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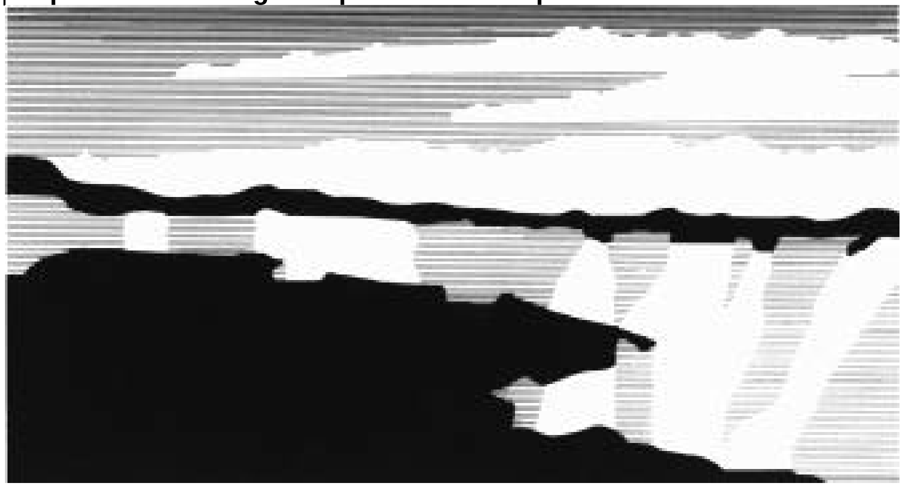

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Reversibility of Sorption of Plutonium-239 onto Colloids of Hematite, Goethite, Smectite, and Silica

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SUMMARY

Sorption of ^{239}Pu onto colloids of iron oxide, clays, and silica in groundwater plays an important role in transport of ^{239}Pu. Natural groundwater and carbonate rich synthetic groundwater were used as media in this study. We performed laboratory batch sorption experiments to evaluate: 1) sorption of ^{239}Pu as a function of different colloids (e.g., hematite, goethite, smectite, and silica), 2) sorption kinetics of colloidal Pu (IV) and soluble Pu (V) onto these colloids, and 3) desorption of ^{239}Pu from ^{239}Pu-loaded colloids as a function of time over a long period (~ 1 year). To confirm the influence of bicarbonate on ^{239}Pu sorption, an additional set of experiments was conducted using sodium nitrate ($NaNO_3$) solutions under carbon dioxide-free environments. Our results show that colloidal Pu(IV), as well as soluble Pu(V), was rapidly adsorbed by colloids of hematite, goethite, smectite, and silica in natural and synthetic groundwater. After 5 days, hematite colloids sorbed all colloidal Pu (IV) and soluble Pu(V) present in the solution, goethite sorbed 97% to 100% of ^{239}Pu, smectite sorbed 94% to 100 % of ^{239}Pu, and silica sorbed 46% to 86% of ^{239}Pu. Sorption kinetics of ^{239}Pu by these four types of colloids show that sorption of soluble Pu(V) is a slow process while sorption of colloidal Pu(IV) is a rapid process. The different sorption behavior of ^{239}Pu among these four types of colloids was due to the differences in their surface characterization. The presence of carbonate did not influence the sorption of ^{239}Pu. Desorption of ^{239}Pu from colloids of hematite, goethite, and smectite was much slower than the sorption process. Desorption of ^{239}Pu from silica colloids was relatively faster than from these tree types of colloids. Our finding suggests that ^{239}Pu contaminated colloids of iron oxide, clay, and silica are formed in the radioactive liquid waste and in groundwater. Different sorption/desorption behavior of ^{239}Pu by these four types of colloids in groundwater facilitates transport of ^{239}Pu along potential flowpaths from radionuclide contaminated areas to the accessible environment.

INTRODUCTION

Colloids are any organic and inorganic particles with sizes ranging from about 1 to 2 nm for organic macromolecules up to 1 μm for fragments of clays, oxides, and other solids in groundwater. It was found that colloids of clays, silica, and iron oxides were formed in the groundwater and the stability of clay and silica colloids is correlated to the ionic strength of groundwater (Triay et al., 1994). These colloidal particles have similar composition and surface characteristics to the immobile aquifer solids but are mobile within aquifers. Colloids are capable of associating with radionuclides (Kosmulski, 1997; Vilks and Degueldre, 1991; Penrose et al., 1990). The large surface area of colloids (10^4 to 5×10^5 m^2 kg^{-1}) can significantly sorb radionuclides even for relatively low mass concentrations of colloidal particles in the aquifer (McCarthy and Degueldre, 1992). In porous media, the size of colloids is smaller than the pores, which allows colloids to migrate over long distances. Therefore, these mobile colloids may enhance the transport of the strongly sorbing radionuclides along flowpaths. It was reported that about 75% of the Pu was associated with colloids which were rapidly transported when groundwater was pumped through undisturbed aquifer cores (Champ et al., 1982). At the Nevada Test Site, transition metals and lanthanide radionuclides were associated with inorganic colloids recovered from groundwater 300 m from a nuclear detonation cavity (Buddemeier and Hunt, 1988). Plutonium and americium were associated with siliceous colloids in an alluvial aquifer at Los Alamos National Laboratory (Penrose et al., 1990). Americium and lead were transported in the vadose zone with organic and inorganic colloids phases (Sheppard et al., 1980). The actual vertical movement of these contaminants was 10^4 times faster than predicted based solely on partitioning between dissolved and stationary solid. Colloidal particles with sizes ranging from 0.1 μm to 1.0 μm were the most mobile during natural gradient flow through a sandy porous medium, with larger and smaller colloids being preferentially removed (O'Melia, 1980).

Mineral oxides / hydroxides, especially those of Si, Fe, and Al, exhibit variable charged surfaces in natural water systems. The net charge changes with pH, being positive at lower pH and negative at high pH. Sorption kinetics of dissolved metals on oxides and hydroxides depend on the type of surface and metal being studied, but generally, is rapid (Sparks, 1995). Keeney-Kennicutt and Morse (1985) found that Pu(V)O_2^+ can be adsorbed from diluted solution and seawater on goethite, aragonite, calcite, and δ-MnO_2. The mechanism that dominates the sorption of actinide contaminants onto oxides or hydroxides in a solid/aqueous interface system is surface complexation (Fuger, 1992). This results in the formation of actinide-hydroxide complexes on the surface of colloids of iron oxides, clay, or silica. It was assumed that adsorption of Pu(IV) onto suspended particulate matter is due to the interaction of the strongly hydrolyzable Pu(IV) oxidation state with the surfaces of natural particulate matter (Sanchez, 1985). Hydrolysis reactions of quadrivalent and pentavalent actinides can be described as follows (Fuger, 1992):

$$q\,M^{4+} + n\,H_2O = M_q\,(OH)_n^{\,(4q-n)+} + n\,H^+ \qquad \mathrm{Log}^*\,\beta_{n.q.} \qquad [1]$$

$$q\,MO_2^{+} + n\,H_2O = (MO_2)_q\,(OH)_n^{\,(q-n)+} + n\,H^+ \qquad \mathrm{Log}^*\,\beta_{n.q.} \qquad [2]$$

According to Fuger (1992), the best value for the formation constant of quadrivalent plutonium hydroxide complex in water at 298 K, $\mathrm{Log}^*\beta^{0}_{1}$, for $Pu(OH)^{3+}$ was estimated to be 1.8 ± 0.7. Lierse et al.,(1985) reported that the best values for the formation constants of pentavalent neptunium hydroxide complexes in perchlorate media at 298 K, $\mathrm{Log}^*\beta_{1.1}$, for NpO_2OH^0, and $\mathrm{Log}^*\beta_{2,1}$, for $NpO_2(OH)_2^-$ was estimated to be -(11.5 ± 0.3) and -(23.0 ± 0.5), respectively. The formation of multiple species may occur simultaneously and may be influenced by the other ions present in groundwater. The sorption behavior of Pu(V)O_2^+ is influenced by oxidation-reduction reactions occurring on the mineral surface. Adsorption of $Pu(V)O_2^+$ onto goethite resulted in a reaction in which Pu(IV) and Pu(VI) are formed on the mineral surface. The Pu(VI) is slowly reduced to Pu(IV), leaving Pu(IV) as the dominant Pu surface species (Keeney-Kennicutt and Morse, 1985). Sanchez et al., (1985) found that adsorption of soluble Pu(IV) onto iron oxide may result in the formation of four hydrolytic species on the surface of the iron oxide. The four species are: $\equiv SO\text{-}Pu(OH)_2^+$, $\equiv SO\text{-}Pu(OH)_2^{2+}$, $\equiv SO\text{-}Pu(OH)_3^+$, and $\equiv SO\text{-}Pu(OH)_4^0$, where ≡SO denotes surface sites on the iron oxides. The adsorption of the more strongly hydrolyzable Pu(IV) occurred in the pH range of 3 to 5 while that for Pu(V) is at pH 5 to 7.

Information on affinity, kinetics, and reversibility, which is critical to evaluate the significance of colloids to Pu transport, is largely unavailable for groundwater particles. The information on sorption behavior of radionuclide colloids (e.g., Pu(IV) colloids) onto iron oxide, clay, and silica colloids in groundwater are unavailable. We performed laboratory batch sorption experiments using natural groundwater and carbonate rich synthetic groundwater as media to evaluate: 1) sorption of ^{239}Pu as a function of colloids of hematite, goethite, smectite, and silica; 2) sorption kinetics of colloidal Pu (IV) and soluble Pu (V) onto these colloids; and 3) desorption of ^{239}Pu from these colloids as a function of time over a long period (~ 1 year). To examine possible influence of bicarbonate on ^{239}Pu sorption, a set of experiments was conducted using sodium nitrate ($NaNO_3$) solutions under carbon dioxide (CO_2)-free environments, while maintaining the same ionic strength as the natural and synthetic groundwater but varying solution pH.

EXPERIMENTAL PROCEDURE

Solutions

The solutions used in this study were natural groundwater and synthetic groundwater. The natural groundwater was collected in the fall of 1994 from the Well J-13 at Fortymile Wash, east of Yucca Mountain, Nevada and referred to as J-13 water. The water was filtered through a 0.05 μm nylon filter membrane to eliminate natural colloids existing in the water. The composition of the filtered water was analyzed using an inductively coupled plasma spectrometry (ICP). The alkalinity of the water was measured by a titration method (Rhoades, 1982). The pH of the water was measured as well.

The synthetic groundwater was prepared by dissolving sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) in nanopure deionized water which was previously filtered through a 0.05 μm nylon filter membrane. The water, referred to as SYN.J-13, was allowed to equilibrate with the atmosphere for 10 days. The alkalinity and pH of the water were measured. The ionic strength of SYN.J-13 was 0.005M.

The $NaNO_3$ solution with ionic strength of 0.005 M, referred to as $NaNO_3$ (pH 6.05), was prepared by dissolving $NaNO_3$ in the filtered nanopure deionized water and allowing $NaNO_3$ to become completely dissolved under CO_2-free environments. The pH of the solution was measured. A portion of the solution was adjusted to pH 8.4 using diluted NaOH solution and referred to as $NaNO_3$ (pH 8.4) solution.

Preparation of Colloidal Solutions

Hematite and Goethite Colloidal Solutions

Commercial synthetic hematite (Fe_2O_3) and goethite (αFeOOH) mineral powders (particle size < 1.0 μm), from Nissan Chemical Industries Ltd., were used. The colloidal solutions, including hematite-J-13 (Fe_2O_3.J-13), hematite-synthetic.J-13 (Fe_2O_3.SYN.J-13), hematite-

$NaNO_3$ (Fe_2O_3-$NaNO_3$), goethite-J-13 (FeOOH.J-13), goethite-synthetic.J-13 (FeOOH.SYN.J-13), and goethite-$NaNO_3$ (FeOOH-$NaNO_3$), were prepared by dispersing a certain amount of hematite or goethite in a given amount of water using a sonifier/ cell disrupter for 10 minutes. The dispersed suspension was allowed to stand for 5 hours at room temperature. Thereafter, the supernatant solution was carefully collected and used as a colloidal solution. The pH of the colloidal solution was measured. The mass of the colloidal particles in the solution was determined by the difference in the weights before and after vaporizing (air-drying) and oven-drying (105^oC) a given amount of each solution. The particle size distribution of colloids in the solution was measured using a high sensitivity liquid in-situ spectroscopy (HSLS) from Particle Measuring Systems Inc. The surface area of hematite or goethite colloidal particles was measured using the sorption procedure of ethylene glycol monoethyl ether (EGME) described by Carter.

The net surface charge of the hematite or goethite colloidal particles was determined by titration methods (Gast, 1977; Zlazny and He, 1996). The titration curve is obtained by plotting the data as net charge ($\Delta H^+ - \Delta OH^-$) (Cmol kg^{-1}) versus pH (Zlazny and He, 1996). The titration curve was used to determine the net surface charge for a given pH and it was used to determine the zero point of charge (ZPC) of colloidal particles. From this, the surface electrical potential, ψ_o , of colloidal particles at a given pH was calculated using the Nernst equation (Gast, 1977; Zlazny and He, 1996):

$$\psi_o = [RT/F] \ln [(\alpha_{H+})/(\alpha_{H+})_{ZPC}] \qquad [3]$$

where ψ_o is the surface electrical potential in mV, R is the gas constant , T is the temperature (Kelvin), F is the Faraday constant, α_{H+} is the hydrogen ion activity at a given pH, and $(\alpha_{H+})_{ZPC}$ is the hydrogen ion activity at the pH of zero point of charge (ZPC).

Smectite Colloidal Solutions

Commercial smectite powder (particle size of < 1.0 μm) was used in this study. The cation exchange capacity (CEC) of smectite was determined using a method described by Sumner and Miller (1996). The colloidal solutions, including smectite -J-13, smectite-synthetic-J-13 (smectite-SYN.J-13) and smectite-$NaNO_3$, were prepared by applying the same method used for preparation of hematite and goethite colloidal solutions. The pH of each solution was measured and the mass of the colloidal particles, the particle size distribution, and the surface area of smectite colloidal particles in the solution were also determined by applying the same procedures used for hematite or goethite colloids.

Colloidal Silica Solutions

Synthetic colloidal silica solutions of PST-1 and SNOWTEX-ZL(ST-ZL), from Nissan Chemical Industries Ltd., were used. The solutions were manufactured by dispersing negatively charged amorphous silica particles in water. To clean the colloidal silica from surfactants (e.g., Na^+ and K^+), the following dialysis procedure was used. Approximately 50 ml of manufactured silica solution was diluted to 200 ml with nanopure water. The diluted colloidal solution was transferred to a 12,000-14,000 molecular weight cut-off membrane, referred to as dialysis tubing. The tubing was sealed and placed in a container with nanopure water. The surfactants of silica colloidal solution were washed by a diffusing-dialysis process. During the 50 days, the water in container was changed with fresh nanopure water at various periods of time. At the same time, 10 ml of cleaning colloidal silica solution were collected and filtered through a 0.05 μm nylon membrane by air-pressure method. The concentrations of Na, K, Ca, Mg, Si, and Al in the filtered solution were analyzed by ICP. The pH of colloidal solution and filtered solution was measured. After the colloidal solution was cleaned, the pH of the cleaned silica colloidal suspensions was adjusted to 8.4 by adding solid $NaHCO_3$ and Na_2CO_3. Then the silica colloidal suspension was stored in a refrigerator for later use. The mass of the colloidal particles in the cleaned solution was determined. Six work colloidal solutions, refereed to as PST-1.J-13, PST-1.SYN.J-13, PST-1.$NaNO_3$, ST-ZL.J-13, ST-ZL.SYN.J-13, and ST-ZL.$NaNO_3$, were prepared by diluting a certain volume of each cleaned silica colloidal solution to natural groundwater, synthetic groundwater, or $NaNO_3$ solution.

Plutonium Tracer Solutions

The Pu(V) stock solution contained 7.65 x10^{-4} M of Pu with 99.7% of Pu(V), 0.3% of Pu(VI), and consists of 93.9% of ^{239}Pu. Three diluted Pu(V) work solutions, referred to as Pu(V)-J-13, Pu(V)-SYN.J-13, and Pu(V)-$NaNO_3$, were prepared. The concentration of Pu for each solution was 2.74 x 10^{-7} M. The activities of the work solutions were determined using a liquid scintillation analyzer. The α activity of Pu(V) was 128,072 Bq kg^{-1} in Pu(V)-J-13, 124,790 Bq kg^{-1} in Pu(V)-SYN.J-13, and 126,819 Bq kg^{-1} in Pu(V)-$NaNO_3$. The pH values of the three work solutions are 8.22, 8.22, and 8.44, respectively.

Pu(IV) colloidal stock contained 0.012 M of Pu with 100% of Pu(IV) and consists of 93.8% of ^{239}Pu. A diluted Pu(IV) colloidal solution was prepared. The concentration of Pu(IV) was 5.12 x 10^{-4} M. The Pu(IV) colloidal particle size was 100Å. Three additional Pu(IV) colloidal work solutions, referred to as colloidal Pu(IV).J-13, colloidal Pu(IV).SYN.J-13, and colloidal Pu(IV)-$NaNO_3$, were prepared. The concentrations of Pu(IV) was 2.40 x10^{-7} M in the colloidal

Pu(IV).J-13 and colloidal Pu(IV).SYN.J-13 and 2.35 x10^{-7} M in the colloidal Pu(IV)-$NaNO_3$. The α activity of Pu (IV) was 116,095 Bq kg^{-1} in the colloidal Pu(IV)-J-13, 121,057 Bq kg^{-1} in the colloidal Pu(IV)-SYN.J-13, and 114,025 Bq kg^{-1} in the colloidal Pu(IV)-$NaNO_3$ solution. The pH values of these three work solutions were 8.18, 8.33, and 8.44, respectively. Throughout the experiment, the activity of each Pu work solution was frequently measured.

Sorption Procedure

Three sorption experiments, referred to as Sorption #1, Sorption #2, and Sorption #3 were performed in duplicate at room temperature. In Sorption #1, approximately 250 ml of hematite, goethite, smectite, or silica colloidal solutions were centrifuged at 38,300 g for 1 hour, resulting in the separation of colloidal particles from solutions. After separation, approximately 0.5 g of a colloid (e.g., hematite, goethite, smectite, or silica colloids) was transferred to an Oak Ridge centrifuge tube (50-ml). 20 mℓ portions of each ^{239}Pu work solution (e.g., Pu(V)-J-13, Pu(V)-SYN.J-13, colloidal Pu(IV).J-13, or colloidal Pu(IV).SYN.J-13) was added to the colloids and agitated on an orbital shaker at 150 rpm for 5 days. Blank samples were also set up using 20 mℓ portions for each ^{239}Pu work solution without hematite, goethite, smectite, or silica colloids. At the end of the sorption process, the samples and blanks were centrifuged at 38,300 g for 1 hour. The supernatant was filtered successively through a 0.45-μm and a 0.2-μm nylon syringe filter for hematite colloids, a 0.45-μm and a 0.1-μm nylon syringe filter for goethite and smectite colloids, and a 0.1-μm and a 0.05 -μm nylon filter membranes for silica colloids. The α activity of the filtered solutions was analyzed by the liquid scintillation analyzer. The adsorbed values of ^{239}Pu onto colloids of hematite, goethite, smectite, or silica were corrected with results from blank samples.

In Sorption #2, 20 ml portions of hematite, goethite, smectite, or silica colloidal solution and 1 mℓ of each ^{239}Pu work solution (e.g., Pu(V)-J.13, Pu(V)-SYN.J-13, colloidal Pu(IV).J-13, or colloidal Pu(IV).SYN.J-13) were placed into an Oak Ridge centrifuge tube (50-ml). The mixture was agitated on an orbital shaker at 150 rpm. The contact periods for colloids with Pu were 10, 30, 60, 240, 360, 1440, 2880, and 5760 minutes. At the same time, blank samples were also set up using 20 mℓ portions of iron oxide-free, smectite-free or silica-free J-13, or SYN.J-13 solution and 1 mℓ of each Pu work solution. At the end of each contact period, the solutions were separated by applying the same centrifuge and filter procedures used in Sorption #1. The adsorbed values of ^{239}Pu onto colloids of hematite, goethite, smectite, or silica were also corrected with results obtained from blank samples.

To examine possible influence of bicarbonate/carbonate on ^{239}Pu sorption, Sorption #3 was conducted to examine the adsorption of ^{239}Pu onto colloids of hematite, goethite, smectite, and silica in $NaNO_3$ solutions with pH 6.05 and pH 8.44. The ionic strength was kept the same as the natural and synthetic groundwater. The same procedures used in Sorption #2 were applied. The adsorption of ^{239}Pu onto silica colloids in $NaNO_3$ solution with pH 6.05 did not conduct due to silica colloids not being stable at pH < 7.0.

The sorption distribution coefficient (Kd_S) of ^{239}Pu onto colloids of hematite, goethite, smectite, or silica is calculated using the following equation:

$$Kd_S = [(A_oV_o - A_i)/M]/A_j \qquad [4]$$

where A_o is the initial α activity of Pu(V) or Pu(IV) per milliliter solution, V_o is the adsorptive solution volume (ml) in contact with colloidal particles, A_i is the total α activity of Pu(V) or

Pu(IV) remaining in the solution after sorption, A_j is the α activity remaining per milliliter solution, and M (g) is the mass of colloids used in the sorption process.

Desorption Procedure

Plutonium-239-loaded colloidal particles were obtained from Sorption #1. At the end of the sorption process, the colloidal particles were separated from liquid by centrifuge. After the wet weights of the colloids were obtained, the colloids were sequentially extracted several times. The extract periods were 2, 13, 35, 36, 21, 21 and 22 days. Each time, 5 ml of Pu-free J-13 or SYN.J-13 water was used. The same agitate, centrifuge, and filter procedures used in the sorption experiments were applied. The activity of ^{239}Pu in the extracts was measured using the liquid scintillation analyzer. Accumulated desorption data for 2, 15, 50, 86, 107, 128, and 150 days were reported.

The desorption distribution coefficient (Kd_D) of ^{239}Pu on colloids of hematite, goethite, smectite, or silica is calculated using the following equation:

$$Kd_D = [(A_S + A_rV_r - A_D)/M]/A_j \qquad [5]$$

where A_S is the sum of α activity of Pu(V) or Pu(IV) sorbed onto colloids, A_r is the radioactivity of Pu(V) or Pu(IV) remaining in per milliliter solution after sorption, V_r is the residual solution volume (ml) remaining after colloidal particles were separated from liquid at the end of the sorption process, A_D is the sum of α activity of Pu(V) or Pu(IV) desorbed from colloids into water at each extraction period, A_j is the desorbed radioactivity in unit solution, and M (g) is the mass of colloids used in the sorption process.

RESULTS AND DISCUSSION

Composition of the Waters

The natural groundwater from Well J-13 had a pH of 8.2 and an alkalinity of 22.5 meq L^{-1} and an ionic strength of 0.005 M. It contained 1.0 ppm of total organic carbon (TOC), 30.3 ppm of Si, 46 ppm Na, 13.3 ppm Ca, 1.9 ppm Mg, and 5.4 ppm K. It also contained small amounts of

Al (< 0.1 ppm), Fe (< 0.01 ppm) and Mn (< 0.01 ppm). The synthetic groundwater had a pH of 8.47, an alkalinity of 25 meq L^{-1}, and an ionic strength of 0.005 M.

Characterization of Hematite, Goethite, Smectite, and Silica

The synthetic hematite contained 99.6% of Fe_2O_3 and < 0.05% of SiO_2. X-ray diffraction showed that the mineral was a hematite. Approximately 51% of hematite particles were in size of 0.2 to 0.4 μm and 48% of particles were in size of 0.4 to 1.0 μm. The surface area of the hematite colloids was 5.35×10^4 m^2 kg^{-1}. The synthetic goethite contained 100% of αFeOOH. X-ray diffraction showed that the mineral was a goethite. About 97% of goethite particles were in size of 0.1 to 0.2 μm. The surface area of goethite colloids was 6.8×10^4 m^2 kg^{-1}.

The characterizations of hematite and goethite colloidal solutions are summarized in Table 1. The pH at the zero point of charge (ZPC) of the colloidal particles was around 8.0. The pH

Table 1. Characterization of Hematite and Goethite Colloidal Solutions.

Properties	hematite J-13	hematite SYN.J-13	goethite J-13	goethite SYN.J-13
pH	8.44	8.61	8.41	8.56
Particle size distribution (%)				
< 100 nm	0%	0%	0%	0%
100-200 nm	0.4%	0.4%	97.5%	97.5%
200-400 nm	51.6%	51.6%	2.5%	2.5%
400-1000 nm	48.4%	48.4%	0%	0%
Surface area (m^2 kg^{-1})	5.35×10^4	5.35×10^4	6.8×10^4	6.8×10^4
pH at ZPC	7.98	8.01	7.95	7.99
Net surface charge at initial pH (Cmol kg^{-1})	-1.53×10^{-5}	-2.31×10^{-5}	-1.45×10^{-5}	-2.08×10^{-5}
Surface electrical potential ψ_o(mV)	-27.14	-35.4	-27.14	-33.63

values of the colloidal solutions ranged from 8.4 to 8.6. At this pH range hematite and goethite colloidal particles exhibited net negative charge and the surface electrical potential, ψ_o , ranged from -27.14 mV to -35.4 mV. In natural groundwater, both hematite and goethite have the same surface electrical potential, while they have higher surface electrical potential in synthetic groundwater. However, in synthetic groundwater hematite colloidal particles have higher surface electrical potential than goethite colloidal particles.

The smectite mineral contained 52.0% of SiO_2, 16.2% of Al_2O_3, 1.34% of Fe_2O_3, 5.16% of MgO, 1.88% of CaO, 0.98% of Na_2O, 0.12% of K_2O, and 8.17% of water as well as CO_2 and volatile organic compounds. X-ray diffraction showed that the mineral was a smectite. Approximately 92% of smectite colloidal particles was in size of 0.1 to 0.2 μm and 7.4% of the particles was in size of > 0.2 μm (Table 2). The surface area of the smectite colloids was 8.33 x 10^4 m^2 kg^{-1}. The CEC of smectite was 152.4 Cmol kg^{-1}.

Table 2. Characterization of Smectite Colloidal Solutions.

	Smectite-J-13	Smectite-SYN.J-13.
pH	8.43	8.47
mass of colloids (g L^{-1})	1.07	0.89
Particle size distribution (%)		
< 100 nm	0	0
100 -200 nm	92	92
200-400 nm	7.4	7.4
>400 nm	0.5	0.5
Surface Area (m^2 g^{-1})	83.3	83.3
CEC (Cmol kg^{-1})	152.4	152.4

Manufactured colloidal silica solution of PST-1 contained 20% of SiO_2 and 80% water. The pH was 9.0. Particle size distribution analyses showed the work solutions of silica-PST-1 consisted of 71.4% colloidal particles with a size of 25 nm to 100 nm, 28.6% of the particles were < 25 nm. The work solutions of silica ST-ZL contained 85.5% colloidal particles with a size of 25 nm to 100 nm, and 15.5% of the particles were < 25 nm (Table 3). Stabilization was achieved by the repulsion between negative charges of particles (Nissan Chemical Ind. Ltd. 1994). A test showed that the stability of silica colloidal particles would be 250 years for both PST-1 and ST-ZL colloids at solution pH > 7.5 (Noell, 1996).

Table 3. **Characterization of Silica Colloidal Solutions.**

	Silica-PST-1 J-13	Silica-PST-1 SYN.J-13	Silica-ST-ZL J-13	Silica-ST-ZL SYN.J-13
pH	8.43	8.40	8.44	8.43
mass of colloids (g L^{-1})	1.0	1.0	1.0	1.0
Particle size distribution (%)				
< 25 nm	28.6	28.6	15.5	15.5
25 - 100 nm	71.4	71.4	85.5	85.5
> 100 nm	0.0	0.0	0.0	0.0
SiO_2 in colloidal silica stock (%)	20	20	40	40

Sorption of ^{239}Pu onto Colloids of Hematite, Goethite, Smectite, and Silica

The results obtained from Sorption #1 show that colloidal Pu(IV), as well as soluble Pu(V), was rapidly adsorbed by colloids of hematite, goethite, smectite, and silica in both natural and synthetic groundwaters. After 5 days, hematite colloids sorbed 100% of ^{239}Pu, goethite sorbed 97% to 100% of ^{239}Pu, smectite sorbed 94% to 100 % of ^{239}Pu and silica sorbed 46% to 86% of ^{239}Pu (Fig. 1).

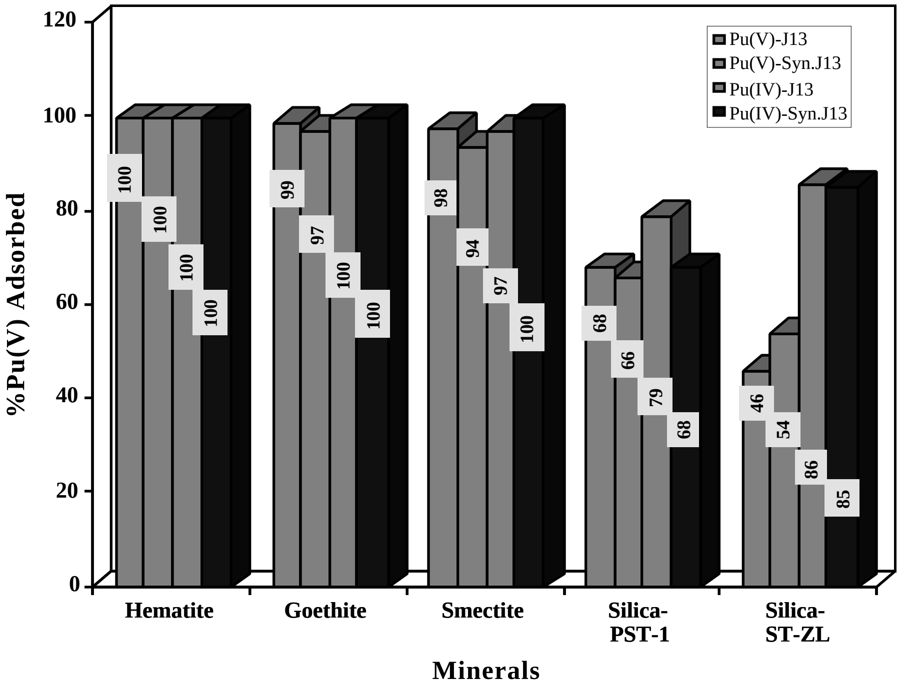

Fig. 1. **Percentage of ^{239}Pu Adsorbed onto Colloids of Hematite, Goethite, Smectite, and Silica in Natural and Synthetic Groundwater After 5 Days.**

Calculations show that one gram of hematite or goethite colloids sorbed 97,600 pCi of Pu(V) from both waters, 87,300 pCi of Pu(IV) from natural groundwater, and 97,100 pCi of Pu(IV) from synthetic groundwater (data not shown). In the case of smectite colloids, one gram of smectite colloids sorbed about 92,600 pCi of Pu(V) from both waters, 81,300 pCi of Pu(IV) from natural groundwater, and 94,100 pCi of Pu(IV) from synthetic groundwater. This indicates that these three colloids have a high capacity to sorb soluble Pu(V) as well as colloidal Pu(IV). Moreover, per gram of hematite, goethite, or smectite colloids sorbed almost the same amount of Pu(V) from both natural and synthetic groundwater. However, they sorbed more Pu(IV) from synthetic ground water than from natural groundwater.

In the case of silica colloids, silica-PST-1 colloid sorbed more Pu(V) than silica ST-ZL colloids did in both natural and synthetic groundwater. Silica-ST-ZL colloids sorbed more

Pu(IV) than silica-PST-1 colloids did. Generally, per gram of silica colloids sorbed a smaller amount of ^{239}Pu than hematite, goethite, or smectite colloids. One gram of silica-PST-1 colloids sorbed about 64,900 pCi of Pu(V) and 61,900 pCi of Pu(IV) from both waters. Silica-ST-ZL colloids sorbed about 45,700 pCi of Pu(V) and 80,800 pCi of Pu(IV) from both waters (data not shown).

Kinetics of ^{239}Pu Sorption

Adsorption of ^{239}Pu onto Hematite and Goethite Colloids

Adsorption of soluble Pu(V) In natural groundwater, the sorption of soluble Pu(V) by hematite or goethite was a slow process which involved two phases: a fast phase occurred in the first 60 minutes, followed by a slow phase of 5700 minutes (Fig. 2 and Fig. 3). In the fast phase, approximately 74% of soluble Pu(V) was adsorbed by hematite colloids and 81% of Pu(V) was adsorbed by goethite colloids. In the slow phase, an additional 19% to 26% of Pu(V) was adsorbed. At the end of the sorption process, the sorption distribution coefficient (Kd_S, ml g^{-1}) on the colloidal particles reached 10^5 order for both hematite and goethite colloids (Table 4).

In synthetic groundwater, the sorption of Pu(V) was faster than in natural groundwater. After 10 minutes, approximately 93% to 95% of Pu(V) was adsorbed (Fig. 2 and Fig. 3). At the end of the sorption process, 100% of Pu(V) was adsorbed by hematite or goethite.

Adsorption of colloidal Pu(IV) Sorption of colloidal Pu(IV) onto hematite and goethite colloids was rapid in both natural and synthetic groundwater. The sorption kinetics of colloidal Pu(IV) show a rapid process. After 10 minutes, approximately 95% to 100% of the Pu(IV) was adsorbed in natural groundwater, and 99% to 100% of Pu(IV) was adsorbed in synthetic groundwater (Fig. 2 and Fig. 3). The sorption distribution coefficient (Kd_S, ml g^{-1}) on the colloids reached 10^5 order for hematite and goethite in both waters (Table 4).

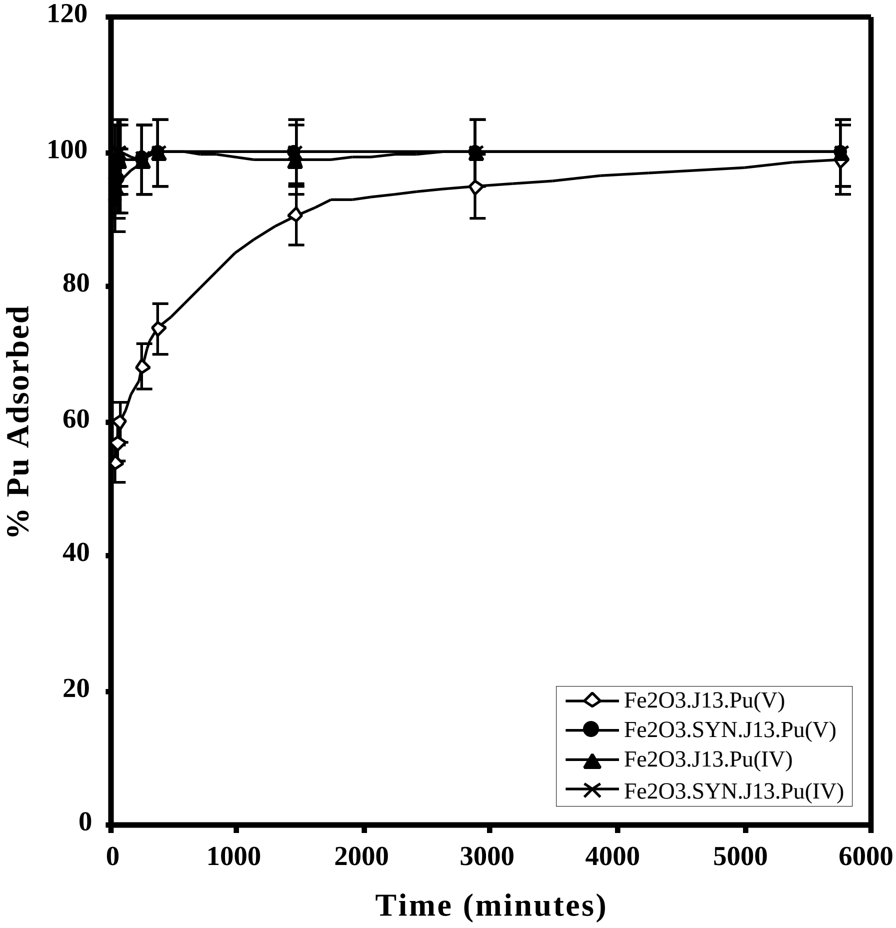

Fig. 2. Percentage of ^{239}Pu Adsorbed onto Hematite Colloids as a Function of Time in Natural and Synthetic Groundwater.

Adsorption of ^{239}Pu onto Smectite Colloids

Generally, smectite colloids sorbed less Pu(V), as well as colloidal Pu(IV), than hematite and goethite colloids did in both natural and synthetic groundwater. Moreover, smectite colloids sorbed more Pu in synthetic groundwater than in natural groundwater.

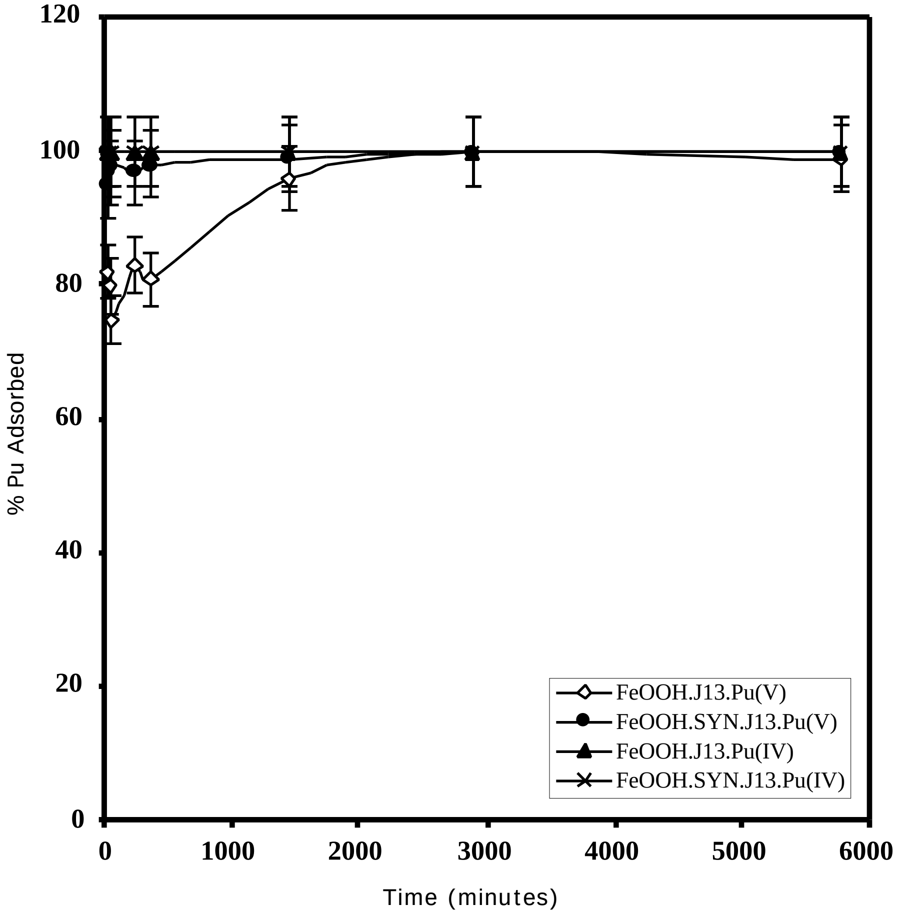

Fig. 3. Percentage of ^{239}Pu Adsorbed onto Goethite Colloids as a Function of Time in Natural and Synthetic Groundwater.

Adsorption of soluble Pu(V) Sorption of soluble Pu(V) by smectite colloids showed a typical curve of sorption rate versus time in both natural and synthetic groundwater. The adsorption of Pu(V) onto smectite colloids also involved two phases: a fast phase which occurred in the first 60 minutes, followed by a slow phase of 5700 minutes (Fig. 4). In the fast phase, approximately 55% of soluble Pu(V) was adsorbed in both waters. In the slow phase, an additional 35% to 42% of Pu(V) was adsorbed. At the end of the sorption process, the Kd_S values on smectite colloidal particles were 10 to 100 times lower than the Kd_S values on hematite and goethite colloids (Table 5).

Table 4. Sorption Distribution Coefficients (Kd_S, ml g^{-1}) of ^{239}Pu on Hematite and Goethite Colloids as a Function of Time in Natural and Synthetic Groundwater.

Mineral	Time (min.)	J-13. Pu(V)	SYN.J-13. Pu(V)	J-13. Pu(IV)	SYN.J-13. Pu(IV)
Hematite	10	1.2×10^3	1.7×10^4	1.6×10^4	2.2×10^5
	30	1.3×10^3	2.8×10^4	5.3×10^4	2.5×10^5
	60	1.5×10^3	2.8×10^4	9.7×10^4	2.6×10^5
	240	2.3×10^3	2.1×10^5	1.5×10^5	9.6×10^4
	360	3.0×10^3	6.0×10^5	2.1×10^5	2.0×10^5
	1440	9.9×10^3	-----	1.1×10^5	-----
	2880	1.9×10^4	-----	-----	-----
	5760	2.0×10^5	-----	-----	-----
Goethite	10	3.9×10^3	2.5×10^4	3.5×10^5	4.9×10^5
	30	3.2×10^3	3.6×10^4	1.5×10^5	2.3×10^5
	60	2.6×10^3	5.9×10^4	4.1×10^5	-----
	240	4.3×10^3	3.5×10^4	1.2×10^5	-----
	360	3.8×10^3	5.7×10^4	-----	-----
	1440	2.5×10^4	1.3×10^5	-----	2.4×10^5
	2880	2.0×10^5	2.6×10^5	-----	-----
	5760	1.2×10^5	3.5×10^5	1.5×10^5	3.3×10^5

Adsorption of colloidal Pu(IV) Sorption of colloidal Pu(IV) onto smectite was rapid in both waters. The sorption curve of colloidal Pu(IV) by smectite colloids showed a parabolic shape in natural groundwater. Approximately 71% of colloidal Pu(IV) was adsorbed onto smectite colloids during the first 10 minutes. The percentage of adsorbed Pu(IV) increased with time until it reached a maximum (86%) at 240 minutes, followed by a decrease to 77% at 2880 minutes where it remained throughout the final sorption period. This indicates that desorption may occur after 240 minutes. At the end of the sorption process, the Kd_S values for Pu(IV) were 10^3 to 10^5 order (Table 5).

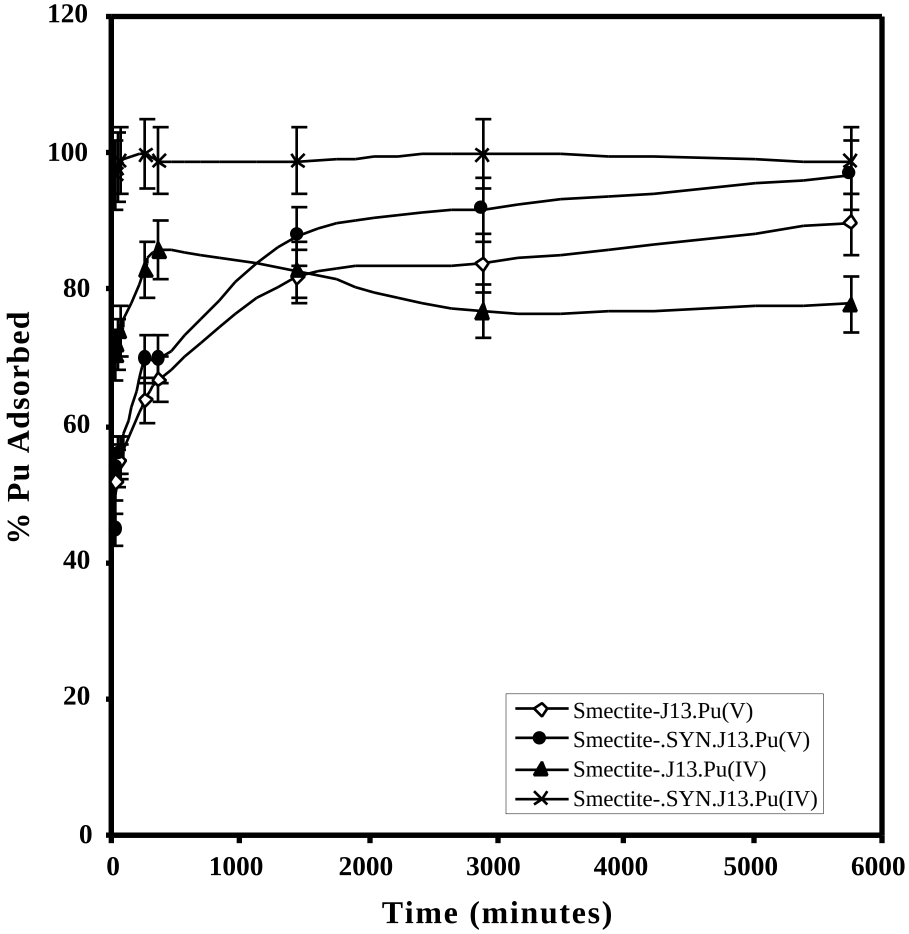

Fig. 4. **Percentage of ^{239}Pu Adsorbed onto Smectite Colloids as a Function of Time in Natural and Synthetic Groundwater.**

Adsorption of ^{239}Pu onto Silica Colloids

Generally, silica colloids sorbed less of Pu(V), as well as colloidal Pu(IV), in both waters than hematite, goethite, or smectite colloids did. Similarly, silica colloids sorbed more Pu from synthetic groundwater than from natural groundwater.

Adsorption of colloidal Pu(V) Sorption of soluble Pu(V) by colloidal silica PST-1 and ST-ZL in both waters is also a slow process. However, the sorption of ^{239}Pu by silica colloids is much slower than by hematite, goethite, or smectite colloids. After 60 minutes, approximately

Table 5. Sorption Distribution Coefficient Kd_S (ml g^{-1}) of ^{239}Pu on Smectite Colloids in Natural and Synthetic Groundwater.

Time (min.)	J-13.Pu(V)	SYN.J-13.Pu(V)	J-13.Pu(IV)	SYN.J-13.Pu(IV)
10	1.1×10^3	9.8×10^2	2.3×10^3	4.6×10^4
30	1.2×10^3	1.5×10^3	2.4×10^3	5.5×10^4
60	1.2×10^3	1.5×10^3	2.8×10^3	1.0×10^5
240	1.8×10^3	2.8×10^3	4.8×10^3	3.0×10^5
360	2.0×10^3	2.8×10^3	5.9×10^3	1.3×10^5
1440	4.2×10^3	8.3×10^3	5.3×10^3	1.8×10^5
2880	5.1×10^3	1.3×10^4	3.7×10^3	2.4×10^5
5760	6.4×10^3	3.8×10^4	3.5×10^3	1.4×10^5

20% of Pu(V) was adsorbed by both silica colloids (Fig. 5 and Fig. 6). An additional 34% to 43% of Pu(V) was adsorbed in 5700 minutes. At the end of the sorption process, 54% to 63% of Pu(V) was adsorbed. The Kd_S values on silica colloidal particles were 100 times lower than the Kd_S values on hematite and goethite colloids (Table 6).

Adsorption of colloidal Pu(IV) Silica colloids sorbed less of colloidal Pu(IV) in both waters than hematite, goethite or smectite did. Sorption of colloidal Pu(IV) was faster than sorption of soluble Pu(V). After 30 minutes, 69% to 76% of Pu(IV) was adsorbed by both PST-1 and ST-ZL colloids (Fig. 5 and Fig. 6). At the end of the sorption process, 78% to 96% of Pu(V) was adsorbed. The Kd_S values on the silica colloidal particles were 10 to 100 times lower than the Kd_S values on the hematite and goethite (Table 7).

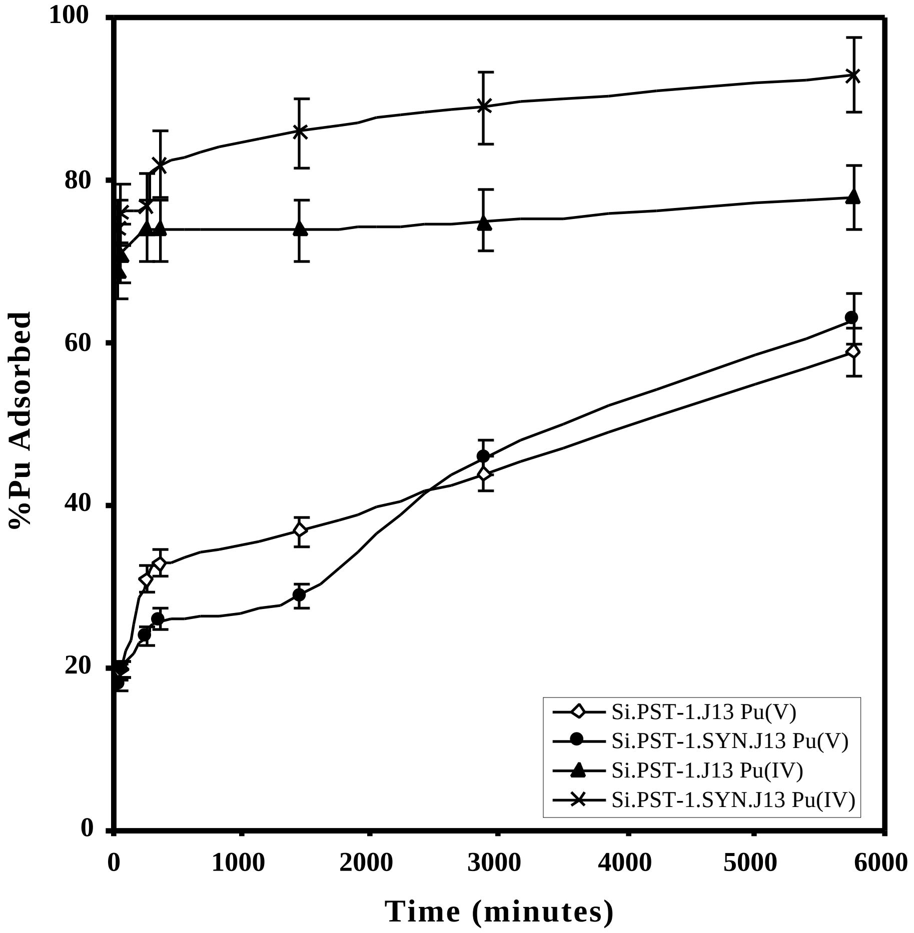

Fig. 5. Percentage of ^{239}Pu Adsorbed onto Colloidal Silica-PST-1 as a Function of Time in Natural and Synthetic Groundwater.

We observed that the sorption curve of soluble Pu(V) by colloids of hematite, goethite, or smectite in natural groundwater shows a typical curve of a first order reaction, in which the sorption rate depends upon the Pu concentration in the water. This mechanism can be described by following equation:

$$-\Delta[Pu] / \Delta t = k[Pu] \qquad [6]$$

where t is time, k is the rate constant.

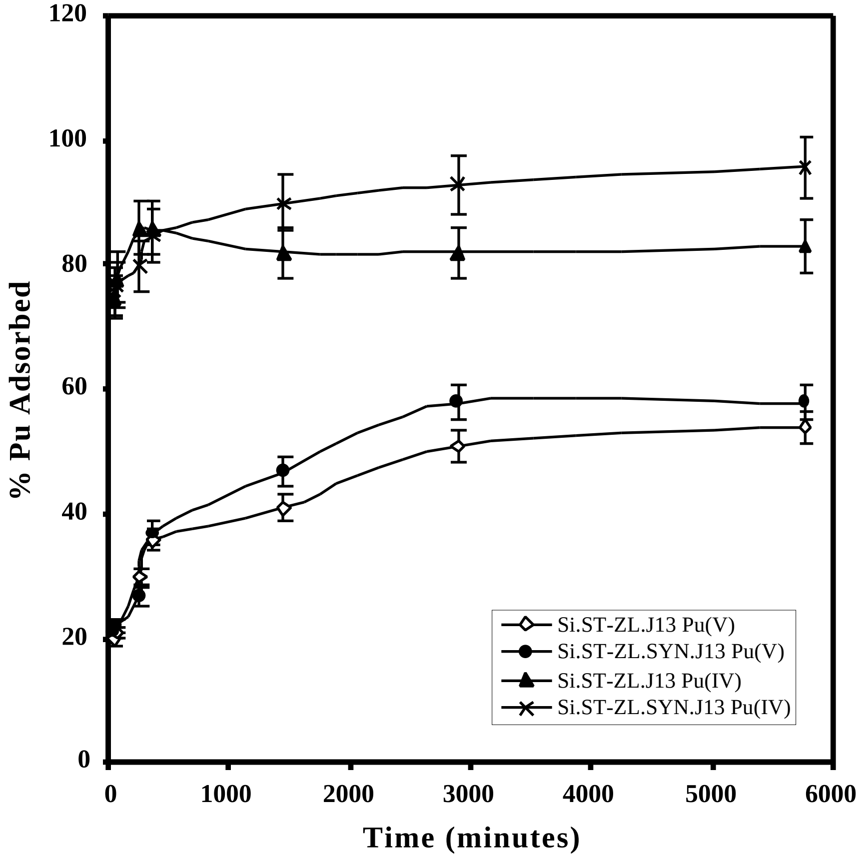

Fig. 6. **Percentage of ^{239}Pu Adsorbed onto Colloidal Silica-ST-SL as a Function of Time in Natural and Synthetic Groundwater**.

However, the sorption of Pu(V) by these four types of colloids in natural groundwater was slower than in synthetic groundwater. This is probable that hematite, goethite, and smectite, colloids may sorb dissolved organic carbon present in natural groundwater (1.0 ppm of TOC), resulting in less Pu being adsorbed. The concentrations of Na, K, and Mg did not change much in natural groundwater after sorption process. However, approximately 53% of Si was sorbed by hematite or goethite colloids, and 50% of Ca was sorbed by smectite colloids. This indicates that the presence of Si (30.3 ppm) and Ca (13.3 ppm) in natural groundwater may influence the adsorption of Pu. The pH of the waters did not Change much after sorption process, thus the

Table 6. Sorption Distribution Coefficient Kd_S (ml g^{-1}) of ^{239}Pu on Colloidal Silica-PST-1 in Natural and Synthetic Groundwater.

Time (min.)	J-13.Pu(V)	SYN.J-13.Pu(V)	J-13.Pu(IV)	SYN.J-13.Pu(IV)
30	2.5×10^{2}	2.2×10^{2}	3.2×10^{3}	3.7×10^{3}
60	2.5×10^{2}	2.5×10^{2}	3.2×10^{3}	3.7×10^{3}
240	4.5×10^{2}	3.1×10^{2}	3.4×10^{3}	4.0×10^{3}
360	4.7×10^{2}	3.5×10^{2}	3.3×10^{3}	6.2×10^{3}
1440	6.1×10^{2}	4.1×10^{2}	3.3×10^{3}	7.2×10^{3}
2880	8.0×10^{2}	8.5×10^{2}	3.5×10^{3}	1.0×10^{4}
5760	1.5×10^{3}	1.8×10^{3}	4.0×10^{3}	1.6×10^{4}

influence of pH can be ignored. It was reported that competition for site with Ca^{2+} significantly reduced NpO_2^{+} adsorption by smectite (Kozai et al. 1995).

Surface area of colloidal particles plays a major role in controlling the sorption rate of Pu(V) (Langmuir, 1997; Gast, 1977). Goethite colloids did have large surface area than hematite (Table 1). Therefore, goethite colloids provide a larger number of sorption sites for Pu(V) than hematite colloids, resulting in a faster sorption rate of Pu(V). Smectite colloids used in our study are a 2:1 layer silicate and Ca^{2+} is the exchangeable cation. The surface of smectite includes external and internal. As much as 80% of the total surface area of smectite colloids is due to internal surfaces (Borchardt, 1977). Although smectite colloids have a larger total surface area (83×10^{4} m^{2} kg^{-1}) than hematite and goethite colloids, the external surface area is smaller than the surface area of hematite and goethite colloids. Therefore the amount of Pu adsorbed onto

Table 7. Sorption Distribution Coefficient Kd_S (ml g^{-1}) of ^{239}Pu on Colloidal Silica-ST-ZL in Natural and Synthetic Groundwater.

Time (min.)	J-13.Pu(V)	SYN.J-13.Pu(V)	J-13.Pu(IV)	SYN.J-13.Pu(IV)
30	2.5×10^2	2.2×10^2	3.2×10^3	3.7×10^3
60	2.5×10^2	2.5×10^2	3.2×10^3	3.7×10^3
240	4.5×10^2	3.1×10^2	3.4×10^3	4.0×10^3
360	4.7×10^2	3.5×10^2	3.3×10^3	6.2×10^3
1440	6.1×10^2	4.1×10^2	3.3×10^3	7.2×10^3
2880	8.0×10^2	8.5×10^2	3.5×10^3	1.0×10^4
5760	1.5×10^3	1.8×10^3	4.0×10^3	1.6×10^4

the external surface of smectite is less than on the surface of hematite and goethite colloids. Even if smectite has a large internal surface area, colloidal Pu(IV) particles may not penetrate into the internal surface. Adsorption of Pu(V) onto the internal surface of smectite may occur but it is very slow. The Pu(V) ions must exchange with cations such as Al, Fe, and Mg which exist in the interlayer of the smectite structure. The Pu(V) as a PuO_2^+ ion in the water does not easily penetrate into the interlayer of the smectite structure and exchange with Al, Fe, or Mg ions.

Sanchez (1985) suggested that the sorption mechanism of soluble Pu(IV) onto goethite included four chemical reactions which formed four Pu(IV) hydrolysis species on the surface of goethite. The four species were $\equiv SO\text{-}Pu(OH)^{3+}$, $\equiv SO\text{-}Pu(OH)_2^{2+}$, $\equiv SO\text{-}Pu(OH)_3^{+}$, and ≡SO-

$Pu(OH)_4^0$, where ≡SO denotes surface sites on the colloids. However, in our research, sorption of colloidal Pu(IV) onto colloids of hematite, goethite, smectite, or silica may not necessarily follow this sorption mechanism. The Pu(IV) used in our experiments was in a colloidal form with a particle size of 100Å. The sorption mechanism of colloidal Pu(IV) onto these four types of colloids may include electric binding and particle interactions. In the case of electric binding, the pH of natural and synthetic groundwater ranged from 8.2 to 8.6. Under this pH range, the surface of colloidal Pu(IV) exhibits four positive charges. The surface electrical potential of hematite and goethite colloids ranged from -27.1 to -35. 4 mV (Table 1). The primary functional groups on the surface of hematite and goethite colloidal particles are OH^- . The surface of smectite particles also exhibits a negative charge and had a larger CEC (152.4 Cmol kg^{-1}). Smectite, as well as other 2:1 type of clay minerals, consists largely of Si^{4+} or Al^{3+} in tetrahedral coordination, and Fe^{3+}, Fe^{2+}, Al^{3+}, and Mg^{2+} in octahedral coordination. Ion size limitation generally results in a substitution of cations of lower valence for those of higher valence. This results in a net negative charge on the smectite structure (Gast, 1977). This charge is a permanent charge on the colloidal particles and it does not change with solution pH. The primary functional groups on the surface of smectite colloidal particles are also OH^- . The silica colloidal particles were spherical. Groups of -SiOH and -OH exist at the surface of the particles when the solution pH is greater than 7.0. Therefore, the negatively charged surface of these colloidal particles may electrostatically sorb (or bind) charged Pu(IV) colloids. At the same time, other cations, such as Si and Ca present in natural groundwater would compete with Pu(IV) for sorption sites on the surface of hematite, goethite, smectite, or silica colloids. This results in a less amount of Pu(IV) being adsorbed from natural groundwater than from synthetic groundwater. Colloidal particles of hematite, goethite, and smectite have a higher net negative charge than silica, thus these three colloids may have a stronger attractive force to colloidal Pu(IV) than silica.

In the case of particle interactions, the colloidal particles of hematite, goethite, smectite, or silica interact with Pu(IV) colloidal particles. Interactions between charged colloidal particles are the result of a balance between van der Waals attractive forces and several repulsive forces including electric double-layer repulsion and other short range repulsive forces (Van Olphen, 1963). In a clay-water system, or an iron oxide-water system, the electric double-layer repulsive forces are less than the van der Waals forces, resulting in a net particle attraction.

Sorption of soluble Pu(V) may be the result of a chemisorption or complexation process, in which the soluble Pu(V) or its hydrolysis species bind to hydroxyl (OH^-) groups on the surface of colloids of hematite, goethite, smectite, or silica. In both natural and synthetic groundwaters, the Pu(V) exists as PuO_2^+ form when the solution pH is less than 9 at room temperature (Clark, 1995). Assuming that Pu (V) binds to the surface (OH^-) groups analogous to aqueous coordination reactions, the adsorption of Pu(V) onto colloids of hematite, goethite, smectite, or silica can be chemically described by the following equation (Ling and McCarthy, 1995; Clark, 1995):

$$\equiv SOH + PuO_2^+ + H_2O \Leftrightarrow \equiv SO\text{-}PuO_2(OH)^0 + 2H^+ \qquad K_{1,\,app} \qquad [7]$$

where $\equiv SOH$ denotes a surface site, and $\equiv SO\text{-}PuO_2(OH)^0$ is the complex on the surface sites of colloids. $K_{1,\,app}$ is the apparent surface equilibrium constant and is defined as:

$$K_{1,\,app} = \{\equiv SO\text{-}PuO_2(OH)\}[H^+]^2/\{\equiv SOH\}[PuO_2^+] \qquad [8]$$

The complexes of $\equiv SO\text{-}Pu(OH)_2^{2+}$, $\equiv SO\text{-}Pu(OH)_3^{+}$ and $\equiv SO\text{-}Pu(OH)_4^{0}$ may also formed. However, the hydrolysis constants for adsorption of Pu(V) onto these colloids are not well known (Sanchez et al., 1985).

Influence of Carbonate

To examine possible influence of carbonate/bicarbonate on the sorption of ^{239}Pu, additional experiments were performed using $NaNO_3$ solutions with pH 6.05 and 8.44. Because colloidal silica is not stable at pH <7, we did not conduct the experiments with colloidal silica using $NaNO_3$ solution with pH 6.05. Results, obtained for the experiments using $NaNO_3$ with pH 8.44, show that the amounts of ^{239}Pu adsorbed by colloids of hematite, goethite, smectite, and silica were the same as those from synthetic groundwater (Table 8). This suggests that carbonate did not influence the adsorption of colloidal Pu(IV) or soluble Pu(V).

In natural groundwater, synthetic groundwater, or $NaNO_3$ solution with pH 8.44, the Pu(V) exists as PuO_2^{+} form because PuO_2^{+} does not hydrolyze below pH 9 (Clark, et al., 1995). The PuO_2^{+}, which is the dominant species, reacts with OH^- groups on the surface of colloidal particles, forming a $PuO_2(OH)$ complex on the surface of colloids. Synthetic groundwater has an alkalinity of 22.5 meq L^{-1} and a pH range of 8.4 to 8.6. Under this alkalinity level, HCO_3^- and CO_3^{2-} anions exist and the HCO_3^- anion is the dominant anion in the water. Some Pu(V), as PuO_2^{+} ions, may react with HCO_3^- and CO_3^{2-} ions to form $PuO_2(HCO_3)^0$, $PuO_2(CO_3)^-$, and $PuO_2(CO_3)_3^{5-}$ complexes (Clark et al., 1995). In the pH range of 8.4 to 8.6, the surface of colloidal particles of hematite, goethite, smectite, and silica exhibits net negative charges. The net surface charge is the sum of negative and positive charge effects. Thus, colloidal particles

Table 8. Comparison of ^{239}Pu Adsorbed onto Colloids of Hematite, Goethite, Smectite, and Silica in $NaNO_3$ Solutions with pH 8.44 to Synthetic Groundwater.

Minerals	Time (min.)	% Pu(V) adsorbed		% Pu(IV) adsorbed	
		$NaNO_3$ (pH 8.44)	SYN.J-13 (pH 8.44)	$NaNO_3$ (pH 8.44)	SYN.J-13 (pH 8.44)
Hematite	60	75	96	100	96
	1440	98	100	100	100
	5760	100	100	100	100
Goethite	60	99	91	100	92
	1440	100	97	94	100
	5760	100	98	100	100
Smectite	60	38	56	100	99
	1440	83	70	100	99
	5760	94	92	100	99
Silica-PST-1	60	18	18	84	76
	1440	38	29	96	86
	5760	61	63	97	93
Silica-ST-ZL	60	22	22	80	77
	1440	44	47	98	90
	5760	59	58	97	96

have a dominance of a negative charge for PuO_2^+ adsorption. However, at this same pH, the same number of coexisting positive sites can sorb $PuO_2(CO_3)^-$ and $PuO_2(CO_3)_3^{5-}$ anions. Therefore, the presence of carbonate/bicarbonate could not significantly influence the adsorption of Pu(V) by these four types of colloids.

Results, obtained from the experiments using $NaNO_3$ solution with pH 6.05, show the solution pH did not influence the sorption of colloidal Pu(IV) by hematite, goethite, or smectite (Table 9). The solution pH did not influence the sorption of soluble Pu(V) by goethite or smectite colloids either. However, the solution pH did influence the sorption of soluble Pu(V) by hematite. Amounts of Pu(V) adsorbed by hematite colloids in the solution with pH 6.05 were less than that in the solution with pH 8.44 (Table 9).

Table 9. Comparison of ^{239}Pu Adsorbed onto Colloids of Hematite, Goethite, and Smectite in the $NaNO_3$ Solutions in pH 6.05 and pH 8.44

mineral	time (minutes)	% Pu(V) adsorbed		% Pu(IV) adsorbed	
		pH 6.05	pH 8.44	pH 6.05	pH 8.44
Hematite	60	41	75	100	100
	1440	72	98	99	100
	5760	94	100	100	100
Goethite	60	95	99	100	100
	1440	100	100	100	94
	5760	100	100	100	100
Smectite	60	41	38	100	100
	1440	78	83	99	100
	5760	94	94	100	100

As mentioned above, sorption of colloidal Pu(IV) is rapid. The primary mechanism of adsorption of Pu(IV) colloidal particles is due to electric binding and particle interactions. Solution pH does not significantly influence these processes. Sorption of soluble Pu(V) may be the result of a chemisorption process, in which the soluble Pu(V) or its hydrolysis species bind to hydroxyl (OH^-) groups on the surface of colloids of hematite, goethite, and smectite. Solution pH does influence this process. Langmuir (1997) stated that adsorption of actinide cations increases with pH and has a strong pH dependence. This partly reflects competition with H^+ ions for adsorption sites. Cations whose adsorption edges occur at low pH values must form the strongest bonds with sorbent surface sites. The adsorption edges of weaker-bonding cations then occur at higher pH values.

In the case of hematite colloids, when the $NaNO_3$ solution pH value was 6.05 which was below the pH (8.0) of ZPC (Table 1), the surface of hematite colloidal particles exhibits positive charges (Gast, 1977). The positive charge sites on the hematite colloidal particles would expel some $Pu(V)O_2^+$ ions from the surface of hematite colloids lowering the amounts of Pu adsorbed. When the solution pH value was 8.44 which was above the pH of ZPC, the surface of the hematite colloidal particles exhibits negative charges. This results in a mutual attraction between the OH^- groups on the surface of colloids and PuO_2^+ ions to form surface complexes.

In the case of goethite colloids, goethite colloids had larger surface area than hematite colloids. The surface area controls the sorption rate of PuO_2^+ ions. Therefore, in the pH range of 6 to 8.44, the effect of pH on the sorption of PuO_2^+ ions may not be stronger than the effect of the surface area.

In the case of smectite, the negative surface charge formed due to structural imperfections resulting from ion substitutions. The CEC (152.4 Cmol kg^{-1}) represents the surface charges of smectite colloids. This charge is a permanent charge which does not change with solution pH. Therefore, the pH of the $NaNO_3$ solutions did not influences the sorption of PuO_2^+ ions. Amounts of Pu adsorbed by smectite colloids from the solution with pH 6.05 were the same as that from the solution with pH 8.44 (Table 9).

Desorption of Pu From Colloidal Particles

When the desorption process is compared with the sorption process, we found that the desorption process is much slower than the sorption process. After 5 days of sorption, about 97600 pCi g^{-1} of Pu(V) and 87300 to 97100 pCi g^{-1} of Pu(IV) were adsorbed by hematite and goethite colloids in both waters. After 150 days, less than 0.02% of Pu(V) was desorbed from hematite colloids in both waters (Table 10), which accounts for less than 13 pCi of Pu(V) being desorbed. The desorption distribution of Pu(V) on the hematite colloids ranged from 10^4 to 10^5 order (Table 11). Little colloidal Pu(IV) was desorbed from hematite colloids in both waters during the 150 days even when using sequential extraction under vigorous shaking conditions. At the end of the 150 day desorption process, the Kd_D value was in the order of 10^6 to 10^7

Desorption of Pu(V), as well as Pu(IV), from goethite and smectite colloids is rapid (Table 10). Even though desorption of Pu(V), as well as Pu(IV), from goethite and smectite colloids was faster than from hematite colloids in both waters, less than 1% of Pu was desorbed from goethite colloids after 150 days. This means that as much as 580 pCi of Pu was desorbed from goethite colloids during this period. Approximately 1.5% of Pu(V) and 2.5% to 11% of Pu(IV) were desorbed from smectite. This accounts for about 880 pCi of Pu(V) and 1570 to 6000 pCi of Pu(IV) being desorbed from smectite after 150 days. The Kd_D values on goethite or smectite colloids were 100 times lower than Kd_D values on hematite colloids (Table 11). The desorbed Pu may be readsorbed again by colloidal particles. Due to the rapid adsorption and slow desorption of Pu by these three types of colloids, the transport of ^{239}Pu along the potential flowpaths is facilitated by these colloidal particles passing through the porous media.

Desorption of Pu from silica colloids was much faster than from the other colloids. After 150 days, 6% to 11% of Pu(V) and 14% to 25% of Pu(IV) were desorbed from silica colloids. This means that as much as 4900 pCi of Pu(V) and 12350 pCi of Pu(IV) were desorbed during the

Table 10. Percentage of ^{239}Pu Desorbed From Colloids of Hematite, Goethite, Smectite, and Silica as a Function of Time in Natural and Synthetic Groundwater.

Minerals	Time (days)	% Pu(V) desorbed		% Pu(IV) desorbed	
		J-13	SYN.J-13	J-13	SYN. J-13
Hematite	2	0.005	0.0002	0.00	0.00
(< 1 μm)	15	0.006	0.0002	0.00	0.00
	50	0.011	0.0002	0.00	0.00
	86	0.011	0.0002	0.00	0.00
	107	0.012	0.0009	0.00	0.0003
	128	0.015	0.001	0.00	0.0005
	150	0.018	0.002	0.0001	0.0005
Goethite	2	0.14	0.09	0.07	0.11
	15	0.34	0.11	0.16	0.27
	50	0.57	0.20	0.36	0.34
	86	0.67	0.22	0.51	0.39
	107	0.74	0.24	0.53	0.41
	128	0.80	0.26	0.55	0.43
	150	0.86	0.27	0.60	0.45
Smectite	2	0.16	0.45	3.41	0.27
	15	0.33	0.64	5.24	0.44
	50	0.44	0.91	6.99	1.00
	86	0.53	1.02	7.98	1.25
	107	0.60	1.13	9.23	1.63
	128	0.68	1.28	10.41	2.09
	150	0.74	1.42	11.10	2.42
Silica-PST-1	2	5.32	3.63	9.34	3.54
	15	8.30	5.50	15.89	4.77
	50	9.62	5.87	18.70	11.58
	86	10.07	5.99	19.97	12.59
	107	10.44	6.09	21.52	13.41
	128	10.72	6.16	23.11	13.88
	150	10.94	6.19	23.46	14.01
Silica-ST-ZL	2	4.81	5.62	13.56	11.17
	15	6.59	9.41	19.04	15.24
	50	7.03	10.28	23.13	18.71
	86	7.23	10.42	23.61	20.50
	107	7.38	10.59	24.21	21.98
	128	7.48	10.67	24.81	24.17
	150	7.55	10.73	24.98	24.58

Table 11. Desorption Distribution Coefficient (Kd_D, ml g^{-1}) of ^{239}Pu on Colloids of Hematite, Goethite, Smectite, and Silica as a Function of Time in Natural and Synthetic Groundwater.

Minerals	Time (days)	% Pu(V) desorbed		% Pu(IV) desorbed	
		J-13	SYN.J-13	J-13	SYN.J-13
Hematite	2	1.33×10^5	2.88×10^6	----	----
(< 1 µm)	15	1.12×10^5	2.88×10^6	----	----
	50	6.61×10^4	2.88×10^6	----	----
	86	6.61×10^4	2.88×10^6	----	----
	107	5.96×10^4	7.83×10^5	----	----
	128	4.83×10^4	7.53×10^5	----	2.12×10^6
	150	4.33×10^4	4.95×10^5	1.15×10^7	2.08×10^6
Goethite	2	5.18×10^3	8.12×10^3	1.08×10^4	6.48×10^3
	15	2.08×10^3	6.11×10^3	4.57×10^3	2.56×10^3
	50	1.24×10^3	3.32×10^3	2.00×10^3	2.07×10^3
	86	1.04×10^3	3.09×10^3	1.38×10^3	1.78×10^3
	107	9.49×10^2	2.81×10^3	1.34×10^3	1.71×10^3
	128	8.87×10^2	2.67×10^3	1.29×10^3	1.63×10^3
	150	8.41×10^2	2.60×10^3	1.21×10^3	1.58×10^3
Smectite	2	3.83×10^3	1.55×10^3	2.00×10^2	2.63×10^3
	15	2.02×10^3	1.06×10^3	1.28×10^2	1.60×10^3
	50	1.51×10^3	7.49×10^2	9.52×10^1	6.93×10^2
	86	1.26×10^3	6.68×10^2	8.29×10^1	5.51×10^2
	107	1.12×10^3	6.03×10^2	6.91×10^1	4.23×10^2
	128	1.01×10^3	5.45×10^2	6.09×10^1	3.45×10^2
	150	9.52×10^2	5.04×10^2	5.66×10^1	3.06×10^2
Silica-PST-1	2	1.25×10^3	1.89×10^2	6.81×10^1	1.92×10^2
	15	7.98×10^1	1.23×10^2	3.86×10^1	1.42×10^2
	50	6.88×10^1	1.15×10^2	3.26×10^1	5.64×10^1
	86	6.57×10^1	1.13×10^2	3.04×10^1	5.17×10^1
	107	5.83×10^1	1.06×10^2	2.55×10^1	4.64×10^1
	128	5.47×10^1	1.02×10^2	2.15×10^1	4.42×10^1
	150	5.25×10^1	1.01×10^2	2.00×10^1	4.12×10^1
Silica-ST-ZL	2	1.44×10^2	1.22×10^2	4.63×10^1	5.77×10^1
	15	1.06×10^2	7.16×10^1	3.23×10^1	4.15×10^1
	50	9.91×10^1	6.53×10^1	2.61×10^1	3.32×10^1
	86	9.62×10^1	6.44×10^1	2.55×10^1	3.02×10^1
	107	8.69×10^1	5.92×10^1	2.14×10^1	2.53×10^1
	128	8.47×10^1	5.61×10^1	1.88×10^1	2.12×10^1
	150	8.18×10^1	5.47×10^1	1.73×10^1	1.97×10^1

150 day period. The forms of desorbed Pu in groundwater are not well understood. This indicates that, in a certain time (months), Pu would exist as both soluble and colloidal forms in groundwater and transport along the flowpaths if adsorbed onto silica colloidal particles.

Plutonium transport by colloids of hematite, goethite, smectite, and silica in groundwater may involve the following mechanisms. In porous media, the colloids with size smaller than the pores may migrate over long distances. O'Melia reported (1980) that colloidal particles with sizes ranging from 0.1 μm to 1.0 μm were the most mobile during natural gradient flow through a sandy porous medium, with larger and smaller colloids being preferentially removed. Moreover, reduction of Fe(III) coated on the clay particles would release the occluded Pu into water. We found that removal of iron oxide from clay particles by a reducing reagent dissolved large amounts of ^{239}Pu into solution (Lu et al., 1998). Anoxic conditions may also result in dissolving the ferric oxyhydroxide coatings which cement the clay particles to the aquifer solids (Ryan and Gschwend, 1990). This enhances the mobilization of clay colloids in groundwater.

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