

Experimental Study on Uranium Sorption onto Silica Colloids: Effects of Geochemical Parameters

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Abstract

In this study, sorption experiments of uranium onto silica colloids were carried out and the effects of important geochemical parameters such as pH, ionic strength, carbonate concentration, colloid concentration, and total concentration of uranium were investigated. The sorption coefficients of uranium for silica colloids named as pseudo-colloid formation constants were about $10^4 \sim 10^5$ mL/g depending on the experimental conditions. The effects of the geochemical parameters were found to be important in the sorption of uranium onto silica colloids. A Langmuir type sorption isotherm of uranium between silica colloids and the solution phase was also presented. The sorption mechanisms were explained by analyzing the effects of the geochemical parameters.

Key Words : pseudo-colloid formation constant (K_{fp}), uranium, silica colloids, sorption mechanism, sorption isotherm, geochemical parameters

1. Introduction

The transport and distribution of radionuclides in groundwater or through geologic media depend upon the radioactive sources, the physicochemical forms of the radionuclides, and interactions with other components present in the groundwater. High-level radioactive waste, especially actinides, can migrate or discharge as various forms that are not simply dissolved ions but colloids or complexes through a geological medium. In particular, it has been reported that the formation of colloidal matter or sorption of radionuclides on negatively

charged naturally occurring colloidal matter could drastically increase the mobility of the radionuclide released from a radioactive waste repository [1-5]. Many scientists have investigated this possibility for several decades [1-12]. The main result of the studies is that colloids can accelerate the migration of radionuclides in the groundwater.

To evaluate the impact of natural colloids on radionuclide migration it is necessary to understand colloid migration itself and to quantify the association of radionuclides with the colloids. The radionuclides released from radioactive wastes may sorb onto the natural colloids present

in groundwater forming pseudo-colloids. For strongly sorbing radionuclides, association with colloids could have a significant influence on migration processes if the colloid concentration is sufficiently high and the colloids are mobile. Smith and Degueldre [4] showed that when irreversible sorption of contaminants on colloids was considered, enhancement of transport distance through fractured porous media could be significant, depending on the extent of interaction between the colloids and the fracture walls. Thus, maximum transport of radionuclides by colloids occurs if sorption is irreversible and no colloid retention occurs in the hydrogeological system [4, 10].

Recent studies have incorporated the possibilities of kinetic limitations and reversibility in the sorption of radionuclides onto colloids, which is critical to evaluate the significance of colloids to radionuclide transport [13, 14]. Therefore, in most of the colloid studies, radioactive pseudo-colloid formation of a radionuclide with natural colloids has been given the highest priority because pseudo-colloids formed in the geosphere (especially in the rock fracture) are likely to migrate faster than dissolved radionuclides [8-12].

In this study, sorption experiments of uranium onto silica colloids were carried out to provide information on the sorption properties of colloids and to determine the pseudo-colloid formation constants of uranium with silica colloids. In our experiments, uranium(VI) was considered a sorbing species because uranium is a major element of strongly sorbing actinides contained in high-level radioactive wastes and is also sensitive to carbonate reactions considered in our study. Silica colloids were considered as colloids because silica is a major component composing rock and aquifer materials and silica colloids are easy to handle comparing to other inorganic colloids.

The effects of the geochemical parameters such

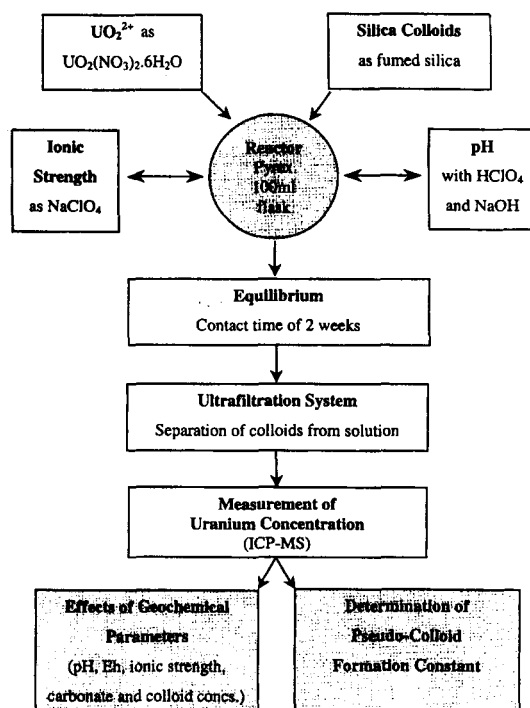


Fig. 1. The Overall Sorption Experimental System

as pH, ionic strength, carbonate concentration, and colloid concentration on the pseudo-colloid formation of uranium with silica colloids were also investigated. A sorption isotherm of uranium between silica colloids and the solution phase was also presented. The sorption mechanism was explained by investigating the effects of the geochemical parameters.

2. Experimental

2.1. Experimental System

In all sorption experiments, uranyl ions (UO_2^{2+}) and synthetic silica colloids were considered as nuclides and colloids, respectively. In an aqueous solution, uranyl ions can easily be incorporated with the complex chemical reactions such as

Table 1. Representative Values and Ranges of the Considered Geochemical Parameters

Parameters	Unit	Ranges	Representative values
pH	-	4 ~ 10	7.0
Colloid concentration as [SiO ₂]	g/L	10 ⁻⁹ ~ 10 ⁻⁶	10 ⁻⁸
Uranium concentration as [U ₀]	mol/L	10 ⁻⁷ ~ 10 ⁻⁴	10 ⁻⁵
Ionic strength as [NaClO ₄]	mol/L	10 ⁻³ ~ 10 ⁻¹	10 ⁻¹
Carbonate concentration as [NaHCO ₃]	mol/L	Ambient, 10 ⁻⁴ ~ 10 ⁻²	Ambient

carbonation and hydrolysis, and thus these reactions were considered. Therefore, the considered reaction system can be simply expressed as *Silica/*UO₂²⁺/*H*₂O/*H*₂CO₃. All sorption experiments were conducted by an equilibrium batch method. The overall experimental system performed in this study was presented in Fig. 1. The representative values and their ranges of the considered geochemical parameters were listed in Table 1.

2.2. Materials and Apparatus

The nuclides and colloids used in all sorption experiments were hexa-valent uranyl ions (UO₂²⁺) provided in a nitrate form, UO₂(NO₃)₂ · 6H₂O, and fumed silica colloids (SIGMA, 99.8%), respectively. The average size of the silica colloids was about 14 nm and the surface area of the colloids was 200 ± 25 m²/g. All solutions used were made of AR grade reagents and high purity water with the resistivity of 18.3 MΩ-cm (Milli-Q, Millipore). The ionic strength of each solution was controlled by NaClO₄ · H₂O, which dissolves into Na⁺ and ClO₄⁻ in solution. These ions sorb onto silica colloids and thus affect uranium sorption. The pH of each solution was adjusted by NaOH and HClO₄, and measured by Ion Analyzer EA-940 (ORION).

In general, the behavior of uranium in the solution is greatly affected by the presence of carbonates since uranium tends to form carbonate complexes with carbonate ions. Thus, it is

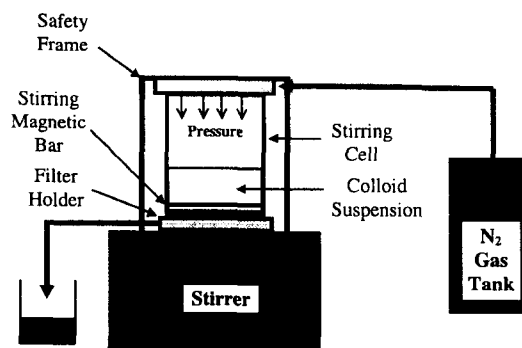


Fig. 2. Ultrafiltration System for Colloid Separation from Solution

necessary to control the amount of carbonates in the solution since the carbonates will affect the sorption of uranium onto silica colloids. To control the concentration of carbonates, NaHCO₃ was used. NaHCO₃ dissolves into Na⁺ and HCO₃⁻, and consecutively HCO₃⁻ dissolves into H⁺ and CO₃²⁻ in solution.

The ultrafiltration system (AMICON 8200) used to separate colloids from solution is shown in Fig. 2. The pore size of the used filter (AMICON, XM-50) was 50,000 NMWL (~3 nm). The total concentration of uranium in the filtrate was measured by ICP-AES (JY 50 P, Jobin Yvon).

2.3. Experimental Method

The reacting solution was prepared by adding a requisite amount of NaClO₄ to make 100 mL of

Table 2. Experimental Results for the Effect of pH on the Uranium Sorption onto Silica Colloids

pH (± 0.1)	[U] (mol/L)	[SiO ₂ -U] (mol/L)	P (%)	K _{fp} (mL/g)
4.0	7.5621×10^{-6}	2.4379×10^{-6}	24.4	3.2238×10^4
5.0	6.3017×10^{-6}	3.6983×10^{-6}	40.0	5.8687×10^4
6.0	5.8816×10^{-6}	4.1184×10^{-6}	41.2	7.0022×10^4
6.8	5.7976×10^{-6}	4.2024×10^{-6}	42.0	7.2485×10^4
7.3	6.3017×10^{-6}	3.6983×10^{-6}	37.0	5.8687×10^4
8.6	7.5621×10^{-6}	2.4379×10^{-6}	24.4	3.2238×10^4
9.8	9.2425×10^{-6}	7.5750×10^{-6}	7.6	8.1968×10^3

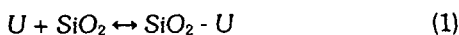
0.1M NaClO₄ in a 125 mL pyrex flask. Uranium was added from a concentrated stock solution to the prepared NaClO₄ solution to make a 10⁻⁵M uranium solution. After the addition of uranium, the pH of each solution was checked and adjusted with dilute NaOH or HClO. The uranium-containing solution was then allowed to stand 24h to allow equilibrium among constituents. A prerequisite amount of silica colloids was added to the pH-adjusted solution and the solution was dispersed by an ultrasonic device. The reaction period was 2 weeks.

After 1 week, the pH of the solution was measured and adjusted again. Two weeks later after adding the silica colloids, the final pH of each solution was measured. The colloids were separated from the solution by the ultrafiltration system. Each 30 mL of the filtrate was sampled for the measurement of the total concentration of uranium in the solution.

3. Results and Discussion

3.1. Analysis Methods

Generally, the sorption of uranium on silica colloids can be defined as:



and the sorption coefficient named as a pseudo-

colloid formation constant can be generally given as [5, 8, 9, 11]:

$$K_{fp} = \frac{[\text{SiO}_2 - U]}{[U][\text{SiO}_2]} \times C \quad (2)$$

where [U] is the concentration of uranium in the solution (mol/L), [SiO₂] is the concentration of the silica colloids in the solution (g/L), [SiO₂-U] is the concentration of uranium sorbed onto the silica colloids per unit volume of the solution (mol/L), K_{fp} is the equilibrium pseudo-colloid formation constant (mL/g), and C is the unit conversion factor of K_{fp} from L/g to mL/g (=10³). It is not difficult to notice that the pseudo-colloid formation constant, K_{fp}, agrees with the distribution coefficient of the uranium between the solution and silica colloids.

The percentage of uranium sorbed onto the silica colloids can be given as:

$$P(\%) = \frac{[\text{SiO}_2 - U]}{[U_0]} \times 100 \quad (3)$$

where [U₀] is an initial loading concentration of uranium (mol/L).

3.2. Effect of pH

The experimental results for the effect of pH on the sorption of uranium onto silica colloids are shown in Table 2 and Fig. 3. As shown in Fig. 3, the pseudo-colloid formation constant, K_{fp},

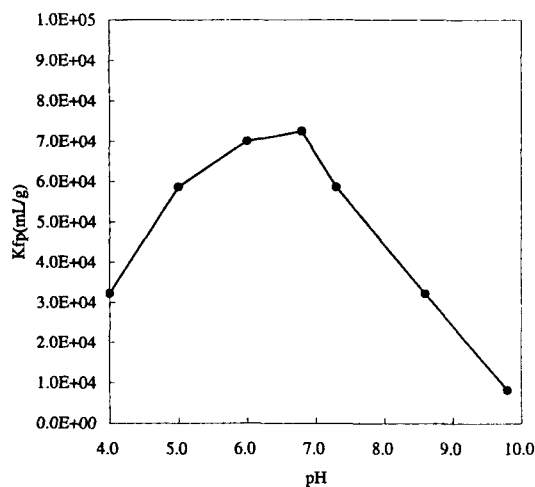


Fig. 3. The Effect of pH on the Sorption of Uranium onto Silica Colloids

increases continuously with pH up to a maximum at about pH 6.8 and decreases at higher pH.

The dependency on pH can give indirect evidence for the sorption mechanisms. The continuous increase of uranium sorption at a lower pH reveals that the sorption is by a surface complexation process rather than an ion exchange process [15-18]. Other studies have shown that for acidic or neutral solutions, the efficiency of uranyl sorption on silica increases with increasing pH [17, 18]. This suggests that sorption is enhanced in the pH range corresponding to the formation of hydrolyzed species. At low pH, the uranyl exists primarily as a mononuclear aqueous ionic species, and outer sphere complexation is the principal method of adsorption [18].

The drastic decrease of K_{fp} above pH 6.8 is due to the fact that in systems open to the air the weak sorption of UO_2^{2+} at high pH values is attributed to the formation of non-sorbing uranyl carbonate complexes, primarily $UO_2(CO_3)_3^{4-}$ [17, 18]. These uranyl carbonate complexes become more important at higher pH values because the total carbonate content in the systems equilibrated with air increases by about tenfold with an increase in pH of one unit. Therefore, K_{fp} will decrease as pH increases since the uranyl carbonate complexes exist as anions and the uranyl carbonate anions are difficult to sorb onto the silica colloids. This result is consistent with the results from the other uranium sorption studies [17-20]. It is also observed that the values of pseudo-colloid formation constants of uranium with silica colloids are similar to those of pseudo-colloid formation constants of uranium with other colloids such as $FeOOH$ and Al_2O_3 (i.e., $K_{fp} \cong 10^4 mL/g$ for Al_2O_3) [21].

3.3. Effect of Ionic Strength

The sorption experiments were carried out to investigate the effect of ionic strength on the sorption of uranium onto silica colloids. These experiments were performed by varying the concentration of $NaClO_4$. The results are shown in Table 3. As shown in Table 3, the percentage of uranium sorbed onto the silica colloids and K_{fp} are decreased as the concentration of $NaClO_4$ or ionic strength increases.

Table 3. Experimental Results for the Effect of Ionic Strength on the Uranium Sorption onto Silica Colloids

Ionic Strength as $[NaClO_4]$ (mol/L)	$[U]$ (mol/L)	$[SiO_2-U]$ (mol/L)	P (%)	K_{fp} (mL/g)
0.1	5.7976×10^{-6}	4.2024×10^{-6}	42.0	7.2485×10^4
0.01	3.1118×10^{-6}	6.8882×10^{-6}	68.9	2.2136×10^4
0.001	1.7760×10^{-6}	8.2240×10^{-6}	82.2	4.6306×10^5

Table 4. Experimental Results for the Effect of Carbonate Concentration on the Uranium Sorption onto Silica Colloids

Carbonate concentration as [NaHCO ₃] (mol/L)	[U] (mol/L)	[SiO ₂ -U] (mol/L)	P (%)	K _{fp} (mL/g)
Ambient	5.7976×10^{-6}	4.2024×10^{-6}	42.0	7.2485×10^4
10 ⁻⁴	4.6213×10^{-6}	5.3787×10^{-6}	53.8	1.1639×10^5
10 ⁻³	7.1420×10^{-6}	2.8580×10^{-6}	28.6	4.0017×10^4
10 ⁻²	7.5621×10^{-6}	2.4379×10^{-6}	24.4	3.2238×10^4

Table 5. Experimental Results for the Effect of Colloid Concentration on the Uranium Sorption onto Silica Colloids

Colloid concentration as [SiO ₂] (g/L)	[U] (mol/L)	[SiO ₂ -U] (mol/L)	P (%)	f _p (mL/g)
10 ⁻⁶	N.D.	-	-	-
10 ⁻⁷	4.2015×10^{-7}	9.5799×10^{-6}	95.8	2.2801×10^5
10 ⁻⁸	5.7976×10^{-6}	4.2024×10^{-6}	42.0	7.2485×10^4
10 ⁻⁹	6.4496×10^{-6}	3.5504×10^{-6}	35.5	5.5048×10^5

N.D. = Not detected by ICP-AES

When the ionic strength of the solution is increased, the thickness of the electric double layer is reduced and the affinity of uranyl ions for surface sites is finally reduced [22]. Thus, it appears that the sorption of uranium onto silica colloids can occur at the outer sphere rather than inner sphere of the electric double layer. However, it cannot be concluded that sorption occurs only at the outer sphere because the ionic strength effects are not great. Recently, it was suggested that adsorption of uranyl onto silica surface appears to occur via an inner sphere complexation [18].

In other study [12], the stability of silica colloids was measured as a function of ionic strength by varying the concentration of NaClO₄. A sharp increase of the size of silica colloids at the ionic strength above 1.0M was observed. This result indicated that above this value silica colloids are not stable. If the size of silica colloids increases, the surface sorption sites and then the sorption capacity of the silica colloids will be reduced.

3.4. Effect of Carbonates

The effect of carbonate concentration on the sorption of uranium onto silica colloids is shown in Table 4. As shown in Table 4, the percentage of uranium sorbed onto silica colloids and K_{fp} are decreased as the concentration of carbonate increased. This behavior is due to the formation of carbonate complexes of uranyl ions with carbonate ions as described in the effect of pH. It is noticeable that the effect of carbonate concentration begins to decrease above 10⁻³ mol/L of carbonate concentration. This may be due to the carbonate species competing with uranyl ions for the surface sorption sites of silica colloids and the surface sorption sites that can contribute to the sorption of carbonates will be gradually saturated as the concentration of carbonates increases.

Table 6. Experimental Results for the Effect of Uranium Concentration on Uranium Sorption onto Silica Colloids

Uranium concentration as $[U_0]$ (mol/L)	$[U]$ (mol/L)	$[SiO_2-U]$ (mol/L)	P (%)	f_p (mL/g)
1×10^{-4}	8.4560×10^{-5}	1.5440×10^{-5}	15.4	1.8259×10^4
5×10^{-5}	3.5290×10^{-5}	1.4710×10^{-5}	29.4	4.1683×10^4
1×10^{-5}	5.7976×10^{-6}	4.2024×10^{-6}	42.0	7.2485×10^4
5×10^{-6}	2.3890×10^{-6}	2.6110×10^{-6}	52.2	1.0929×10^5
1×10^{-6}	N.D.	-	-	-

N.D. = Not detected by ICP-AES

3.5. Effect of Colloid Concentration

The effect of colloid concentration on the sorption of uranium onto silica colloids is shown in Table 5. As shown in Table 5, the percentage of uranium sorbed onto silica colloids increases as the concentration of colloids increases because the number of sorption sites for uranium increases as the concentration of silica colloids increases. If the concentration of colloids is above 10^{-7} g/L, most of the uranium can sorb onto the silica colloids. However, K_{fp} does not show a remarkable dependency on the colloid concentration and this was also observed in other studies [8, 9].

3.6. Effect of Initial Concentration of Uranium

Sorption experiments were carried out to investigate the effect of uranium concentration on the sorption of uranium onto silica colloids by varying the initial loading concentration of uranium, $[U_0]$, as shown in Table 6. The percentage of uranium sorbed onto silica colloids and the pseudo-colloid formation constant decreased as $[U_0]$ increased. This can be explained on the basis of the existence of a relatively small number of strong surface sites and a large number of weak sites. Such two-site models have been

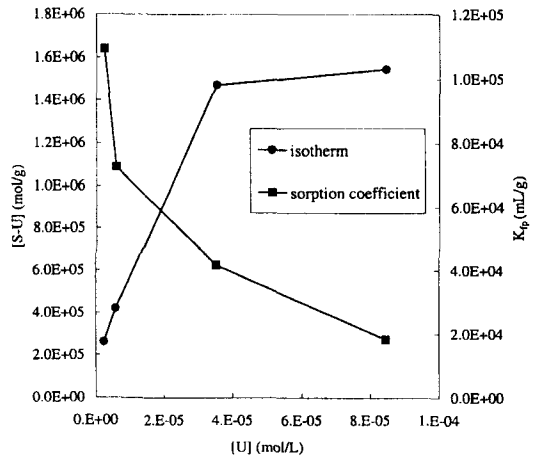


Fig. 4. The Isotherm and Sorption Coefficient of Uranium Between Solution Phase and Silica Colloids

found to be applicable to the sorption of various nuclides or metals on ferrihydrite [15].

3.7. Sorption Isotherm

A sorption isotherm of uranium for silica colloids and the calculated distribution coefficient of uranium are shown in Fig. 4. The shape of the sorption isotherm is similar to that of the Langmuir isotherm because the amount of uranium sorbed onto silica colloids increases continuously with the concentration of uranium in

the solution up to a maximum and then saturates at higher concentration. In contrast to the sorption isotherm, K_{fp} increases continuously with the concentration of uranium in the solution because K_{fp} means the slope of the isotherm.

4. Conclusions

In this study, sorption experiments of uranium onto silica colloids were carried out and the effects of important geochemical parameters such as pH, ionic strength, carbonate concentration, colloid concentration, and total concentration of uranium were investigated. The sorption isotherm of uranium between silica colloids and the solution phase was also studied. The pseudo-colloid formation constant was defined and determined. The pseudo-colloid formation constants of uranium for silica colloids (K_{fp}) were about $10^4 \sim 10^5$ mL/g depending on the experimental conditions.

The sorption mechanisms of uranium onto silica colloids were explained by analyzing the effects of the geochemical parameters such as pH, ionic strength, and total concentration of uranium. It was inferred that 1) the sorption of uranium onto silica colloids might be due to a surface adsorption process, 2) the surface complexation can also occur at the outer sphere as well as inner sphere of the electric double layer of the surface, and 3) there are a large number of weak sorption sites on the surface of silica colloids.

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