Factors influencing plutonium sorption in shale media

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Summary. The extent and factors influencing sorption of plutonium (Pu) in shale media have been studied in batch-type experiments. The equilibrium time and isotherm of Pu sorption have been firstly determined. The effect of shale grain size, aqueous pH, water/solid ratio, co-existing ions (cations and anions) and temperature were studied as the factors likely to influence Pu sorption. The experimental variables included the following: grain sizes in five ranges, 0.12 to 0.15 mm, 0.15 to 0.18 mm, 0.18 to 0.25 mm, 0.25 to 0.38 mm, and 0.38 to 0.83 mm; solution pH values of 4, 6, 8, and 10; water/solid ratios of 10 : 0.25, 10 : 0.5, 10 : 0.75, and 10 : 1; temperatures of 20 °C, 40 °C, and 60 °C); and selected co-existing conventional cations including Na^+, Fe^+, Al^{3+}, Ca^{2+}, and K^+ and anions including SO_4^{2-}, CO_3^{2-}, NO_3^-, and Cl^- in each case in solutions of the same total ionic strength. The experimental results demonstrate that the equilibrium time of Pu sorption is 9 d, that the sorption behavior of Pu in the solution is well described by the Freundlich sorption isotherm ($C_s = kC_{eq}^N$), and that Pu is strongly sorbed on shale media. The extent of Pu sorption increased with decreasing grain size, apparently in response to the increase in specific surface area and total pore volume. The results also show that Pu sorption increases with increasing solution pH and with increasing water/solid ratio. The influence of co-existing anions on Pu sorption was much stronger, under the same conditions, than that of the cations; this was attributed to Pu complexation in solution, *i.e.*, the complexing apparently weakened the sorption of Pu on shale particles in the solution. Finally, the influence of varying temperature on Pu sorption is found to be less important than that of other factors, but should never be ignored.

1. Introduction

Clay rocks, shale in particular, represent approximately two-third of all shallow crustal sediments. In oil and gas drilling operations, shales constitute 80% of all drilled sections, mainly because they overlie most hydrocarbon bearing reservoirs (immature shale). Furthermore, several countries are considering clay rocks as possible host lithologies for radioactive waste repositories, and have been carrying out active research programs to evaluate the feasibility of such solutions [1]. It is therefore important to understand sorption behavior and factors affecting nuclide sorption in shale media.

It is widely accepted that the migration of radioactive contaminants in groundwater can be substantially affected by the presence and magnitude of contaminant sorption on the porous media. In recent years, a great deal of specific work has been conducted to improve our understanding of sorption and of the factors affecting the mobility of radio-elements in the environment. Examples include studies addressing: the effect of pH, soil humic/fulvic acid and ionic strength on the sorption of thorium(IV) onto silica [2], the relation of particle size and radionuclide distributions in Irish Sea surface sediments [3], the effect of solution composition on release of actinides (Np, Pu, Am) and Tc from nuclear glasses [4], the impact of clay mineral content and type, organic content, pH, ammonium content and potassium status on the environmental mobility of cesium [5], the effect of fulvic acid over a concentration range of 0–5 mg/L DOC on the sorption of ^{85}Sr, ^{137}Cs, ^{233}U, ^{238}Pu and ^{241}Am by crushed granite, biotite, goethite, montmorillonite and quartz [6], the effect of temperature, ionic strength and colloid concentration on the sorption and desorption behaviors of $^{239}Pu(V)$ [7], and so on. The present study focused on the factors affecting plutonium sorption in shale media.

Plutonium is one of the most toxic radioactive elements. Concerns arise because of the chemical and radioactive toxicities of α-particle-emitting ^{239}Pu, the very long half-lives of most of its isotopes, their tendency to accumulate in the human skeleton, and their high radio- and bio-toxicities. In the human body, Pu entering the blood rapidly associates with the Fe-transporting and storage proteins, transferrin and ferritin, and with the components of bone; it also forms insoluble deposits within the cells. From a purely chemical viewpoint, there is an important factor, the oxidation state of the element, which controls the element's solubility [8]. The knowledge of the oxidation states of Pu is important for predicting Pu mobility in waste solutions, and for predicting the nature and the charge of complexes formed, which influence the solubility in groundwater and the migration rate through the geo-media.

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Plutonium can exist in four major oxidation states from Pu(III) to Pu(VI) in solution [9]. Each of the different valence states undergoes hydrolysis, the tendency to do so decreasing in the order Pu(IV) $\gg$ Pu(VI) > Pu(III) > Pu(V) [10]. The higher oxidation states will form relatively soluble PuO_2^+ or PuO_2^{2+} species whereas the lower oxidation states will be more prone to hydrolysis and sorption [11]. Pu(IV) is the most readily hydrolyzed oxidation state, with the hydrolysis starting below pH 2.0. With increasing pH value, the (IV) and (VI) states can undergo polymerization, while disproportionation is a common feature of the chemistry of the (IV) and (V) states [10]. In moderate pH or oxygenated groundwater, Pu(III) is readily oxidized to Pu(IV). The aqueous phase concentration of plutonium is usually controlled by the presence of $Pu(OH)_4(s)$ or PuO_2, due to the extremely low solubility of these compounds. At concentrations high enough to cause homogenous precipitation of polymeric plutonium hydroxide or oxy-hydroxide species, colloidal forms of plutonium are produced *via* aggregation of $Pu(OH)_4(s)$ or $PuO_2(s)$. These colloidal forms of plutonium must be separated from the aqueous phase in order to differentiate between aqueous and solid plutonium phases [12].

Releases from nuclear reactors may contain Pu incorporated in fuel particles, Pu-colloids, oxidized forms [Pu(V), Pu(VI)], reduced forms [Pu(III) and Pu(IV)], or organic complexes [13]. Several field and laboratory studies have been carried out in an attempt to understand the relationship between Pu solubility and redox status of sediments. Studies of distributions in the solid phase have been interpreted to demonstrate a degree of Pu mobility [8], but this can be difficult to discern since the solid-phase concentration is much greater than the dissolved phase concentration.

For radioactive waste disposal sites, the groundwater is the main pathway for potential transport of radioactivity to the biosphere. The mobility of the element in geological media is governed by complex physico-chemical interactions which depend largely on the properties and characteristics of the element, the aquifer and the solid surface. The size distribution of actinides in natural waters depends on water chemistry (pH, ionic strength, inorganic components, and organic properties) and transport processes. Moreover, the groundwater chemistry of the radioactive elements in concentration ranges less than 10^{-12} M is very complex, and is affected by the presence of various anions, cations, carbonates and bicarbonates [14, 15].

The mobility of Pu depends largely on the extent to which it enters solution and is transported in the dissolved phase, as in the interstitial solution of soils, sediments or (especially) deep groundwater. The solubility of Pu, as noted above, is controlled by the oxidation state, and by some chemical reactions, such as adsorption and/or precipitation reactions. The way in which Pu partitions itself between possible species in any given environmental system is known to depend upon the chemical form in which it enters the system, as well as on redox conditions, pH, ionic strengths, the type and concentration of organic and inorganic complexing agents, and the extent of hydrolytic colloid formation [15]. In the simplest cases, the partitioning extent can be expressed through K_d, the distribu-

tion (or partition) coefficient, which is the ratio of the radionuclide concentration in the solid phase to the radionuclide concentration in the solution [16]. Sorption process is dynamic and complicated in groundwater within most geological media. For a quantitative evaluation of solute migration in geological media, the distribution coefficient is calculated from laboratory test data by means of Eq (1) [17].

$$K_d = \left(\frac{C_0}{C} - 1\right) \frac{V}{M} \tag{1}$$

Where K_d is the distribution coefficient; C_0 and C are the initial and the equilibrium concentrations in the liquid phase; V is the volume of the liquid (mL); M is the mass of the fine-particle soil (g). A higher K_d value means a higher sorption ability of soils with respect to the radionuclide and its correspondingly lower concentration in pore solution. The use of a distribution coefficient as calculated by Eq. (1) is dependent on numerous assumptions; among these, the most serious are the implicit assumptions that: (a) the reaction can be adequately represented by a reversible equilibrium between solution and solid, in which case K_d is simply the equilibrium constant for the reaction; (b) the system is actually at equilibrium.

Experimental determinations of K_d values are relatively easy to perform, commonly by "batch tests". However, the initial experimental conditions must be considered for K_d values being used to predict partitioning, as, for a given element, the distribution coefficient may depend on many environmental factors and/or experimental conditions, such as pH, the time needed for reaching equilibrium, the nature of particle and so forth [18]. Although there have been prolific K_d measurements, the experimental conditions affecting the measurements have often been insufficiently controlled during the experiments, and have rarely been described in adequate detail. The experimental conditions affecting K_d measurements include pH, solute concentration, temperature and pressure, physical, chemical and mineralogical characteristics of available sorbing surfaces, stirring rates and/or flow rates [19]. In other words, the factors affecting the sorption behavior of Pu in natural aquatic ecosystems are multiple and complex.

The distribution coefficient has been widely accepted in expressing the concentration ratio between the particulate phase and the dissolved phase under equilibrium conditions [20, 21]. However, in practice, detailed analysis of the speciation of transuranic elements in environmental samples is rarely possible. More commonly, K_d measurements form the basis of interpretation, with high K_d values (10^6-10^7) being used as evidence for the presence of reduced species and low K_d values (10^4-10^5) suggesting the presence of oxidized species [8].

The objectives of the present work were: (a) to confirm the equilibrium time of plutonium sorption on shale rock samples; (b) to determine Pu sorption isotherms and to analyze experimental data with an appropriate sorption model; and (c) to analyze the different influences of rock grain size, solution pH, water/solid ratio, temperature, and ion strength on Pu sorption in shale media.

2. Materials and methods

2.1 Samples

All groundwater and shale samples were collected from the candidate VLLW (very low level waste) disposal site in the Southwest of China, and all groundwater samples were taken from shallow groundwater by pumping from a bore-hole in the experiment field on Sep. 26, 2005. The pumped flow from the bore-hole was 0.3 L/s. The diameter and depth of the bore-hole were 130 mm and 34.5 m, separately. The water table was -7.5 m from the surface, and the sampling point was 1 m below the water table; the temperature of the groundwater was 16.5 °C. The groundwater samples were collected and transported following the protocols given in "Technical Specifications for Environmental Monitoring of Groundwater in China" [22]. The samples were colleted in polyethylene bottles of 5 L volume, one at a time, and were stored in a cool and dark place.

All rock samples were collected from the fresh and widely distributed shale rock of the experiment field, and were washed and oven-dried at 105 °C for 2 h, and then refrigerated to room temperature and crushed to different size fractions. The elemental compositions of powdered rock samples were analyzed by X-ray diffraction (XRD). Results for groundwater and shale samples were presented in Table 1.

2.2 Procedures of sorption experiments

All sorption experiments were performed in duplicate, and were carried out under constant temperature (20 ± 1 °C) (except for experiments specifically targeting the effects of t temperature variation) and at pH $= 7$ (except for experiments specifically targeting the effects of pH variation). The experimental procedures were as follows:

(1) Use a Pu standard solution (^{239}Pu(NO$_3$)$_4$, purchased from the National Institute of Meteorology, P.R. China), of a concentration of 40 Bq/mL, at an uncertainty of

6%, (no additional attempt was made to determine the oxidation state). Use a dilution concentration at 1.6 Bq/mL for the experiments;

(2) Weigh a rock sample of 0.5 g and put into a container of 20 mL, then pipet 10 mL groundwater, which was taken from the collected groundwater sample, and was deposited statically for a week;

(3) Add ^{239}Pu reagent (40 μL), then cover and shake vigorously and intermittently for 4 h every day. Shaking intermittently served to mimic a natural process and achieve adequate mixing;

(4) After centrifugal separation (15 min at 3000 rpm for the separation of solid phase from aqueous phase), measure the Pu concentration in the supernatant by a multi-channel low-background α counter, with a detection limit is 2×10^{-4} Bq. "Analytical Methods of Plutonium in Water" (Chinese National Criterion GB11125-89) was referenced [23];

(5) Repeat the same operation for the duplicate experiment;

(6) Calculate the K_d value according to Eq. (1); all the experimental data were the average of duplicate experiments. The relative errors of data were about 5%.

2.3 Design of sorption experiments

The sorption behavior of Pu in shale was investigated in seven group experiments to determine the equilibrium time and, sorption isotherm, and to study the effects of varying pH and other factors using a batch technique. Every individual sorption experiment was carried out according to the general steps and procedures given above; individual differences, are discussed below:

(1) Equilibrium time: the shale samples were divided and designated A and B. Sample A was tested to determine a general trend of the calculated K_d value with experiment time, using a relatively long shaking time (28 d); the testing points were chosen at the 1st, 4th, 8th, 10th, 16th and 28th day. And sample B was designed to determine the exact equilibrium time, using a small and exact interval according to the results of test A, the testing point was taken at every two days from the 3rd to 21st day.

(2) Sorption isotherms: the tested samples were divided and designated X and Y. The experimental data were obtained in the same way for each, except for the initial experimental concentration of Pu. The experiments on sample X were carried out with Pu initial concentrations of 0.087, 0.174, 0.348, and 0.522 Bq/mL; for sample Y, smaller initial concentrations of Pu were used, 0.0016, 0.0032 and 0.0048 Bq/mL .

(3) Rock grain size: the oven dried and crushed rock was sieved and divided into 5 test groups according to the grain sizes. The sieve sizes used were 20–40, 40–60, 60–80, 80–100, and 80–120 mesh (the number of holes per linear inch in a sieve), the conversions for particle diameter were 0.38–0.83 mm, 0.25–0.38 mm, 0.18–0.25 mm, 0.15–0.18 mm, and 0.12–0.15 mm.

(4) Aqueous pH value: in this test, the rock grain size used was that of the 0.18–0.25 mm sample, and the aqueous pH value was varied through values of 4, 6, 8 and 10. The pH values of the system were adjusted by adding

Table 1. Result of the groundwater and rock analysis.

	Groundwater data		Shale data	
Constituent	Data (mg/L)		Element/ oxide	Abundance (μg/g or %)
Ca^{2+}	66.53		As	1.32
Cl$^-$	6.03		Cd	0.097
CO$_3^{2-}$	0		Co	18.2
HCO$_3^-$	220.88		Cr	112
K$^+$/Na$^+$	6.67		Cu	40.6
Mg^{2+}	5.59		Mn	280
SO$_4^{2-}$	13.45		Ni	52.5
Total hardness	189.17		Pb	14.5
			Sc	20.4
pH	8		Ti	4344
			V	137
			Zn	117
			Zr	161
			Al$_2$O$_3$	18.70%
			CaO	0.20%
			MgO	1.80%
			Na$_2$O	0.30%
			SiO$_2$	61.20%

negligible volumes of 0.01 M HCl, and 0.01 M NaOH to achieve the desired pH;

(5) Water/solid ratio: the initial water/solid ratio was varied through the range 10 : 0.25, 10 : 0.5, 10 : 0.75 and 10 : 1 using a fixed rock grain size represented by the 0.18–0.25 mm shale sample;

(6) The influence of different co-existing conventional groundwater anions and cations were also investigated in 9 individual tests; the solutions used contained concentrations of, respectively, 0.1 mol/L of NaCl, NaNO$_3$, Na$_2$SO$_4$, or Na$_2$CO$_3$ (for the influence of anions) and 0.1 mol/L of NaCl, KCl, CaCl$_2$, AlCl$_3$, or FeCl$_3$ (for the influence of cations) reagents 2 mL under otherwise the same experimental conditions (0.18–0.25 mm rock grain size, 20 °C, water/rock ratio 10 : 0.5);

(7) Temperature: in these tests, the various temperatures were held at values of 20, 40 and 60 °C, respectively.

3. Results and discussion

3.1 Equilibrium time

Fig. 1 showed the relation between the sorption distribution coefficient of Pu and the contact time of the solid and liquid; this indicated the time required for Pu sorption to reach equilibrium.

The results showed that the Pu distribution coefficient initially increased with an increasing contact time, and tended to stabilize after a certain time. Test A showed a distinct sorption inflection point at about 10 d contact time, and Test B determined the equilibrium time more exactly to be 9 d. From the results of Test A and B, it could be seen that the K_d value was obviously increasing before the equilibrium time of 9 d, after which the sorption of Pu attained the equilibrium state. Therefore, for the subsequent experiments, a minimum shaking contact time of 9 d was maintained in order to assure that sorption equilibrium had been attained.

The necessity for a minimum time period to reach apparent equilibrium in the sorption of Pu from solution was also observed in prior work by Roussel-Debet [16] and the results ranged from approximately 200 to 300 h or more depending on the soil. Another prior result for the equilibrium time of Pu sorption was approximately 330 h [24].
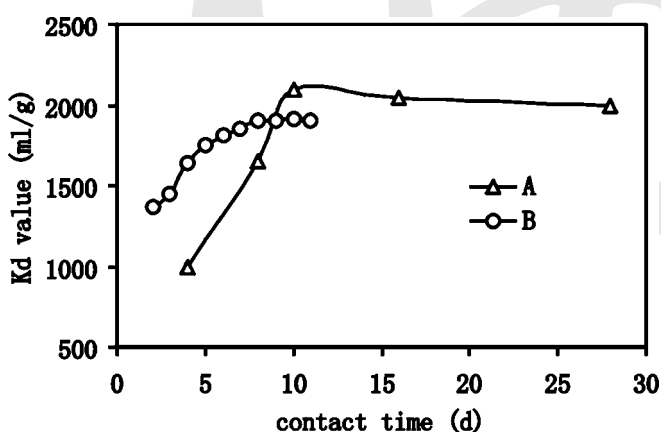
However, although the controlling initial experimental condition was the same, due to this difference of the consistent equilibrium time between A and B (no additional attempt we made can be the cause), some difference existed in the two results (Fig. 1). It was inferred that the possible reason for this difference was the slight difference of the mineral components between sample A and B, despite of the same sample weight.

3.2 Sorption isotherms

Fig. 2 showed the sorption isotherms of Pu onto shale rock at pH 7. Although the initial experimental concentration of the two samples (X and Y) was obviously different, a similar variation order could be seen in the sorption isotherms.

The Freundlich sorption model is an empirical relationship describing the sorption of solutes from a liquid to a solid surface; the equation is as follows:

$$C_s = k C_{eq}^N$$

or

$$\ln C_s = N \ln C_{eq} + \ln k .$$

Where C_s is the amount of Pu adsorbed per mass unit of solid, C_{eq} is the concentration of Pu in the supernatant after sorption and centrifugation, and N and k are empirical constants. Rock shale samples of 0.5 g and solutions of 10 m/L initial concentration were used in the isotherm experiments. The data from the isotherm experiments was shown in Table 2.
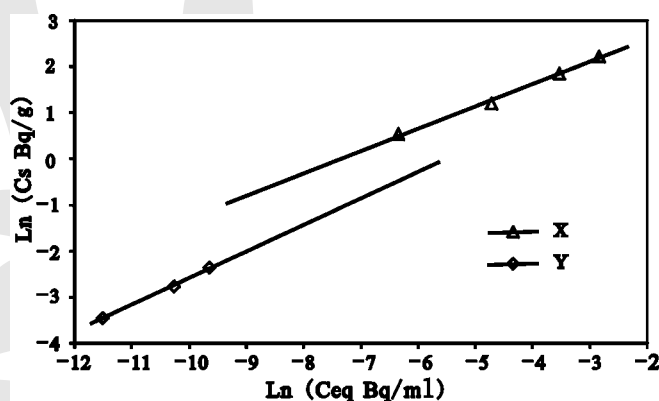

Fig. 2. Sorption isotherm of Pu.

Table 2. Data of the isotherm experiments.

Sample	Initial conc. (Bq/mL)	C_{eq} (Bq/mL)	C_s (Bq/g)	Relation equation
X	0.087	0.0175	1.705	$\ln C_{S(X)} = 0.4829 \ln C_{eq(X)}$
	0.174	0.09	3.3	$+3.5537$
	0.348	0.294	6.372	$R^2 = 0.9935$
	0.522	0.59	9.26	
Y	0.0016	0.0001	0.0318	$\ln C_{S(Y)} = 0.5781 \ln C_{eq(Y)}$
	0.0032	0.00035	0.0633	$+3.1987$
	0.0048	0.00065	0.0947	$R^2 = 0.9981$

Fig. 1. Time evolution of distribution coefficients.

Fitted isotherm parameters for Plutonium were presented in Table 2 and Fig. 2; the Freundlich model fit the sorption of Pu well. The N values approximately fluctuated near 0.5, which showed a strongly nonlinear sorption of Pu in the shale rock. It should be noted that the Freundlich isotherm has the capability of simulating an increasing ratio of adsorbing to aqueous concentration with increasing aqueous concentrations [19].

In prior work, results similar to those found in this study were obtained by Turin *et al.* [25], who performed field-scale unsaturated-zone tracer tests at Busted Butte, Nevada, near the potential high-level radioactive waste repository at Yucca Mountain, their conclusion was that plutonium sorption was markedly nonlinear, and that the Freundlich isotherm described Pu sorption quite well. Turin *et al.* attributed the behavior of Pu to the redox reactions, at higher concentrations, the disproportionation of Pu(V) leaded to an increased proportion of strongly sorbing Pu(IV) and an increase in apparent sorption [25]. However, a major problem limiting the application of the Freundlich model is that it only considers the total aqueous concentrations of the component, ignoring the thermodynamic properties of the constituent aqueous species (such as Pu with multiple oxidation states); it also ignores the speciation of the sorbing surface.

3.3 Influence of rock grain size

For this set of experiments, sieved samples were divided into 5 groups; every group was a mixture of particles falling within the designated sieve range; for example, for particles in the sieve interval from 0.12 to 0.15 mm, the diameter of all particles in the group fell between 0.12 and 0.15 mm, and the calculated K_d values were plotted against the average size of each range. Fig. 3 showed the trend of sorption of Pu with the different rock grain sizes used in the experiment.

The results showed that, the general trend of distribution coefficient of Pu with rock grain size was that the K_d value decreased with increasing grain size; the trend was obviously rapid when the grain size was less than 0.2 mm, while above that ranged the rate of decrease in distribution coefficient with increasing grain size was slowly reduced.

In prior work, Gouzy *et al.* obtained a similar decreasing trend at grain sizes smaller by an order of magnitude (< 50 μm), they concluded that the plutonium adsorption was a predominantly non-selective surface process and depended on the specific surface area of the sediment, which dramat-

ically increased as the average decreased grain size [26]. Thus it can be inferred that, because the surface texture of the shale grain varies with the grain size of rock, the specific surface area and total pore volume should increase with decreasing grain size [27], and the sorption of Pu should be enhanced with it. However, a problem remains in that the surface areas of the various particle size fractions is unknown both in the present study and in prior work, and without that information it is difficult to explain the drastic change in the data trend below the 0.2 mm particle size.

3.4 Influence of aqueous pH value

The pH value often has a major influence on the mobility and the adsorption process of radionuclides in soil. The influence of aqueous pH value on the sorption of Pu, as derived from the experiments targeting that issue, was shown in Fig. 4.

The results showed that pH value clearly influences the sorption distribution coefficient of Pu. The sorption of Pu increased with increasing pH within the pH range from 4 to 10, although the increasing trend was a bit slow when pH < 6. The results could reflect that the hydrolysis behavior of Pu has a strong effect on sorption.

Under typical environmental conditions, plutonium is known to exist in four different oxidation states (*i.e.*, +3, +4, +5, and +6). Under reducing conditions, the +3 and +4 oxidation states would be the most stable, with the +3 state dominating at pH values below 8.5, and the +4 state dominating at pH values above 8.5. Under oxidizing conditions, the +4, +5, and +6 oxidation states exist at pH values above 4.0 [28]. Choppin and Morgenstern concluded that "in most natural systems", plutonium was found in the +4 and +5 oxidation states, and that while dissolved plutonium could be in either the +4 or +5 redox state, "most adsorbed plutonium" is found to be in the +4 redox state [29]. In noncomplexing media, the hydrolysis of Pu(III) occurs around pH 5, whereas the hydrolysis of Pu(IV) was already significant by pH 1. Under slightly acidic conditions, the hydrolysis of Pu(IV) could result in the formation of a hydroxy polymer which ages to the intractable oxo polymer. Choppin *et al.* (1997) has shown the speciation of the Pu(IV) mononuclear hydrolysis products as a function of pH [30].

More detailed descriptions of the influence of pH in sorption experiments were given by Lujanlene *et al.*, Dhami *et al.* [31, 32] and Banik *et al.* [24]. Banik *et al.* found that
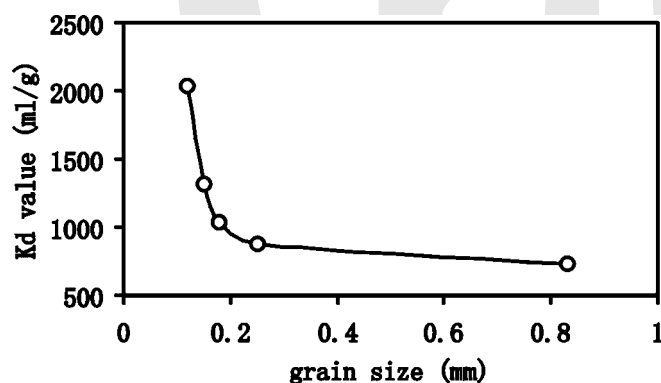
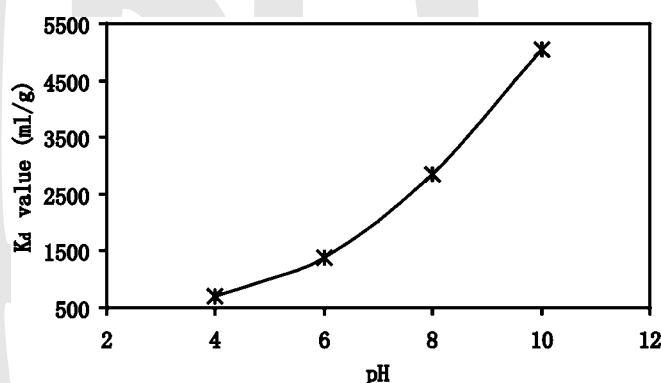**Fig. 3.** Influence of rock grain size on the sorption of Pu.

Fig. 4. Influence of aqueous pH value on the sorption of Pu.

the initially added Pu(IV) at pH 4 to pH 6 had been partially oxidized in solution to Pu(V) and that the sorption of Pu(V) onto kaolinite was weaker than that of Pu(IV) for that pH range.

3.5 Influence of water/solid ratio

Fig. 5 showed the influence of water/solid ratio on Pu sorption in the shale rock as given by the experimental results.

The water/solid ratio is a parameter for describing the relative influences of rock and solution composition on the nature of alteration processes during fluid-rock reaction. From Fig. 5, as expected, it was clear that the distribution coefficient of Pu sorption decreased with the decreasing water/solid ratio, and that the trend of the K_d values was the same changing consistent with the sample ratio. In this study, the water/solid ratio was taken as the reactant mass of fluid divided by the reactant mass of solid. Under this definition the grain-size of starting solids was assumed to be small enough for the entire mass of solids to be available for reaction. At higher values of water/solid ratio, there were fewer grain-size groups of rock, and greater sorption mass of Pu, so that the distribution coefficient was enhanced, and these groups could achieve strong complexes. Therefore, the extent of these effects depended upon the ratio between the water/solid and the mineral phases.

In prior work, without question, the water/solid ratio had been shown to have a large effect upon the nature of fluid and solid products during hydrothermal reactions (*e.g.*, Seyfried and Bischoff 1977) [33]. The water/solid ratio defined by area/volume may be a more meaningful parameter (Lasaga 1984) [34]. In an example of an interaction of granite with meteoric fluid, Savage (1988) indicated that at low water/solid ratios, the character of hydrothermal alteration products was dominated by the chemical composition, while conversely, hydrothermal alteration at high water/solid ratios leading to the replacement of the rock constituents by chemical components from the fluid and the alteration [35].

3.6 Influence of different ions (cations and anions)

In order to investigate the influence of different ions, including some cations and anions, the K_d value of Pu in a series of different ionic solutions was investigated. These experiments were performed in the presence of the crushed rock samples, the results were shown in Fig. 6.
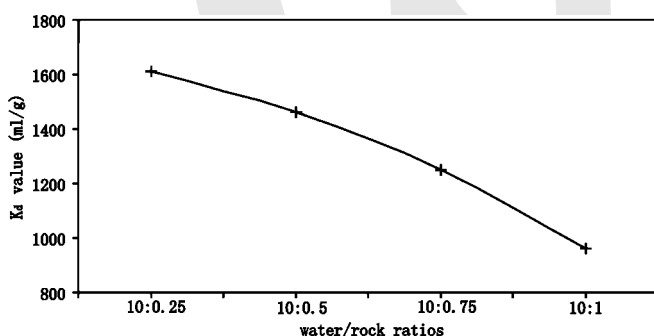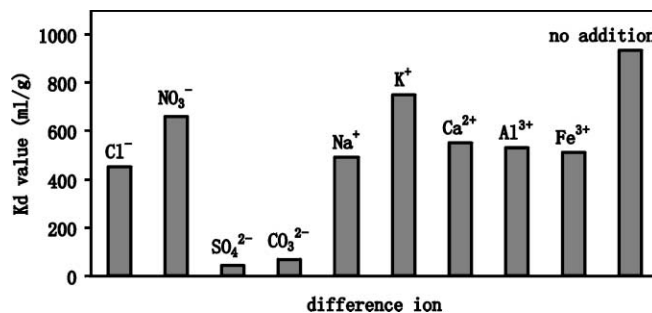

Fig. 6. Influence of different ions (4 cations and 5 anions) on the sorption of Pu.

For the cations, in contrast to the test without added ions, the K_d value of Pu were only weakly influenced to decrease somewhat. The order of the influence of cations was $Na^+ > Fe^+ > Al^+ > Ca^+ > K^+$, which suggested that the K^+ affected the Pu sorption the least. In contrast to the cation effect, the addition of certain anions had a significant influence on K_d values; the sorption of Pu was strongly influenced by adding SO_4^{2-} and CO_3^{2-}. A similar result was reported by Xia *et al.* [36], who concluded that "the distribution ratio of Pu(IV) between the organic and aqueous phases was found to decrease as the concentrations of sulfate were increased". On the other hand, the effects on Pu sorption by NO_3^- and Cl^- were weak. Overall, the results showed that the influence of complex divalent anions was much more important than that of other anions. The reason may be that the complexation of strong complex ions with the Pu ion in solution buffered the sorption capacity with shale particles. In summary, compared with the anions, the effect on K_d values by the cations was smaller under the same conditions. This suggested that cation exchange capacity could not be the mechanism of sorption of Pu.

In prior work, the general trend in the strength of the complexed species for actinides and various groundwater ligands has been investigated and reported as follows: $OH^- \geq CO_3^{2-} > F^- > HPO_4^{2-} > SO_4^{2-} > Cl^- > NO_3^-$ [37]. In investigating the sorption behaviors of $^{239}Pu(V)$ on three types of inorganic colloids (hematite, montmorillonite and silica), it was found that: ionic strength did not significantly affect the adsorption of $^{239}Pu(V)$ onto hematite colloids, while an increasing in ionic strength decreased the adsorption of ^{239}Pu onto montmorillonite and silica colloids [7]. In research on the adsorption of Pu(IV) and Pu(V) on goethite (α-FeOOH) from $NaNO_3$ solution, it was found that increasing ionic strength (from 0.1 to 3 M NaCl or $NaNO_3$ and 0.03 to 0.3 M Na_2SO_4) did not affect Pu(IV) or Pu(V) adsorption [38].

3.7 Influence of temperature

The correlation of K_d value of Pu and temperature was shown in Fig. 7.

It could be seen from Fig. 7 that as temperature rising from 20 to 40 °C, the distribution coefficient value increased, and then decreased slowly as the temperature increases further to 60 °C; the turning point appears approximately at 40 °C. The K_d values ranged from 1200 to 1800 mL/g at above temperature. The influence of temperature on Pu sorption was smaller than that of the other factors (*e.g.* pH,
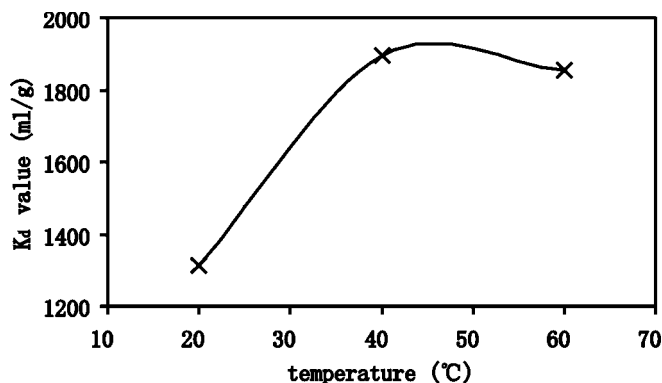

Fig. 5. Influence of water/rock ratio on the sorption of Pu.

Fig. 7. Influence of temperature on the sorption of Pu.

water/solid ratio), but temperature should not be ignored as an influencing factor in the sorption of Pu onto shale media.

In prior work, Runde *et al.* (2002), in a study of Pu-bearing precipitates on inorganic colloidal particulates in J-13 water from the Yucca Mountain site, it was reported that Pu solubility at pH values of 6, 7 and 8.5 and temperatures of 25 °C, 60 °C, and 90 °C, respectively. Their data showed that, at pH of 6, Pu solubility decreased from 5×10^{-8} to 4×10^{-9} mol/L with the temperature changing from 25 °C to 90 °C, and the same changing trend at pH 7 and 8.5 [39]. Lu *et al.* (2003) reported that temperature did not significantly influence the adsorption of ^{239}Pu(V) onto hematite and silica colloids, but that the adsorption of ^{239}Pu(V) onto montmorillonite colloids increased significantly with the increasing temperature [7].

Our experimental results indicated that when the temperature was nearly 40 °C, Pu sorption was at a maximum. Subsequent research should further address this question of the temperature at which maximum sorption of Pu occurs in shale media.

4. Conclusions

There have been relatively few studies of Pu sorption on shale media, although several studies involving other media have been made. The experiments reported herein investigated the sorption behaviors of ^{239}Pu(IV) on shale media, with the adsorption being measured as a function of grain size, pH, water/solid ratio, ionic composition and temperature. From the experimental results, the following conclusions can be made: (1) the sorption of Pu onto shale grains is strong and the sorption equilibrium time is about 9 d; (2) the sorption behavior of Pu in solution can be expressed well by the Freundlich sorption isotherm ($Q = kC^N$); (3) the sorption extent of Pu increases with decreasing grain size owing to the specific surface area and total pore volume of the finer particle; (4) the diversification of the oxidation state of Pu in the sorption reaction, and consequently the K_d value for shale media, increases with increasing pH of the solution; (5) the sorption of Pu decreases as the water/solid ratio decreases; (6) the presence of other cations in solution has a smaller effect on the K_d value for Pu than does the presence of anions under the same conditions, which suggests that cation exchange

is not the mechanism of sorption of Pu; (7) the influence of temperature should be considered as a sorption factor for Pu on shale, although it is not as significant as other factors.

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