Reactive transport of uranium(VI) and phosphate in a goethite-coated sand column: An experimental study

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Abstract

The migration of uranium(VI) in subsurface environments is strongly influenced by its adsorption/desorption reactions at the solid/solution interface. Phosphate is often present in subsurface systems and was shown to significantly affect U(VI) adsorption in previous batch experiments. In this study, column experiments were conducted to investigate the effects of phosphate on U(VI) adsorption and transport under flow conditions. The adsorption of U(VI) and phosphate was very low on pure quartz sand with negligible effects on U(VI) and phosphate transport. However, U(VI) and phosphate transport was retarded in a column packed with goethite-coated sand. The presence of phosphate, either as a co-solute with U(VI) or pre-adsorbed, greatly increased U(VI) adsorption and retardation. U(VI) and phosphate adsorption in our column experiments were rate-limited, and the adsorption of U(VI) and phosphate was not reversible, with kinetic limitations more pronounced for desorption than for adsorption. This study demonstrated the importance of phosphate in controlling U(VI) mobility in subsurface environments and helped illustrate some phenomena potentially applicable to U(VI) adsorption and transport in natural systems, especially where U(VI) adsorption is rate-limited.

Keywords: Adsorption/desorption on goethite; Uranium(VI); Phosphate; Solute transport; Kinetics; Batch and column experiments

1. Introduction

Reactive transport of solutes in porous media is affected by advection, dispersion, and adsorption. The migration of uranium(VI) as well as other radionuclides and transition metals in subsurface environments is strongly influenced by their adsorption/desorption reactions at the solid/solution interface. Batch adsorption experiments have been widely used to investigate the adsorption of U(VI) to subsurface media (e.g., Waite et al., 1994; Payne et al., 1996; Villalobos et al., 2001; Barnett et al., 2002; Logue et al., 2004) and to derive adsorption isotherms (or $K_D$), which may then be used to model U(VI) transport in porous media. However, prominent differences between the conditions in batch experiments and those encountered during solute transport through porous media exist because: (1) relatively low solid-to-solution ratio (SSR) is used in most batch experiments, and (2) batch experiments are often conducted over a long enough time frame to reach adsorption equilibrium. The influence of reaction kinetics on adsorption is often neglected. However, during solute transport through porous media, adsorption is often rate-limited and controlled by both thermodynamics and kinetics of adsorption reaction. Therefore, batch experiments may have only limited applicability to solute transport in porous media (Cheng et al., 2006).

Phosphate is often present in subsurface systems and is important in governing the mobility of U(VI) (Sandino and Bruno, 1992; Payne et al., 1996; Bostick et al., 2002). At low pH, a U(VI)–phosphate ternary surface complex formed on iron oxides can be the dominant adsorbed U(VI) species and the formation of this complex can greatly increase U(VI) adsorption (Payne et al., 1996;
Cheng et al., 2004). In our previous study of U(VI) adsorption on goethite-coated sand (Cheng et al., 2006), we found that at an SSR of 33.3 g l\(^{-1}\) and pH 4.2, U(VI) adsorption increased in the order: no phosphate < phosphate pre-adsorbed < simultaneous addition of phosphate and U(VI) at a total (dissolved + adsorbed) phosphate concentration of 10\(^{-4}\) M. Therefore, it is expected that at low pH the presence of phosphate would reduce U(VI) mobility in porous media (dominated by iron oxide-coated materials) due to the increased U(VI) adsorption caused by the formation of the U(VI)-phosphate ternary surface complex. However, to our knowledge, there have been no reported studies on the effects of phosphate on U(VI) transport under flow conditions. Due to strong interactions between U(VI) and phosphate, and large difference in the SSR in batch and column experiments, it is not clear if the increased U(VI) adsorption in the presence of phosphate observed in batch systems will also occur in column and field conditions (Cheng et al., 2006). Moreover, in subsurface environments, the interaction between phosphate and the porous media may be in equilibrium before any radionuclides or heavy metals are introduced (i.e., they are not necessarily co-solutes). Hence, the adsorption and transport characteristics of U(VI) or heavy metals in media with pre-adsorbed phosphate may better mimic actual natural processes (Bostick et al., 2002; Wang and Xing, 2004).

In this investigation, we studied the reactive transport of U(VI) and phosphate in a goethite-coated sand column, with particular emphasis on the effects of phosphate on U(VI) transport. Our goal was to determine if the effects of phosphate on U(VI) adsorption observed in batch systems (Payne et al., 1996; Cheng et al., 2004, 2006) are also applicable to flow conditions and to provide an improved understanding of U(VI) transport in subsurface media in the presence of phosphate, either pre-adsorbed, or as a co-solute with U(VI).

2. Materials and methods

2.1. Materials

All chemicals used were certified ACS grade and were obtained from Fisher Scientific (Pittsburgh, PA). The acids were trace metal grade and the uranium standards and stock solutions were prepared from plasma grade uranium standard (depleted uranium). Synthetic goethite-coated sand was used as the adsorbent in the column experiments. Crystalline iron oxide minerals such as goethite (α-FeOOH) are a common coating material for subsurface particles that have been shown to adsorb U(VI) and phosphate in the subsurface. Similar coatings on natural sands have been shown to control adsorption of U(VI) (Barnett et al., 2002; Logue et al., 2004) and metals (Coston et al., 1995) to natural subsurface materials. The use of synthetic iron oxide-coated sand allowed us to more closely approximate real subsurface materials and flow conditions while still maintaining a chemically well-controlled system (e.g., no pre-adsorbed phosphate). The preparation of goethite-coated sand was described previously (Cheng et al., 2004). The DCB (dithionite-citrate-bicarbonate) extractable Fe (Jackson et al., 1986) of the goethite-coated sand was 94.3 ± 2.6 μmol of Fe g\(^{-1}\) of sand and the specific surface area of the goethite-coated sand, as measured by BET (Brunauer, Emmett, and Teller) surface analysis (Brunauer et al., 1938) was 1.25 m\(^2\) g\(^{-1}\).

2.2. Column experiments

Column experiments were conducted at room temperature (~295 K) using a glass chromatography column with 1.0 cm inner diameter and a constant ionic strength of 0.1 M. A total mass of 2.00 g of dry material (goethite-coated sand or pure quartz sand) was dry-packed to a uniform bulk density of 1.6 g cm\(^{-3}\), with a porosity of 0.45 and a length of 1.6 cm. The length of the column could be adjusted by the Teflon end-plate assemblies at both ends of the column. Glass wool was used between the goethite-coated sand and Teflon end-plate assemblies to hold the porous media in place. The bulk density and porosity of the packed column was close to those packed with subsurface materials from U(VI)-contaminated US Department of Energy (DOE) sites (Barnett et al., 2000).

The columns were slowly flushed from the bottom using 0.1 M NaNO\(_3\) background solution until air spaces were no longer visible. Two reciprocating-piston high performance liquid chromatography pumps were connected into a four-way valve at the column entry. Short tubing with small inner diameter was used to connect the four-way valve to the column entry and at the column exit to minimize the dead volume. The two pumps provided a steady flow of either the background solution (U(VI)-free and phosphate-free 0.1 M NaNO\(_3\) solution at pH 4.2) or the reactant solution (U(VI), phosphate, or U(VI) + phosphate in a 0.1 M NaNO\(_3\) background matrix at pH 4.2) into the column. In each column experiment, the column was pre-conditioned using the 0.1 M NaNO\(_3\) background solution for at least 12 h, after which a pulse input of reactant solution was introduced into the column for the desired duration (~256 pore volumes), which was then followed by again flushing the column with uranium-free and phosphate-free 0.1 M NaNO\(_3\) background solution. The pore water velocity during the preconditioning, pulse input, and desorption parts of the experiment was 2.93 cm min\(^{-1}\), resulting in a fluid residence time in the column of 15 s.

Effluent samples were collected with an automatic fraction collector and analyzed for U(VI), phosphate, and pH until the U(VI) and phosphate concentrations were below ~1% of their concentration in the initial input pulse. The effluent pH of all the column experiments was fairly constant and close to that of the influent (change <0.2 units). After each column run, the column was disassembled and the sand in the column was completely removed and weighed. The sand was divided into two equal parts (by weight) and treated with 0.1 M HNO\(_3\) or 0.1 M NaOH.
solution to fully extract any adsorbed U(VI) or phosphate respectively. The extracted U(VI) and phosphate in the extracting solution was then analyzed. The mass balance of U(VI) and phosphate of the column experiments was checked by numerical integration of the experimental breakthrough curves (BTC). After each experiment, the column was soaked in 0.1 M HNO₃ overnight and then rinsed with distilled and deionized water to fully remove any U(VI) that may have adsorbed to the column.

In all the column experiments, the pH of the influent solution was fixed at 4.2 (±0.1 pH unit). We used pH 4.2 in our experiments for several seasons: (1) soils with pH ranging from 4.1 to 4.7 have been reported at U(VI)-contaminated DOE sites (Barnett et al., 2000; Bostick et al., 2002), (2) at pH 4.2, goethite is a more stable phase than ferric phosphate, (3) at this pH, the U(VI)–phosphate ternary surface complex formed on goethite surfaces could have important effects on U(VI) adsorption and transport, (4) the uptake of CO₂ (g) from the atmosphere is minimized at this pH. In our column experiments (Table 1, Experiments 1–4), the U(VI) concentrations in effluents were in the range of below detection limit (ca. 10⁻¹⁰ M) to ~10⁻⁶ M. These U(VI) concentrations fall within the ranges used by other workers to represent typical U(VI) concentrations in contaminated groundwater (Sandino and Bruno, 1992; Waite et al., 1994; Payne et al., 1996; Villalobos et al., 2001). The total phosphate concentration used was 10⁻⁴ M in experiments with phosphate. The fixed phosphate concentration simulates subsurface environments where the total phosphate (dissolved and adsorbed) concentration is constant. The environmental relevance of using a total phosphate concentration of 10⁻⁴ M was discussed previously (Cheng et al., 2004). Aqueous U(VI) concentration was analyzed by a kinetic phosphorescence analyzer and phosphate concentration by ion chromatography as previously described (Cheng et al., 2004). The BTC in the control column packed with uncoated quartz sand (Experiment 1) showed practically no retardation in phosphate transport (Fig. 1, (□)), which is consistent with our previous observation that the quartz sand was insignificant with respect to phosphate adsorption (and therefore transport) compared to the goethite-coating (Cheng et al., 2004). The BTC of phosphate of goethite-coated columns when U(VI) and phosphate were present as co-solutes in the pulse input and when only phosphate was present in the pulse input are also shown in Fig. 1 (⟨⟨⟩⟩ and ⟨Δ⟩). Phosphate transport was retarded in the goethite-coated sand column, and those two curves (⟨⟨⟩⟩ and ⟨Δ⟩ in Fig. 1) were practically identical, indicating the presence of a relatively small amount of U(VI) (~10⁻⁶ M) did

### Table 1

Experimental conditions for U(VI) and phosphate column experiments

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Total phosphate (M)</th>
<th>Total U(VI) (M)</th>
<th>pH</th>
<th>Phosphate state</th>
<th>Sand</th>
<th>Fig. 1 symbol</th>
<th>Fig. 2 symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10⁻⁴</td>
<td>7.98 x 10⁻⁴</td>
<td>4.2</td>
<td>Co-solute</td>
<td>Quartz</td>
<td>□</td>
<td>○</td>
</tr>
<tr>
<td>2</td>
<td>BDL b</td>
<td>7.98 x 10⁻⁴</td>
<td>4.2</td>
<td>No phosphate</td>
<td>Goethite-coated quartz</td>
<td>None</td>
<td>○</td>
</tr>
<tr>
<td>3</td>
<td>10⁻⁴</td>
<td>7.98 x 10⁻⁴</td>
<td>4.2</td>
<td>Co-solute</td>
<td>Goethite-coated quartz</td>
<td>●</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10⁻⁵</td>
<td>7.98 x 10⁻⁴</td>
<td>4.2</td>
<td>Pre-adsorbed</td>
<td>Goethite-coated quartz</td>
<td>△</td>
<td>×</td>
</tr>
</tbody>
</table>

a Ionic strength was 0.1 M for all column experiments.

b BTL means below detection limit, phosphate detection limit of our analysis is ca. 3 x 10⁻⁶ M.

3. Results and discussion

3.1. Phosphate breakthrough curves (BTC)

The BTC in the control column packed with uncoated quartz sand (Experiment 1) showed practically no retardation in phosphate transport (Fig. 1, (□)), which is consistent with our previous observation that the quartz sand was insignificant with respect to phosphate adsorption (and therefore transport) compared to the goethite-coating (Cheng et al., 2004). The BTC of phosphate of goethite-coated columns when U(VI) and phosphate were present as co-solutes in the pulse input and when only phosphate was present in the pulse input are also shown in Fig. 1 (⟨⟨⟩⟩ and ⟨Δ⟩). Phosphate transport was retarded in the goethite-coated sand column, and those two curves (⟨⟨⟩⟩ and ⟨Δ⟩ in Fig. 1) were practically identical, indicating the presence of a relatively small amount of U(VI) (~10⁻⁶ M) did

![Fig. 1](image-url)
not noticeably affect phosphate (10^{-4} M) adsorption (and therefore transport), which was expected. The overlap of these two BTCs also demonstrated the good reproducibility of our column experimental data. In either case, about 35% of the total phosphate in the influent was retained on the column material at the end of the experiment (Table 2), indicating irreversible (or slowly-desorbing) adsorption of phosphate under our experimental conditions.

Two relevant factors of our column experiments bear further discussion. First, analysis of break-through curves of non-reactive tracers from some of the columns (and numerous similar columns packed in an identical manner in our laboratory over the years) has shown that our packing method produces uniformly-packed columns free of preferential flow paths that could cause physical non-equilibrium (Barnett et al., 2000). Second, the pore water velocity during the preconditioning, pulse input, and desorption parts of the experiment was the same at 2.93 cm min^{-1}. For practical reasons, it is difficult to replicate actual groundwater flow velocities, which are normally very low, in laboratory column experiments. Initially, however, we attempted to use a ~20x slower flow velocity to better approximate field conditions (Kohler et al., 1996; Gabriel et al., 1998; Barnett et al., 2000). However, at this low velocity, the mass amount of U(VI) in the effluent plus the mass amount of U(VI) adsorbed to the goethite-coated sand was only ~70–80% of the mass amount of U(VI) in the influent, even after we used 0.1 M HNO_3 to completely extract U(VI) adsorbed to the goethite-coated sand. Our previous results also showed that U(VI) has a very strong tendency to adsorb to the inner surfaces of reaction vessels. Therefore, we suspect that the 20–30% loss of U(VI) was due to adsorption to the inner surfaces of our experimental flow system and not related to its interaction with the goethite-coated sand. In order to achieve ~100% U(VI) recovery, we utilized a much higher flow velocity of 2.93 cm min^{-1}. The use of a small column and high pore water velocity make the effect of mass transport processes (advection, longitudinal dispersion, etc.) on breakthrough curves insignificant and the retardation in breakthrough curves only sensitive to adsorption/desorption processes (Pignatello, 2000), the focus of our study.

In our column experiments, the duration of phosphate input, which was equal to the total time the goethite-coated sand being exposed to phosphate adsorption, was 1 h, while our previous batch kinetics experiments showed that it took 48–96 h for phosphate to approach adsorption equilibrium (Cheng et al., 2006). These facts suggest phosphate adsorption in our column experiments was probably rate-limited. The conclusion that phosphate adsorption in our column was rate-limited was further supported by the shape of the phosphate breakthrough curve for experiments with goethite-coated sand. These phosphate breakthrough curves were asymmetric (Fig. 1), indicative of rate-limited adsorption (Jardine, 1991).

### 3.2. Effects of phosphate on U(VI) adsorption and retardation in column experiments

The U(VI) breakthrough curves for all column experiments are shown in Fig. 2. Similar to the breakthrough curve of phosphate, in the experiment with uncoated quartz sand, practically no retardation in U(VI) transport was observed, consistent with previous observations that the quartz sand was insignificant with respect to U(VI) adsorption (Cheng et al., 2004) compared to the goethite coating. Thus, any U(VI) retardation that occurred in the goethite-coated sand column experiments can be attributed to the interaction between U(VI) and/or phosphate and the goethite coatings. The results of the control column also demonstrate that simple precipitation of U(VI) and phosphate solids did not occur under our column experimental conditions. The chart below shows the experimental breakthrough curves (BTC) of U(VI) in a control column (pure quartz sand, ○) and in goethite-coated sand columns (U(VI) only (●); phosphate pre-treated column (×); and U(VI) and phosphate as co-solutes in the input (●)). I = 0.1 M, T = ~295 K, pH 4.2.

### Table 2

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Total U(VI) recovered (%)</th>
<th>U(VI) recovered in effluent (%)</th>
<th>U(VI) recovered from sand (%)</th>
<th>Total phosphate recovered (%)</th>
<th>Phosphate recovered in effluent (%)</th>
<th>Phosphate recovered from sand (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>101.9</td>
<td>101.9</td>
<td>&lt;0.01</td>
<td>99.3</td>
<td>99.3</td>
<td>&lt;3b</td>
</tr>
<tr>
<td>2</td>
<td>101.1</td>
<td>101.1</td>
<td>&lt;0.01</td>
<td>N/A</td>
<td>N/Ac</td>
<td>N/Ac</td>
</tr>
<tr>
<td>3</td>
<td>94.2</td>
<td>72.9</td>
<td>21.3</td>
<td>100.4</td>
<td>67.3</td>
<td>33.1</td>
</tr>
<tr>
<td>4</td>
<td>98.9</td>
<td>87.9</td>
<td>11.0</td>
<td>103.8</td>
<td>66.2</td>
<td>37.6</td>
</tr>
</tbody>
</table>

a U(VI) was not detected. U(VI) detection limit of our analysis is ca. 10^{-10} M.
a Phosphate was not detected. Phosphate detection limit of our analysis is ca. 3 × 10^{-6} M.
c N/A means not applicable.
calculated saturation indices for U(VI) minerals in the column influent were also negative (Table 3).

There was a small but noticeable difference between the BTC for U(VI) in the goethite-coated sand column (without phosphate) (Experiment 2) and the control column (Experiment 1) (Fig. 2). Slight retardation, due to adsorption of U(VI) to the goethite-coating, occurred when U(VI) flowed through the goethite-coated sand packed column. In a goethite-coated sand column, complete breakthrough occurred at ~120 pore volumes and the maximal normalized U(VI) concentration in effluent was ~1.0 (Experiment 2). In both the control column and the goethite-coated sand column, U(VI) was completely recovered (101.9% and 101.1%) in the effluent (Table 2). The presence of phosphate, either prior to or concurrent with U(VI), caused a marked increase in U(VI) retardation (Experiments 3 and 4, (x) and (●) in Fig. 2), and resulted in the formation of some irreversible or slowly-desorbing U(VI)–phosphate surface complexes as evidenced by the U(VI) extracted from the goethite-coated sand at the end of the experiment (Table 2). When U(VI) and phosphate were present as co-solutes in the pulse input (Experiment 3), the U(VI) recovered in the column effluent was 72.9%, with 21.3% remaining in the column at the end of the experiment (indicative of irreversible adsorption or slow desorption) for a total U(VI) recovery of 94.2% (Table 2). Given the relatively small amounts of U(VI) involved (total U(VI) input was ~27 μg), close to complete recovery of U(VI) within experimental errors was obtained. In a column with pre-adsorbed phosphate (Experiment 4), the degree of U(VI) retardation was intermediate between that observed in the U(VI) only experiment (Experiment 2) and the U(VI) and phosphate as co-solute experiment (Experiment 3). The U(VI) recovered in the column effluent in Experiment 4 was 87.9%, and the amount extracted from the sand at the end of the experiment was 11.0%, for a total U(VI) recovery of 98.9% (Table 2). Irreversible (or slow as compared to adsorption) desorption of U(VI), has been reported in some recent studies, in both batch experiments (Dong et al., 2005) and in column transport experiments (Qafoku et al., 2005). These results suggest that assumptions of rapid reversible adsorption/desorption, which are sometimes used in modeling contaminant transport in porous media, might not be appropriate under certain conditions, particularly in the presence of reactive co-solutes. In addition, kinetic limitations might be more pronounced for desorption than for adsorption.

The relative degree of U(VI) retardation and irreversible adsorption (or slow desorption) exhibited in each column experiment were: no phosphate < phosphate pre-adsorbed < simultaneous presence of phosphate and U(VI). This order is consistent with the degree of adsorption observed in the batch-measured isotherms at an SSR of 33.3 g l\(^{-1}\) (Cheng et al., 2006). The presence of phosphate greatly increased U(VI) adsorption in both batch systems (with an SSR of 33.3 g l\(^{-1}\)) and column systems (with an SSR of ~3750 g l\(^{-1}\)). In the presence of phosphate, the increased U(VI) adsorption in batch systems is caused by the formation of strongly adsorbed ternary surface complexes, and the increased retardation in U(VI) transport observed in our column experiments is most probably caused by formation of the same ternary surface complexes. These results show that the effects of phosphate on U(VI) adsorption observed in batch systems are also applicable to column conditions, at least qualitatively.

The U(VI) breakthrough curve for the experiments with goethite-coated sand (Fig. 2) was asymmetric, indicative of either (1) nonlinear adsorption and/or (2) rate-limited adsorption (Jardine, 1991). Calculated U(VI) adsorption isotherms based on a previously-developed surface complexation model (Cheng et al., 2006) indicated that the isotherms were linear at the solid-to-solution ratio used in our column experiments, both in the presence and absence of phosphate. Therefore, the asymmetry of the U(VI) breakthrough curves was most likely caused by rate-limited adsorption. Our batch kinetic experiments showed that U(VI) adsorption required at least 8 h and 2 h to reach equilibrium in the absence and presence of phosphate, respectively (Cheng et al., 2006). In our column experiments, the duration of U(VI) input, which was equal to the time the goethite-coated sand being exposed to U(VI), was only 1 h. These facts suggest U(VI) adsorption in our column experiments was rate-limited, and adsorption equilibrium cannot be assumed in modeling U(VI) adsorption. In a recent study, strong kinetic effects were observed for both U(VI) adsorption and desorption during U(VI) transport in a sediment column from the US DOE Hanford site, and it was suggested that U(VI) release and transport in the vadose zone and aquifer system of the sediment were kinetically controlled (Qafoku et al., 2005). These results demonstrate the importance of kinetic effects on U(VI) adsorption in porous media in natural systems.

4. Conclusions

U(VI) and phosphate transport was retarded in a column packed with goethite-coated sand, due to their mutual adsorption on goethite. A relatively small amount of U(VI) (ca. \(10^{-6}\) M) did not affect phosphate (ca. \(10^{-4}\) M) transport. However, the presence of phosphate greatly increased
U(VI) adsorption and retardation in column experiments. U(VI) and phosphate adsorption in our column experiments was rate-limited, and adsorption equilibrium cannot be assumed. Although U(VI) adsorption in the absence of phosphate was reversible, the adsorption of phosphate and the adsorption of U(VI) in the presence of phosphate were not reversible in our column experiments, and kinetic limitations were more pronounced for desorption than for adsorption. The results of this study indicate several potentially salient features of U(VI) adsorption and transport in natural systems, especially in the presence of phosphate and where U(VI) adsorption is rate-limited.

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References


