Similarly, reduction of U⁶⁺ by the ferrous ion (Fe²⁺) has been reported to be kinetically slow except in the presence of strong acid (4).

It has been speculated that contaminants are removed by ZVI via a heterogeneous surface reaction (e.g., reduction, adsorption, and/or coprecipitation) that is able to render the contaminants insoluble and thus immobilize them onto the ZVI or iron oxide surface. It has also been long understood that the oxidation state of uranium is one of the determining factors that governs its solubility, speciation, and sorptive behavior (3). Therefore, any knowledge gained concerning the chemical speciation of uranium in solution and at the iron surface will provide valuable insight to the sorption/reduction processes.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique (i.e., analysis depth ≈ 100 Å) whose strength lies in its ability to determine the various chemical states of a given surface species. Previous studies have shown that XPS can be a valuable spectroscopic tool when studying the metal sorption processes, such as redox reactions, on oxide, clay, and sulfide systems (5, 6). Recently, Muflikhan et al. (7) used XPS to examine the bimetallic surface of a palladium—iron system in an attempt to understand the dechlorination of VOCs. Other analytical methods, such as wet chemistry, used to determine the quantitative speciation of uranium often underestimate the contribution from U⁴⁺ due to reoxidation (8). In this way, XPS offers a significant contribution in determining uranium speciation, and thus this technique will be used in this study to monitor the uranium oxidation state at the iron surface.

The experimental design used in this study will enable one to monitor the uranium speciation as well as the relative kinetics for the removal of soluble uranium (U⁶⁺) in a synthetic surrogate of Bear Creek Valley groundwater by ZVI under the two limiting conditions of aerobic (oxic) and anaerobic (anoxic) experienced in remediation schemes using ZVI. The uranium speciation in solution will be kept relatively constant...
by carrying out the experiments at constant pH (i.e., ~6.0) (9–11). These experiments will provide boundary conditions in that the aerobic experiment will thermodynamically favor the sorption mechanism of uranium to the Fe\textsuperscript{iii} corrosion products, while the anaerobic experiment will favor the reduction of U\textsuperscript{vi} to U\textsuperscript{iv}. Redox potential (E\textsubscript{h}) pH measurements, dissolved O\textsubscript{2} readings, and γ-counting of the solution will be taken to assist in determining the most thermodynamically stable uranium species and the most kinetically favored mechanism under the varying O\textsubscript{2} solution conditions.

### Experimental Section

**Composition of Surrogate.** The groundwater investigated in this study is representative of that found near groundwater sampling well 087 (GW-087), which is located near the so-called boneyard/burnyard (BBYB) region of the Bear Creek Valley Characterization Area. The BBYB water contains the composition of BYBY groundwater (see Table 1).

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<table>
<thead>
<tr>
<th>compound</th>
<th>concentration (as formulated) (mg/L)</th>
<th>value reported in authentic BBYB (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgSO\textsubscript{4}·7H\textsubscript{2}O</td>
<td>Mg = 6.02; SO\textsubscript{4} = 23.8</td>
<td>Mg = 5.0 = 21.5 (5.5)</td>
</tr>
<tr>
<td>CaCl\textsubscript{2}·2H\textsubscript{2}O</td>
<td>Ca = 20; SO\textsubscript{4} = 8–21 (23.5)</td>
<td>Ca = 38–76 (51.7)</td>
</tr>
<tr>
<td>Ca(OH)\textsubscript{2}</td>
<td>Ca = 19.6</td>
<td>Ca = 20–33 (12.6)</td>
</tr>
<tr>
<td>NaHCO\textsubscript{3}</td>
<td>Na = 12.3</td>
<td>Na = 13–18 (2)</td>
</tr>
<tr>
<td>K\textsubscript{2}CO\textsubscript{3}·1.5H\textsubscript{2}O</td>
<td>K = 7.2</td>
<td>K = 3.9–6.1 (5.4)</td>
</tr>
<tr>
<td>NO\textsubscript{3}</td>
<td>NO\textsubscript{3} = 0.06 (1)</td>
<td>NO\textsubscript{3} = 12 (4)</td>
</tr>
<tr>
<td>total alkalinity (as CaCO\textsubscript{3}, mg/L)</td>
<td>132</td>
<td>81–238 (160)</td>
</tr>
<tr>
<td>pH\textsuperscript{b}</td>
<td>[6–0.5]</td>
<td>(6.8)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Range of values, as summarized in Bostick et al. (12). These samples were not filtered prior to analysis, and thus, etc., add to the values reported for Al, Si, and Fe. (Total suspended solids for this data set was 23–326 mg/L). Values in brackets (i) are the median of values from two batches of filtered samples as reported in Table 2 of Bostick et al.

\textsuperscript{b} Simulant was prepared by adding the stated chemicals to deionized water; calcium ion was solubilized; and the final pH was adjusted by bubbling a gas mixture (80% N\textsubscript{2}/20% CO\textsubscript{2}) into slurry overnight. After the solution is stored for several days, excess CO\textsubscript{2} is lost, gradually raising the solution pH value to 7.2 (authentic BBYB samples behave similarly).
three-neck flask that was fitted with calibrated electrodes to monitor the solution’s \( E_0 \), pH, and dissolved \( O_2 \) values. The ZVI coupon was suspended in solution by tying a piece of Kevlar string through a small hole that was drilled into the coupon. The experimental setup for both aerobic and anaerobic solutions is illustrated in Figure 1.

**Aerobic.** Aerobic solution conditions were maintained by purging the surrogate solution with \( O_2 \). To sustain \( \sim 100\% \) relative humidity, the purged gas streams were passed through a bubbler containing \( H_2O \) before entering into the surrogate. A constant pH (i.e., \( \sim 6.0 \)) in the solution was obtained by concurrently purging with an \( 80\% N_2/20\% CO_2 \) gas mixture. The \( CO_2 \) in the gas stream forms \( H_2CO_3 \) (i.e., bicarbonate) in solution that behaves like a buffer. With \( CO_2 \) bubbling in the solution, it is a concern that siderite (i.e., \( FeCO_3 \)) can precipitate onto the surface of the iron coupon. In a laboratory test using a similar experimental design, it was estimated that the maximum iron substrate loss over \( 40 \) h due to aerobic corrosion would correspond to \( \sim 3.6 \times 10^{-4} \) M. It should be noted and emphasized that under anaerobic conditions the corrosion and substrate loss will occur at a much slower rate. Therefore, assuming that \( FeCO_3 \) begins to precipitate when the \( Fe^{2+} \) concentration reaches \( 3 \times 10^{-4} \) M, very little siderite formation is expected under our experimental conditions (18). Thus, in contrast to long-term operation of relatively high solid surface/liquid volume, our geometry and experimental conditions for the relatively short-term coupon test (low solid surface/liquid volume) are not favorable to saturation and precipitation of siderite.

After \( 9.5 \) h in the aerobic U-traced solution, the iron coupon was removed. It was immediately rinsed with deionized water purged of \( CO_2 \) to remove any unbound corrosion products and placed on a planchet for subsequent XPS analysis. The remaining solution was filtered using a \( 0.45-\mu m \) pore size filter from Millipore. The filtrate was sampled and analyzed for activity. The corrosion products remaining on the filter were scraped off and subsequently analyzed using XPS.

**Anaerobic.** Anaerobic conditions were maintained within a radiological glovebox using a continuous gas purge stream consisting of \( 80\% N_2/20\% CO_2 \). It was found that the pH of the solution rose over time if \( N_2 \) was used alone. The purge gas was first bubbled into a sealed scrubber tower containing water, to maintain \( \sim 100\% \) relative humidity, and then passed into a radiological glovebox. The moistened purge gas was then fed into a three-neck flask containing a test solution (see Figure 1). In a preliminary test lasting \( \sim 24 \) h using these experimental conditions, it was demonstrated that the gas purge maintained the test solution in the flask at a pH value near 5.7.

The glovebox was purged with the \( N_2 \). This was done to ensure that the iron coupon would be exposed to a similar atmosphere when taken out of solution. The contents of the flask, with coupon, were purged with the \( N_2/CO_2 \) mixture for \( \sim 100 \) h. At this time, the iron coupon was removed, rinsed with deionized water purged of \( CO_2 \) to remove loosely bound soluble uranium, and placed into a sealable airtight sample holder to transport to the X-ray photoelectron spectrometer. In this manner, the reacted iron coupon would never be exposed to air.

### Results and Discussion

**Theoretical Thermodynamic Considerations.** Assuming that the uranium species has reached equilibrium with the dominant Fe redox couple, the equilibrium speciation of soluble and adsorbed uranium can be predicted from the solution \( E_0 \) and pH values for each experiment listed in Table 2. The solution conditions in the aerobic experiment favor \( UO_2^{2+}/H_2O \) as the most thermodynamically stable solid species and the uranyl ion (\( UO_2^{2+} \)) as the most stable aqueous species, as indicated by the Pourbaix diagram (\( E_0 \) vs pH) for the uranium–water system considering \( UH_3, U, UO, UO_2, U_3O_8, \) and \( UO_2^{2+}/H_2O \) (14). The Pourbaix diagram also indicates that \( U^{4+} \) should be reduced to \( U^{3+} \) at the potential of the Fe(II)/Fe(III) redox couple, \( E^{\circ} = -0.44 \) mV (14). Although the solution conditions predict \( U^{4+} \) as the stable uranium oxidation state, conditions at the zero-valent iron surface theoretically predict that reduction to \( U^{4+} \) is possible.

MINEQA2 solution modeling of the aerobic coupon experiment also predicts that the dissolved uranium will be in the \( U^{4+} \) state in the form of complex ions with dissolved carbonate ion. The modeling indicates that the most predominant uranium containing species, \( UO_2CO_3^{2-} \), accounts for 67% of the total soluble uranium, while 32% of the uranium exists in decarbonate complexes as \( UO_2(CO_3)\)\(^{2-} \).

The final solution \( E_0 \) and pH values in the anaerobic experiment listed in Table 2 correspond to \( U^{4+} \) as the thermodynamically favored oxidation state. MINEQA2 solution modeling also predicts \( U^{4+} \) as the predominant uranium species and indicates that at equilibrium more than 99% of the total uranium precipitates from solution as \( U_2O_5 \) (c). However, because only 55% of the total uranium was removed from solution by the termination of the experiment, the modeling indicates that the dissolved uranium is not in equilibrium with the \( E_0 \) of the bulk solution.

**Spectroscopic Characterization.** Standard Fe Coupon. The overall XPS spectrum for a freshly acid-washed iron coupon is illustrated in Figure 2A. The main elements on the coupon surface are iron, oxygen, and carbon. The overall XPS spectrum also indicates the presence of a small amount of chlorine, most likely a residue of the acid-washing procedure. An enlargement of the Fe 2p binding energy region from Figure 2A is shown in panel B. The Fe 2p spectrum indicates that iron oxide is the predominant surface species and that Fe\(^0\), as indicated by the arrow, is a minor component. The position of the Fe 2p\(_{3/2}\) peak at 710.8 eV is indicative of ferric iron, which may be present in any one

<table>
<thead>
<tr>
<th>experiment</th>
<th>elapsed time (h)</th>
<th>final uranium concn (C/C(_0))</th>
<th>final ( E_0/pH/D_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>aerobic</td>
<td>10</td>
<td>0.78</td>
<td>+510 mV/5.8/17 ppm</td>
</tr>
<tr>
<td>anaerobic</td>
<td>72</td>
<td>0.45</td>
<td>−35 mV/6.0/0 ppm</td>
</tr>
</tbody>
</table>

TABLE 2. Final Conditions of the Iron Coupon Experiments
of several possible species including hydrated ferric oxide (FeOOH), magnetite (Fe₃O₄), or hematite (Fe₂O₃). It is difficult for XPS to differentiate between these three Fe³⁺ containing species, but thermodynamic considerations would favor hydrated ferric oxide as the surface species (7). This analysis indicates that the iron surface reoxidizes rapidly, and thus any acid washing procedures must be performed under anaerobic conditions.

Aerobic: XPS - U Region. The U 4f spectra from the four samples obtained from the aerobic and anaerobic coupon experiments are plotted in Figure 3. The two lines indicate the U 4f 7/2 peak positions of a U⁶⁺ species and a U⁴⁺ species.

Figure 3A shows a curve fitted spectrum of Figure 3C. The curve fitted U 4f envelope uses the individual peak areas to semi-quantitatively estimate the contributions of U⁶⁺ and U⁴⁺. Curve fitting variables for the individual uranium species, such as peak position (i.e., U 4f⁷/₂ of U⁶⁺ = 381.4 eV and U 4f⁷/₂ of U⁴⁺ = 379.9 eV), were approximated from the standards. Curve fitting results indicate that ~75% of the uranium adsorbed on the coupon surface is in the U⁶⁺ oxidation state, while ~25% is in the U⁴⁺ state. These results are consistent with the thermodynamic predictions based on the EₚH/pH measurements, and they are very similar to those reported by Wersin et al. (3), who used similar techniques to demonstrate the partial reduction of U⁶⁺ by sulfide minerals under strongly reducing anaerobic conditions. Thus, even under extremely anaerobic conditions only partial reduction of U⁶⁺ is evident.

Next, the anaerobically reacted iron coupon was removed from the spectrometer and exposed to lab air (~32% relative humidity) for 2.7 h and then reexamined by XPS (Figure 3D). This was done to determine the rate of reoxidation and thus gain an understanding of the crystal nature of the UO₂ species. It has been observed that moist amorphous UO₂·2H₂O will oxidize in air rather quickly to form UO₂·3H₂O (21). However, crystalline UO₂ hydrate is stable in air for several days at...
room temperature (21). Partial reoxidation of U$^{4+}$ to U$^{6+}$ was observed after short exposure to low-humidity air (see Figure 5B). It is estimated that ~25% of the U$^{4+}$ reoxidized, resulting in an overall even distribution of U$^{4+}$ and U$^{6+}$. No further reoxidation occurred after ~16 h of additional exposure to air.

Aerobic: XPS - U Region. Figure 3B represents the U 4f envelope for the iron coupon that was reacted under aerobic conditions. The U 4f$_{7/2}$ peak position of 381.6 eV corresponds to the presence of a U$^{6+}$ surface species. Therefore, if appreciable oxygen is available, the predominant mechanism for the removal of soluble U$^{6+}$ by iron is by sorption of U$^{6+}$ to detached hydrolyzed Fe$^{3+}$ corrosion product or to the iron oxide on the surface of the metal.

Aerobic/Anaerobic: XPS - Fe Region. Figure 6 overlays the Fe 2p spectra for the standard "clean" iron coupon, the anaerobically reacted iron coupon, and the aerobically reacted iron coupon. The Fe 2p spectrum of the anaerobically reacted iron coupon (Figure 6B) consists of only one iron component. This component has an Fe 2p$_{3/2}$ binding energy of ~710.8 eV, which is indicative of an Fe$^{3+}$ species. This is an interesting finding since anaerobic corrosion (see eq 2) should produce an abundance of Fe$^{3+}$ species:

$$2\text{H}_2\text{O} + \text{Fe}^{0} = \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \quad (2)$$

However, the presence of a thin surface layer of magnetite, which is a spinel structure that consists of octahedral sites occupied with approximately equal numbers of Fe$^{3+}$ and Fe$^{2+}$ atoms and tetrahedral sites occupied solely by Fe$^{3+}$ atoms, cannot be ruled out (22). In fact, White et al. (22) showed that magnetite had an XPS Fe 2p$_{3/2}$ peak position of 710.7 eV, which is indicative of an Fe$^{3+}$ surface species and in agreement with our findings. Grambow et al. (8) gave further support by correlating the reduction of U$^{6+}$ under anaerobic conditions to the presence of magnetite and attributed this to surface-mediated electron transfer at sorptive sites.

It can be postulated that the formation of a highly hydroxylated iron oxide film may facilitate the reduction of uranium. This hydroxylated layer may act as region where U$^{6+}$ can actively adsorb to form U-O-Fe bonds. Upon adsorption in this manner, the uranium is immobilized long enough so that electrons may be donated to the U$^{6+}$ surface species by the electron-rich iron oxide layer and/or the bulk Fe$^{0}$. A similar mechanism has been proposed for the palladium-iron system (7).

Unlike the anaerobic experiment, the aerobic experiment produced copious amounts of Fe$^{3+}$ corrosion products that sloughed off into solution. It appears that under aerobic conditions iron corrosion products are formed, loosely bound to the ZVI matrix and easily removed by a simple rinsing and/or agitation. To analyze the corrosion products for the sorption of uranium, the surrogate solution was filtered with a 0.45-μm silver filter from Millipore. Figure 6C represents the XPS Fe 2p region of the Fe corrosion products. The Fe 2p$_{3/2}$ binding energy position of ~710.8 eV is suggestive of
an Fe$^{3+}$ surface species. Figure 3A shows the U 4f XPS spectrum for the Fe$^{3+}$ corrosion products. The U 4f$^{7/2}$ peak position of 381.6 eV indicates the presence of a U$^{6+}$ surface species. Thus, sorption of U$^{6+}$ to the highly hydrated Fe$^{3+}$ most likely occurs via a proton exchange with the hydroxyl sites. Again, this finding is consistent with the thermodynamic predictions.

Figure 6B shows the Fe 2p XPS region of the iron coupon that was reacted aerobically. It is interesting to note that this Fe 2p spectrum is very similar in peak shape to that of the standard clean iron coupon (Figure 6A). In fact, both spectra show the presence of a surface Fe metal component and a thin layer of iron(III) oxide. A possible explanation of this phenomenon is that the formation and eventual removal of the iron(III) oxide layer due to aerobic corrosion enables the surface of the aerobic Fe coupon to be continuously replenished so that a clean surface is formed.

Kinetics. Figure 7 illustrates the relative kinetics for removal of soluble uranium under the limits of aerobic and anaerobic conditions: (●) iron coupon exposed to aerobic conditions, (○) iron coupon exposed to anaerobic conditions, (▲) iron oxide coated iron coupon exposed to anaerobic conditions.

Presuming the reduction of U$^{6+}$ is a surface-mediated effect, the lag period seen in the anaerobic experiment could be caused by the formation of sorptive sites. These sites could correlate with the growth of a thin highly porous layer of iron oxide due to anaerobic corrosion. To investigate this postulation, a ZVI coupon was exposed to an CO$_2$ atmosphere at 800 °C in attempt to prepare a thin layer of magnetite (Fe$_3$O$_4$) coating. Magnetite is geologically stable, has sorptive capabilities, and is conductive. These properties make it an ideal surface coating. However, X-ray diffraction (XRD) analysis indicated that both magnetite and hematite (Fe$_2$O$_3$) were present on the surface of the coupon in roughly equal proportions. The surface-coated coupon was exposed to the solution under anaerobic conditions in attempt to compare the kinetics with that of the ZVI coupons reacted under anaerobic and aerobic conditions. It is readily apparent from Figure 7 that the oxide-coated coupon (▲) eliminates the lag phase, indicating that reduction is a surface-mediated effect. However, it does not accelerate the kinetics ($t_{1/2} = 72.9$ h) for reduction of U$^{6+}$ to U$^{4+}$. XPS results for the iron oxide-coated ZVI coupon reacted under anaerobic conditions were analogous to the uncoated ZVI coupon (see Figure 3C) reacted under similar conditions.

Discussions

Some of the more important reactions that may occur during treatment of metals (e.g., inorganics) with ZVI include the following processes:

anaerobic corrosion

\[
2\text{H}_2\text{O} + \text{Fe}^0 = \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^- \tag{3}
\]

aerobic corrosion

\[
\text{O}_2 + 2\text{Fe}^0 + 2\text{H}_2\text{O} = 2\text{Fe}^{2+} + 4\text{OH}^- \tag{4}
\]

\[
\text{Fe}^{2+} + 1/4\text{O}_2 + 5/2\text{H}_2\text{O} = \text{Fe(OH)}_3(s) + 2\text{H}^+ \tag{5}
\]
Most likely reaction mechanisms. The ZVI coupon is first oxidized in solution to form a ferrous iron (Fe(II)) layer. In turn, the ferrous iron (Fe(II)) is rapidly oxidized (eq 5) to form a high surface area and highly porous layer of hydrolyzed ferric (Fe(III)) oxide. Hydrolyzed ferric iron [Fe(OH)(3)(5)] and its polymer, ferrfhydate, are effective in removing U(VI) by sorption (depicted by eq 7) (23–27). In eq 7, the OH represents an exchangeable site on the hydrous metal oxide at the hydrous iron substrate or on its detached corrosion product. Note in the simplified eq 7 that, depending on the solution pH, the surface site may have a net positive charge (>OH-) or negative (-O-) charge. The exchange of protons to and from the oxide surface creates specific site types available for adsorption. For most iron-containing minerals, the solution pH value that results in no net charge on the mineral (i.e., the point of zero charge or pzc) is typically in the range of 6–8 (28). As the solution pH falls below the pzc of the substrate, the net surface charge becomes more positive, favoring the sorption of anionic species; conversely, as the pH is increased above the pzc, the substrate becomes more negatively charge, favoring the sorption of cationic species. For our experiment, the iron surface contained roughly equal amounts of negative and positive charges because the pH (6.0) is close to the pzc of the iron substrate. Since both charges exist on the iron surface at this pH, sorption of U(VI) by the iron surface can take place with the negatively charged UO2(CO3)2–2 species as suggested by Payne and Waite (9) and further supported by the MINTEQA2 modeling performed in this experiment or the positively charged (UO3)(OH)+ species as predicted by Meinrath et al. (11).

For the anaerobic investigation, the “cementation” reaction seen in eq 5 (M = uranium or UO22+) most readily describes the mechanistic pathway by which soluble U(VI) is removed from solution. Our work has shown that, under strongly reducing anaerobic conditions and given enough time, ZVI can partially reduce U(VI) to U(IV). Our results are consistent with the literature for reduction of U(VI) by Fe(II) or H2 in that reduction of U(VI) appears to be kinetically slow. Therefore, the relative significance of soluble uranium removal by reduction using ZVI under treatment trench conditions is uncertain.

Perhaps, with a deep enough treatment zone to provide the necessary anaerobic conditions and the required contact time, this mechanism could represent a significant component to the overall removal of soluble uranium, if any remains after the semi-oxic contact zone, which offers a relatively rapid removal of U(VI) by sorption to corrosion product. Thus, if the residence time in a treatment trench is relatively short (e.g., less than a few hours) and anaerobic conditions are not achieved fairly rapidly, then kinetically slow reduction of U(VI) is not likely to be a significant component of the overall removal.

In the middle of a treatment trench, where anaerobic conditions begin to prevail, the pH values will be considerably higher than pH 6 due to the production of hydroxyl ions from the relatively slow anaerobic corrosion of the iron substrate (eq 3). This is detrimental to the reduction mechanism because higher pH values (>8) tend to disfavor reduction of U(VI) and favor sorption. Therefore, under practical groundwater remediation conditions, sorption appears to have a more significant role than reduction in the removal U(VI) using ZVI. Most of the soluble uranium removal occurs under semi-oxic conditions near the forward portion of the column or trench, where U(VI) can bind avidly to corrosion product containing Fe3+. Thus, there will be little additional uranium removal downstream by reduction due to (a) unfavorable kinetics in the near-neutral to alkaline solution and (b) a low concentration of residual soluble U(VI) available to be reduced.

In conclusion, iron coupons tested under controlled conditions indicate that under fully aerobic conditions sorption of U(VI) to hydrated Fe(III) corrosion products is the predominant removal mechanism. The strong affinity for uranium by iron-containing minerals is well-documented (23–27). However, a potential concern with this removal mechanism is the possible redistribution and/or desorption of U(VI) on detached fine particulate corrosion products. Although, treatment by ZVI of subsurface water, with low levels of dissolved oxygen, should minimize this effect.

When reaction conditions (pH and U speciation) are similar but with the exclusion of dissolved oxygen, soluble uranium is slowly removed at the iron surface by partial reduction of U(VI) to sparingly soluble U(IV) species. Uranium speciation was verified using XPS. These results are similar to those reported by Grambow et al., who suggest that U(VI) in anaerobic brine solution is sorbed to magnetite (Fe3O4) and then slowly and incompletely reduced at the iron surface (8). Analogously, Wersin et al. reported on the kinetically slow partial reduction of U(VI) to U(IV) at the surface of sulfide minerals under strongly reducing anoxic conditions (3). Therefore, reduction of uranium may be beneficial in terms of limiting its solubility and mobility, but the relatively slow reaction kinetics may mandate a long residence time in the reductive medium.

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Literature Cited
(1) For a complete list of references on this subject, please see WEB page maintained by Dr. Paul Tratnyek, www.ece.uconn.edu/tratnyek/ironrefs.html, Department of Environmental Science and Engineering, Oregon Graduate Institute of Science & Technology.

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