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Effect of attapulgite colloids on uranium migration in quartz column

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ABSTRACT

Clay minerals are widely used as backfill and buffer materials, and it is known that clay colloids derived from an engineered barrier system may affect the migration behaviors of radionuclides. Based on a study of the stability of attapulgite colloids and the sorption behavior of uranium on attapulgite, the effect of attapulgite colloids on U(VI) migration was investigated in a quartz column. The results show that attapulgite colloids are stable without disturbance, but changes on pH or addition of an electrolyte can reduce their stability. Quartz column experiments in the presence of attapulgite indicated U(VI) adsorption to the colloid that retarded U(VI) migration. In a system consisting of U-colloid-chloride at pH 6.0, U(VI) migration showed almost no change compared to when only uranium was present. However, U(VI) migration was accelerated significantly in the U-colloid-phosphate system because of the formation of U(VI)-phosphate complexes rather than U(VI) adsorbing on the attapulgite colloid.

1. Introduction

The volume of radioactive waste originating from the operation and decommissioning of nuclear facilities has increased considerably as the nuclear energy industry and nuclear technology have rapidly developed (Poskas et al., 2012; Hwang et al., 2003). Prior to its final disposal, radioactive waste must be treated in ways that ensure its isolation from the biosphere until it can decay to natural background radiation levels (Sartori, 2013). Ideally, the radionuclides should be contained by a multi-barrier system that employs both engineered and natural or geological barriers to achieve the required passive safety (IAEA, 2009; Lee et al., 2016). The buffer or backfilling material, which is the most important component of an engineered barrier, plays a crucial role in ensuring long-term isolation (Zhang et al., 2012). Therefore, when designing and constructing engineered barriers it is important to select a material that strongly retards radionuclide transport and has good mechanical properties. Considering their economic and technical feasibility, clay materials such as bentonite, smectite, and attapulgite have been used in engineered barrier systems (Li et al., 2016; Murray, 2000; Amer et al., 2006).

Attapulgite, also called as palygorskite, is a hydrated octahedral layered magnesium aluminum silicate mineral (Chi et al., 2013) with an abundance of structural hydroxyls, including Si–OH, Mg–OH, and Al–OH, on its surface. Some isomorphous substitutions, such as Al³⁺ for Si⁴⁺ and Fe²⁺ for Al³⁺, provide negatively charged sites that can adsorb a large number of metal ions from aqueous solutions. Previous

research has shown that attapulgite has good adsorption ability for U (Song et al., 2013), Th (Pan et al., 2011), ⁶³Ni (Chen et al., 2011), and ⁶⁰Co (Tan et al., 2011a,b), which suggests that attapulgite has potential as a barrier material. However, it is well known that inorganic colloids can be derived from the degradation of engineered barrier materials (Lahtinen et al., 2010), and these colloids have been shown to influence radionuclide migration (Schäfer et al., 2004). For example, in situ experiments at the Grimsel Test Site showed that the migration behavior of Am and Pu was greatly affected by the presence of bentonite colloids and that recovery in the presence of bentonite colloids (60–80%) was larger than that in the absence of bentonite (20–30%) (Möri et al., 2003). For Sr, a small fraction of the Sr adsorbed on mobile colloids moved un-retarded, while the majority of Sr was transported more slowly than free Sr in solution because of retention by bentonite colloids (Albarran et al., 2011). Thus, the effect of colloids on radionuclide migration is complex and remains unclear; the effects depend on the interactions between the radionuclides, colloids, and host minerals (Li et al., 2004) and are also affected by environmental factors like pH, temperature, and background ions. Attapulgite is abundant in South China and is likely to be selected as a barrier material. To the best of our knowledge, the effect of attapulgite colloids on radionuclide migration has scarcely been researched. To this end, the objectives of the present work are: (1) to investigate the effect of pH and the addition of an electrolyte on attapulgite colloid stability by analyzing the size distribution and zeta potential; (2) to characterize the effect of attapulgite colloids on uranium migration in a quartz column; and (3) to study the

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adsorption behavior of uranium on attapulgite to understand the phenomena observed in column experiments. Uranium was chosen as a representative radionuclide because it is one of the most important component in the nuclear fuel cycle.

2. Experimental

2.1. Materials

A uranyl stock solution was prepared by dissolving uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in deionized (DI) water (conductivity > 18 MΩ cm). Quartz was purchased from Rongsheng Science & Technology Co., Ltd and washed with DI water more than 10 times. Its chemical composition, as reported by the manufacturer, was > 99.0% SiO_2 , < 0.005% chloride, < 0.002% Fe and < 0.2% impurity resolved by HCl, NaCl, NaH_2PO_4 , and all acids and bases used in the experiments were of analytical purity and were used without any further purification.

Attapulgite samples were provided by the College of Water Sciences, Beijing Normal University. The chemical composition (wt%), as analyzed by X-ray fluorescence spectrometry (D/max-2400), was SiO_2 , 70.36%, MgO, 12.17%; Al_2O_3 , 10.35%; Fe_2O_3 , 5.16%; and K_2O , 0.93%. Attapulgite (100 g, < 120 μm) was immersed in a solution of NaCl (2 L, 5%) and stirred magnetically for 48 h and then rinsed with DI water until no chloride was detected in the supernatant by AgNO_3 (0.01 M) testing. The treated sample was dried at 105 °C, and the resulting material was named Na-attapulgite and used in the following experiment.

Na-attapulgite (10.0 g) was added to DI water (200 mL) and shaken for 4 h, and then left undisturbed for 72 h. The milk-white supernatant containing a suspended solid was diluted to obtain an attapulgite colloid stock solution. The concentration of the colloid stock solution was determined by a gravimetric method (The concentration is equal to the dried weight of an aliquot of the colloid solution divided by the aliquot volume). The particle size distribution was measured by dynamic light scattering (DLS) based on analysis of the temporal fluctuations in the intensity of scattered laser light that arises from Brownian motion of the colloid, and the zeta potential was determined by electrophoretic light scattering (Zetasizer Nano ZS90, Malvern).

2.2. Batch experiments

A batch study was performed under ambient conditions to determine the extent of U(VI) sorption on attapulgite. The stock suspension of Na-attapulgite was added to a polyethylene centrifuge tube (10 mL capacity) along with a certain volume of U(VI) stock solution and background electrolyte solution (NaCl, NaH_2PO_4) to make a solution with a final volume of 6.0 mL. A negligible volume of HCl or NaOH was added to adjust the pH to the desired value. The centrifuge tubes were shaken for ~24 h at the desired temperature before they were centrifuged (4000 rpm, 10 min). The supernatant liquid was collected to measure the concentration of U(VI). The sorption percentage (S , %) of U(VI) from aqueous solution, the adsorption capacity (q_e , mg/g) and distribution coefficient (K_d , mL/g) were calculated according to Eqs. (1)–(3), respectively:

$$S = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

$$K_d = \frac{C_0 - C_e}{C_e} \times \frac{V}{m} \quad (3)$$

where C_0 and C_e (mg/L) are the initial and equilibrium liquid phase concentrations of U(VI), respectively. V (mL) denotes the volume of the U(VI) solution in the tubes, and m (g) denotes the amount of adsorbent.

2.3. Column experiments

Column experiments were performed in a polypropylene column (ø 25 mm × 100 mm). Quartz of 0.4–0.8 μm was packed in the column and supported on a Teflon filter (pore diameter of 5 μm). The resulting porosity of the porous media was determined to be 0.42. The injection solution was delivered by a 12-head peristaltic pump (LangerPump Co. Ltd., China) in an upward direction at a flow rate of ~30 mL/h in all column experiments. After the quartz column had been equilibrated with ~6 pore volumes (PVs) of DI water at the desired pH value, U(VI) solutions (10 PVs) with different contents and compositions of background electrolyte and attapulgite colloid were introduced to the column. Finally, ~6 PVs of DI water was flushed through the column to study the release of the retained U(VI) from the column. Before investigating the effect of the attapulgite colloid in the presence of different anions, we investigated the individual effects of attapulgite colloids and various anions on U(VI) migration.

2.4. Measurement of U(VI) and the attapulgite colloid

The U(VI) concentration was determined by UV-Vis spectrophotometry (Shimadzu UV-1800, Japan) at 652 nm using the Arsenazo III method (Ozdemir et al., 2017). Sample (1 mL) and add one drop HCl (2 mol/L) was added into 10 mL volumetric flask, 1 mL Arsenazo III (0.5 g/L) was added and the final volume was completed to 10 mL. After 30 min, the absorbance of U-Arsenazo complex was determined at 652 nm. The correlation coefficient of the standard curve was 0.999. The attapulgite colloid concentration was directly determined by UV-Vis spectrophotometry (at 220 nm). The correlation coefficient of the standard curve was 0.997. The concentration of samples containing U(VI) and colloids was calculated under the assumption that the absorbance at 220 nm was equal to the sum of the absorbance of the colloid and U(VI) and that the colloid did not impact the absorbance of U(VI) at 652 nm. The process for measuring the colloid concentration involved three steps: (1) measuring the absorbance of U(VI) at 652 nm to determine the U(VI) concentration; (2) calculating the absorbance of U(VI) at 220 nm; (3) subtracting the absorbance of U(VI) from the total absorbance of a sample containing U(VI) and colloid at 220 nm to obtain the absorbance of colloid.

3. Results and discussion

3.1. Characterization of attapulgite

Fig. 1A shows a scanning electron microscopy (Nova Nano SEM450) image of a Na-attapulgite sample, demonstrating compact rod-like shapes with diameters of ~20–50 nm and lengths of ~500–1000 nm. The morphology of attapulgite results in a large surface area, giving it high sorption capacity (Tan et al., 2011a,b). The bands at 3620 cm^{-1} and 3560 cm^{-1} in the Fourier transform infrared (Thermo Scientific Nicolet 6700) spectrum of attapulgite (Fig. 1B) correspond to the stretching vibrations of Al–OH and Fe–OH, respectively. The bands at 1018 cm^{-1} and 474 cm^{-1} are attributed to the asymmetric stretching modes of Si–O–Si whereas the peak at 800 cm^{-1} may correspond to the stretching vibration of Al–O–Si. The results of the SEM, X-ray fluorescence (XRF), and FTIR analyses are similar to those of attapulgite reported previously (Niu et al., 2009; Cao et al., 1996), indicating that the attapulgite used in this study possesses a typical composition and structure.

3.2. Attapulgite colloid characterization

3.2.1. Attapulgite colloid

The attapulgite colloid (42.5 mg/L), obtained by a natural sedimentation method in DI water, was homogeneous and remained stable for ~2–3 months at room temperature. The colloid had a pH of 6.62

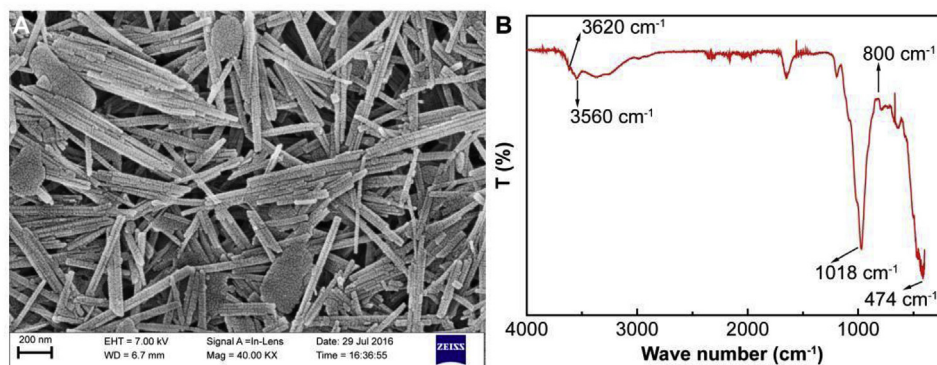


Fig. 1. Characterization of attapulgite. A: SEM image; B: FTIR spectrum.

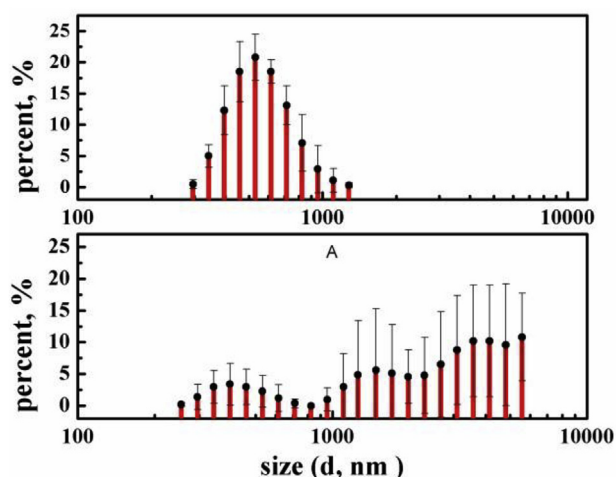


Fig. 2. Size distribution of attapulgite colloids.

A: original attapulgite colloid; B: attapulgite colloid in 0.001 M NaCl.

and a zeta potential of -24.6 mV. Its particle size distribution is shown in Fig. 2A. As seen, the particle size ranged between 290 nm and 1280 nm with an average size of 562 nm, and its polydispersity index was 0.247.

The stability of the suspensions relies on both dynamic stability and agglomeration stability, which refer to its ability to resist gravitational sedimentation by Brownian motion and the ability to withstand aggregation by electrical repulsion, respectively. Dynamic stability depends on the colloid particles being sufficiently small (i.e., on the nano-micrometer scale) and agglomeration stability requires an abundant surface charge; the attapulgite colloidal suspension remained stable because it satisfied both these criteria.

3.2.2. Effect of pH on colloid stability

The effect of pH on the particle size distribution and zeta potential of attapulgite colloids (42.5 mg/L) at room temperature is shown in Fig. 3. As the pH was increased from 5.0 to 8.0, colloid became more negative and the particle size decreased. In general, the tendency of colloids to aggregate depends on changes in the surface charge. When the pH changes, the agglomeration stability is enhanced by increased surface charge whereas decreasing surface charge reduces the stability (Cölfen and Lucas, 2006). The pH that corresponds to the zero-point charge of attapulgite (pH_{zpc}) is about 6.0 (Cao et al., 1996), so the particle surface is negatively charged in its original state (pH 6.62). Reducing the zeta potential led to coagulation because H^+ was adsorbed on the particle surface at pH 5.0–6.0. At pH 7.0–8.0, the particle surface became more negatively charged by the adsorption of OH^- , which increases the repulsive force between colloid particles. Thus, the attapulgite colloid is more stable in weakly basic solutions than in

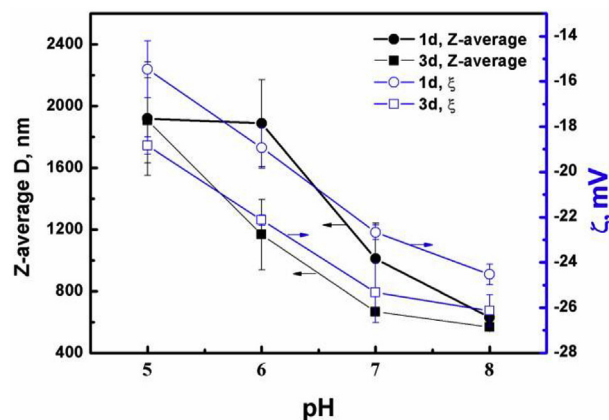


Fig. 3. Influence of pH on colloid diameter and zeta potential.

weakly acidic solutions.

3.2.3. Effect of inorganic salinity on colloid stability

The lyophobic attapulgite colloid remains stable mainly because of surface charge, but its stability is sensitive to charge screening by the presence of an electrolyte. Coagulation is typically observed in electrolyte solutions. Thus, the effects of uranium and other background ions on attapulgite colloid stability must be evaluated to determine the effect of attapulgite colloids on uranium migration in the presence of different background ions. The influence of uranium and salt concentration (NaCl, NaH_2PO_4) on the attapulgite colloid is shown in Table S1 of the Supporting Information; the particle size and the zeta potential increased slightly (by $\sim 10\%$) and decreased, respectively, in the presence of uranium (0.5 mg/L). When NaCl (10^{-3} M) was introduced into the colloid, the zeta potential decreased from -24.7 mV to -17.7 mV, and the average particle size increased drastically from 562 to 2581 nm. As shown in Fig. 2B, the size distribution of the colloid was much wider in the presence of NaCl, ranging from 250 nm to 5560 nm, which indicates that the colloid particles had aggregated. However, the particle size and zeta potential changed little in the presence of NaH_2PO_4 (10^{-3} M) at pH 6.0–8.0, suggesting that the effect of phosphate on the attapulgite colloid was far less than that of chloride. The similar phenomenon was found in research of the stability of montmorillonite colloid. NaH_2PO_4 increases the edge charge density of montmorillonite colloid and changes the type of coagulation, which contributes to the critical coagulation concentration of NaCl that is much lower than that of NaH_2PO_4 (Lagaly and Ziesmer, 2003).

DLVO theory is often used to describe colloid stability. It is generally believed that colloidal stability depends on the balance between the attractive van der Waals force and the repulsive surface charge; if the repulsion is greater than the attraction, the colloid is stable, and vice versa. The evident zeta potential decrease as a result of NaCl

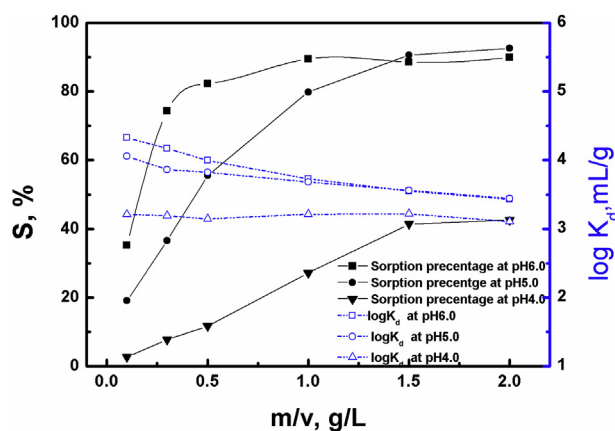


Fig. 4. Influence of m/v on adsorption efficiency
 $T = 25\text{ }^{\circ}\text{C}$, $c_0(\text{U(VI)}) = 5\text{ mg/L}$, $I = 0.01\text{ M NaCl}$, $t = 24\text{ h}$.

introduction contributed to a decreased electric repulsion and caused particle aggregation. However, the zeta potential changed only slightly when NaH_2PO_4 was introduced, and consequently, no significant coagulation was observed.

3.3. Absorption of uranium on attapulgite

3.3.1. Effect of solid content

Fig. 4 shows the effects of 0.01 M NaCl and 5 mg/L uranium on adsorption with a solid-liquid ratio (m/v) of $0.1\text{--}2\text{ mg/L}$. At $\text{pH } 6.0$, the sorption percentage of uranium from aqueous solution to attapulgite increased to 90% as m/v increased to 1.0 g/L , then remained relatively constant as m/v increased to higher values. At $\text{pH } 4.0$, the sorption percentage increased to only $\sim 40\%$ for $m/v < 1.5\text{ g/L}$ and then remained relatively constant for $m/v > 1.5\text{ g/L}$. This result indicates that the sorption percentage increases with both increasing m/v and increasing pH , which is attributed to an increased presence of charged functional groups on the attapulgite surface that provide more adsorption sites for uranium and/or the change on U(VI) aqueous speciation. Generally, the K_d value is assumed to be independent of solid content at low levels (Shao et al., 2009). However, we found that the K_d values decreased slightly with increasing m/v , as reported in previous experimental results (Song et al., 2013). Whereas higher attapulgite content provides more sites for U(VI) binding, competition among the functional groups decreases the sorption and complexation ability of attapulgite, resulting in a decrease in K_d as the attapulgite solid content increases (Tan et al., 2008).

3.3.2. Effect of shaking time

Adsorption kinetics is a consequence of the rate of the adsorption process. The relationship between the sorption percentage and the shaking (contact) time is shown in Fig. 5; the sorption percentage increased with increasing contact time. The percentage increased quickly to 65% in 4 h and then increased slowly after 4 h . Adsorption steady state occurred when the percentage reached 76% at 12 h . We introduced the pseudo-second-order kinetic model (Eq. (4)) to study the kinetic features of U(VI) adsorption on quartz, which was used to describe the chemical sorption (Du et al., 2012):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (4)$$

where k ($\text{kg}/(\text{mg}\cdot\text{h})$) is the rate constant of adsorption, q_e (mg/kg) is the amount of U(VI) adsorbed at equilibrium, kq_e^2 ($\text{mg}/(\text{kg}\cdot\text{h})$) is the initial rate, and q_t (mg/kg) is the amount of U(VI) adsorbed at measurement time t (h).

The data were well described by the pseudo-second-order kinetic model (inset plot in Fig. 5). Fitting the kinetic data to Eq. (3) resulted in

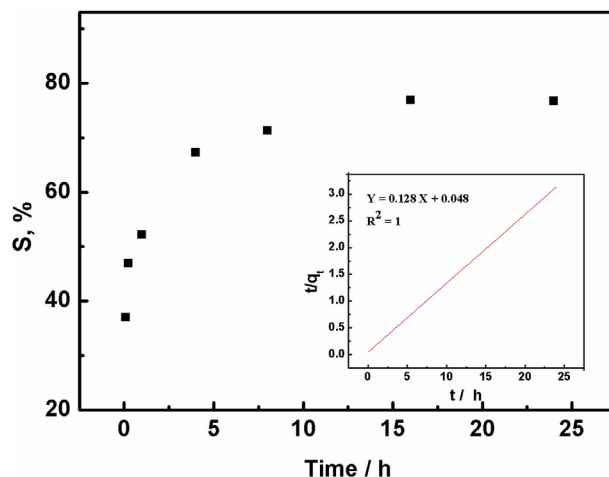


Fig. 5. Effect of shaking time on the sorption of U(VI) on attapulgite
 $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 5.0$, $c_0(\text{U(VI)}) = 5\text{ mg/L}$, $m/V = 0.5\text{ g/L}$, $I = 0.01\text{ M NaCl}$.

an r^2 of 0.999 , q_e of $7.78 \times 10^3\text{ mg/kg}$, and an initial rate kq_e^2 of $2.07 \times 10^4\text{ mg}/(\text{kg}\cdot\text{h})$. The rapid occurrence of adsorption steady state is a characteristic feature of chemical adsorption (Tan et al., 2011a,b; Song et al., 2013). Furthermore, the pseudo-second-order kinetic model suggests that the adsorption velocity varies linearly with the concentrations of sorbent and sorbate and is controlled by a chemical sorption mechanism.

3.3.3. Effect of pH and ionic strength

Fig. 6 shows the sorption curves of uranium on attapulgite as a function of pH in different concentrations of NaCl and NaH_2PO_4 . The concentration of the two different types of background ions had little effect on the sorption percentage, whereas the effect of pH was significant. Generally, surface complexation is pH -dependent and ion exchange is ionic-strength-dependent (Chen et al., 2009; Dong et al., 2012). This result indicates that the sorption of uranium on attapulgite is dominated by surface complexation. The effect of uranium adsorption on attapulgite in previously reported studies was an obvious discrepancy; for example, the adsorption percentage decreased with increasing ionic strength at $\text{pH } 2.0\text{--}7.0$ in some reports (Chi et al., 2012; Xiao et al., 2013). In contrast, other reports showed that adsorption increased by increasing ionic strength under similar experiment conditions (Song et al., 2013). This discrepancy may arise from differences in the experimental material.

In the presence of NaCl , the adsorption of uranium on attapulgite

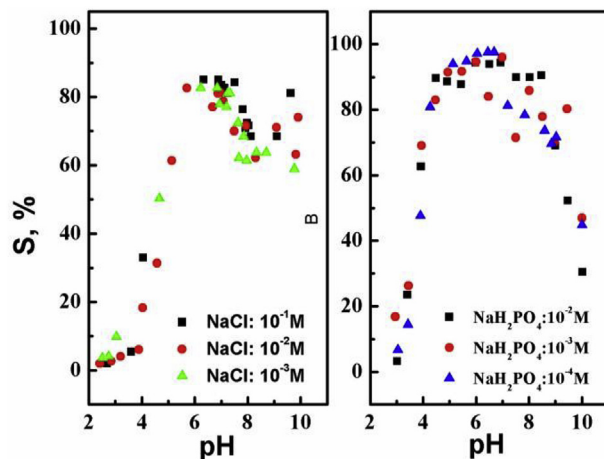


Fig. 6. Effect of ionic strength and pH on U(VI) sorption on attapulgite
 $T = 25\text{ }^{\circ}\text{C}$, $C_0(\text{U(VI)}) = 5\text{ mg/L}$, $m/V = 0.5\text{ g/L}$, $t = 24\text{ h}$.

increased clearly at pH 2.0–6.0, decreased slightly at pH 6.0–8.5, and increased slightly at pH 8.5–10.0. In NaH_2PO_4 , the adsorption of uranium on attapulgite increased clearly at pH 3.0–5.0, increased slightly at pH 5.0–8.0, and decreased slightly at pH 8.0–10.0. The adsorption behavior at different pH values correlates with the type of uranium species and the characteristics of the attapulgite surface. U(VI) sorption is enhanced under conditions that favor the formation of aqueous U(VI) hydroxy complexes (e.g., near-neutral pH for atmospheric p_{CO_2} conditions). Conversely, geochemical conditions that inhibit the formation of U(VI) hydroxy complexes (e.g., low pH and a tendency for carbonate complexes to form) suppress U(VI) sorption (Prikryl et al., 2001). In NaCl at low pH, uranium is mainly present as positively charged ions (such as UO_2^{2+} , UO_2OH^+ , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, as calculated by Visual Minteq 2.52), and the surface of attapulgite is positively charged because of a protonation reaction at $\text{pH} < \text{pH}_{\text{zpc}}$ (i.e., $\equiv\text{S}-\text{OH} + \text{H}^+ \rightarrow \equiv\text{S}-\text{OH}_2^+$, where $\equiv\text{S}$ represents the surface of attapulgite and $-\text{OH}$ represents the functional group). Thus, in strongly acidic conditions, the adsorption of uranium on attapulgite is low, and sorption increases with decreasing acidity because of the resultant decrease in positive charge of the attapulgite surface. However, in basic NaCl, uranium species are primarily negatively charged ions (such as $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$ and $\text{UO}_2(\text{CO}_3)_3$), and the surface of attapulgite is negatively charged because of a deprotonation reaction (i.e., $\equiv\text{S}-\text{OH} \rightarrow \equiv\text{S}-\text{O}^- + \text{H}^+$); thus, adsorption decreases as pH increases. The observed adsorption behavior in NaH_2PO_4 can be explained in a similar way. That is, uranium species are positive or neutral (UO_2^{2+} and UO_2HPO_4) under acidic conditions and negatively charged ($(\text{UO}_2)_2\text{HPO}_4^-$, $\text{UO}_2(\text{CO}_3)_3$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3$, $\text{UO}_2(\text{CO}_3)_3$) under alkaline conditions. Therefore, the adsorption increases with increasing pH under acidic conditions because of the decreased electrostatic repulsion between the attapulgite surface and uranium, and adsorption decreases with increasing pH under basic conditions because of the increased electrostatic repulsion between the attapulgite surface and uranium.

3.4. Effect of the attapulgite colloid on uranium migration

3.4.1. Effect of background ions on attapulgite colloid migration

The effect of background ions on attapulgite colloid migration is shown in Fig. 7, where breakthrough curves (BTCs) were plotted using the relative concentration c/c_0 (c is the effluent concentration and c_0 is the initial influent concentration). As seen, c/c_0 rapidly reached $\sim 100\%$ in the absence of background ions (control group), indicating that the attapulgite colloids were transported almost without retardation through the quartz column. This result suggests that the quartz

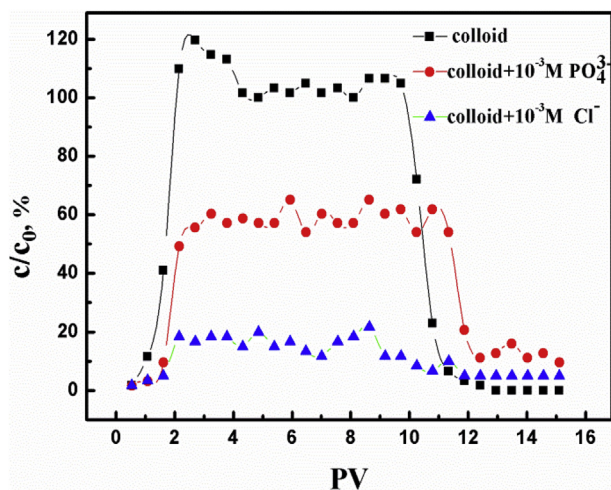


Fig. 7. Effect of background ions on colloid migration in a quartz column $T = 25^\circ\text{C}$, $\text{pH} = 6.0$, $c(\text{colloid}) = 15.0 \text{ mg/L}$.

media did not adsorb attapulgite colloid and that there was no aggregation in the column. However, in the presence of $0.001 \text{ M NaH}_2\text{PO}_4$ or 0.001 M NaCl , c/c_0 decreased to $\sim 60\%$ and 20% , respectively, indicating that NaCl had a more prominent effect than NaH_2PO_4 to decrease migration of the colloid. The decreased colloid migration caused by background ions may be correlated with their effect on colloid stability. The colloid particle size and zeta potential changed slightly in the presence of $0.001 \text{ M NaH}_2\text{PO}_4$ (Table S1), corresponding to a migration of $\sim 60\%$ of the colloid through the column. However, the colloid particle size drastically increased, and the zeta potential clearly decreased in the presence of 0.001 M NaCl (Table S1), which reduced the attapulgite colloidal transport. In previous work on the effect of NaCl on the migration of bentonite colloids through fractured rock (Yoshio and Hiroshi, 2009), the authors observed that the colloids passed through a granite fracture (0.1 cm) in the presence of 10^{-4} M NaCl , whereas it was filtered by the same fracture in the presence of 10^{-3} M NaCl . The difference was attributed to NaCl changing the interaction between the colloid and the rock surface. In our work, the cause of filtration of the attapulgite colloid in the presence of background ions could include: (1) mechanical retardation because of increased colloid particle size; (2) intensive dynamic settlement because of increased particle size; (3) aggregation on the pore surface because of decreased zeta potential.

3.4.2. Effect of attapulgite colloid on uranium migration

The effect of different concentrations of the attapulgite colloids on uranium migration is shown in Fig. 8. As seen, the c/c_0 of uranium decreased with increasing colloidal concentration, suggesting that the presence of the attapulgite colloids increased uranium retardation by the quartz column.

Although field investigations at the Nevada test site (Novikov et al., 1999) and Mayak (Kersting et al., 1999) showed that environmental colloids facilitated migration of radionuclides, the effect of colloids was found to be distinctly different in other laboratory experiments. Laboratory experiments showed that humic acid (HA) accelerated the migration of $\sim 2.4\%$ of the U(VI) in a test sample by the formation of HA-U(VI) (Artinger et al., 2002), but the migration behavior of the remaining 97.6% of the U(VI) was not described. In research of the effect of bentonite colloid on Sr migration in a granite column, Sr migration was only accelerated by 1% by the bentonite colloid, which was much lower than expected. However, the transport velocity of bentonite-adsorbed Sr was decreased because of retention by the bentonite colloid (Albarran et al., 2011). The discrepancy between field investigations and laboratory experiments may arise from the difference

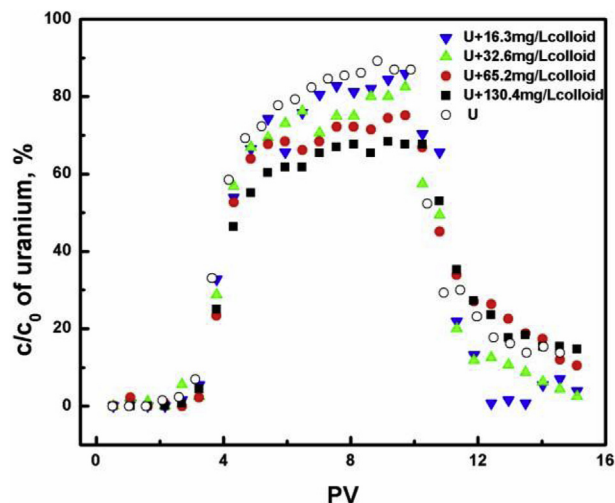


Fig. 8. Effect of colloid concentration on U(VI) migration in quartz $T = 25^\circ\text{C}$, $\text{pH} = 6.0$, $c_0(\text{U(VI)}) = 5.0 \text{ mg/L}$.

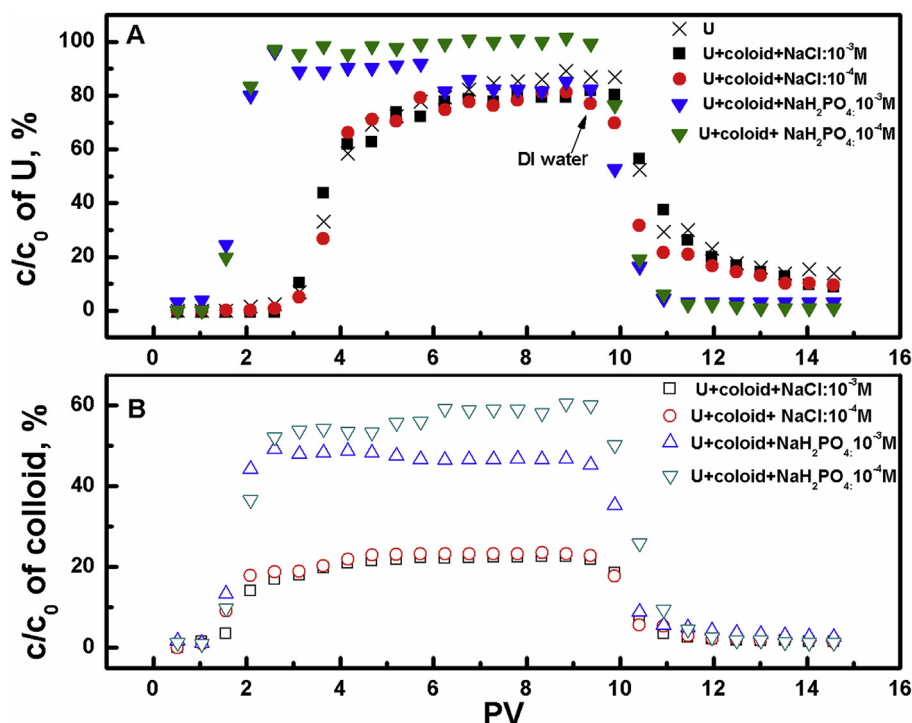


Fig. 9. Co-effects of anion and colloid on U(VI) migration in a quartz column
 $T = 25\text{ }^{\circ}\text{C}$, $\text{pH} = 6.0$, $c_0(\text{U(VI)}) = 5.0\text{ mg/L}$, $c(\text{colloid}) = 13.1\text{ mg/L}$.

in stability of the two colloids (Möri et al., 2003) and other factors (the different porosity or solution composition).

As described in Section 3.1, attapulgite colloid stability decreased at higher uranium concentrations, which led to enhanced aggregation of the attapulgite colloid particles in the quartz column. Furthermore, the colloid sorption sites can be modified by uranium adsorption at higher background uranium concentrations (Akbour et al., 2013), leading to more colloid adsorption on the quartz surface. Accordingly, the retention of colloid decreased the c/c_0 of uranium because of the increased uranium adsorption ability of attapulgite. No facilitation of uranium transport by attapulgite colloids was observed in this study.

3.4.3. Effect of the attapulgite colloid on uranium migration with different anions

Ionic strength can affect the degree to which the colloid influences radionuclide migration (Yoshida and Suzuki, 2006; Xie et al., 2012). The effect of different anions on uranium migration with the attapulgite colloid is shown in Fig. 9. As shown in Fig. 9A, the uranium migration behavior remained almost unchanged in a system of chloride-colloid-U compared to the one containing only uranium. However, the uranium migration behavior changed considerably in the phosphate-colloid-U system as follows. First, the uranium transport velocity increased distinctly. The breakthrough ($\sim 2.5\text{ PV}$) of uranium in the phosphate-U-colloid system was lower than that in both chloride-colloid-U and the control group ($\sim 6.0\text{ PV}$), which suggested that uranium migration was much faster in the presence of phosphate than in the other two groups.

Table 1
 U(VI) species and distributions.

Composition	Species and content/%			
U: 5 mg/L, NaCl: 0.001 M	$(\text{UO}_2)_3(\text{OH})_5^+$, 50.07	$(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$ 24.60	UO_2OH^+ 10.42	$(\text{UO}_2)_4(\text{OH})_7^+$ 5.33
U: 5 mg/L, NaH_2PO_4 : 0.001 M	UO_2HPO_4 (aq.), 69.20	UO_2PO_4^- 30.02	UO_2OH^+ 0.43	

* Calculated by Minteq version 2.52 with the system pH at 6.0.

Second, the c/c_0 value of uranium in the presence of 0.01 M phosphate was 10% greater than that in the absence of phosphate. The higher breakthrough plateaus signified that the column retained less uranium (Shen et al., 2013). The c/c_0 of uranium reached $\sim 90\%$ in the phosphate-colloid-U system, compared to 80% in the chloride-colloid-U system and 85% in the U system, which indicated that uranium migration was facilitated by the presence of phosphate and was retarded in the presence of chloride. Third, the volume of eluting DI water was lower in the presence of phosphate, which means that U(VI) migrated out of the quartz column more quickly in the presence of phosphate. Extended tailing is more obvious in the presence of chloride, but it was hardly observed in the presence of phosphate. The fast migration of uranium in the presence of phosphate was attributed to the formation of a Uranyl phosphate complex. Uranium species exist mainly as negative ions or neutral species in the presence of phosphate at pH 6.0 but form positive ions in the presence of chloride (Table 1). The quartz surface is negatively charged at pH 6 because the pH_{zpc} of quartz is lower than 4 (Tao and Zhang, 2002). Thus, the electric repulsion between U and quartz was lower in the presence of phosphate than in the presence of chloride, and uranium could migrate more easily in the presence of phosphate.

Fig. 9B shows that the c/c_0 value of attapulgite was between 50% and 60% in the phosphate-colloid-U system, but it was only $\sim 20\%$ in the chloride-colloid-U system. This difference further confirmed the phenomenon shown in Fig. 7; that is, attapulgite colloid migration is higher in the presence of phosphate than in the presence of chloride.

Table S1 shows that the attapulgite colloid has smaller particle size and higher zeta potential in the phosphate-colloid-U system than in the chloride-colloid-U system.

4. Conclusions

Based on the preparation of attapulgite colloids and the characterization of its stability, the adsorption of uranium on attapulgite clay and the effect of attapulgite colloids on the migration of uranium in a quartz column were studied. The following conclusions can be drawn:

1. The prepared attapulgite colloids had an average particle size of 562 nm and a zeta potential of -24.6 mV, which were sufficient for colloidal stability. However, adjusting either the pH or adding electrolyte ions may affect this stability. NaCl significantly reduced the attapulgite colloid zeta potential and increased the colloid particle size.
2. Attapulgite clay has a high adsorption capacity for uranium, with sorption reaching steady state within 12 h. The pH and aqueous solution composition significantly affected sorption of uranium on the surface of attapulgite clay.
3. The migration of the attapulgite colloid in the quartz column was reduced by the presence of background ions, which reduced the colloid stability. In uranium-containing solutions, the colloid stability was reduced by the uranyl ion, leading to filtration of the colloid in the quartz column and retention of the uranium adsorbed on the surface of attapulgite in the column. This result shows that attapulgite colloids reduce the migration of uranium in a quartz column.
4. In the phosphate-colloid-uranium ternary system, uranium migration was promoted by phosphate rather than by the attapulgite colloid. The uranyl-phosphate complex migrated rapidly in a quartz column at pH 6.0, leading to accelerated uranium migration. However, in a chloride-colloid-uranium complex, the attapulgite colloid was strongly retained in the column.

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2018.11.009>.

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