FACTORS INFLUENCING U(VI) ADSORPTION ONTO SOIL FROM A CANDIDATE VERY LOW LEVEL RADIOACTIVE WASTE DISPOSAL SITE IN CHINA

by

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The properties of soil at disposal sites are very important for geological disposal of very low level radioactive waste in terms of U(VI). In this study, soil from a candidate very low level radioactive waste disposal site in China was evaluated for its capacity on uranium sorption. Specifically, the equilibrium time, initial concentration, soil particle, pH, temperature, and carbonate were evaluated. The results indicated that after 15-20 days of sorption, the K_d value fluctuated and stabilized at 355-360 mL/g. The adsorptive capacity of uranium was increased as the initial uranium concentration increased, while it decreased as the soil particle size increased. The pH value played an important role in the U(VI) sorption onto soil, especially under alkaline conditions, and had a great effect on the sorption capacity of soil for uranium. Moreover, the presence of carbonate decreased the sorption of U(VI) onto soil because of the role of the strong complexation of carbonate with U(VI) in the groundwater. Overall, this study assessed the behavior of U(VI) sorption onto natural soil, which would be an important factor in the geological barrier of the repository, has contribution on mastering the characteristic of the adsorption of uranium in the particular soil media for the process of very low level radioactive waste disposal.

Key words: uranium, soil, adsorption, influencing factor, batch test, very low level radioactive waste

INTRODUCTION

The rapid development of nuclear power plants has caused an increase in the quantity of radioactive waste (RW) [1], which has led to increasing interest in the treatment of wastewater with low-levels of radioactivity (LLRW). Radioactive uranium, which is one of the main contaminants in LLRW, needs to be managed because of its high toxicity, long half-life ($^{238}\mathrm{U}t_{1/2} = 4.51\ 10^9$ years), and its resistance to degradation methods to remove uranium from wastewater such as chemical precipitation, evaporation concentration, solvent extraction, membrane dialysis, and adsorption [2]. Among these, adsorption is among the most efficient method of treatment. Near-surface and deep geological disposal are the safest and most effective disposal methods for radioactive wastes with different levels of radioactivity [3, 4]. During the RW disposal process and monitoring period, uranium can be discharged into the biosphere through the unsaturated or saturated zone [5] because of geological activity and climate variations.

Adsorption of uranium by soils (including sand, clay, or clay minerals) such as quartz sand [6], illite, bentonite [7], podzol [8], phyllite [9], and diatomite [10] plays an important role in geological disposal and element migration. Previous studies have investigated high quality sorption treatments for the removal of uranium from waste or waste water and examined U(VI) removal from the aqueous environment using different adsorbents with characteristics such as a high specific surface area, negative surface charge, and effective cation exchange capacity [3, 11]. However, for geological disposal of radioactive waste, greater attention should be paid to the role of the geological barrier, and specific conditions that could affect the migration of uranium, such as temperature, equilibrium time, ion concentration, redox conditions, and humic acid (HA) content

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[12-14]. For the sorption of nuclides onto soil, the extent of partitioning could be expressed as K_d, which is the distribution (or partition) coefficient used to describe the distribution ratio of the radionuclide concentration in the solid phase to the radionuclide concentration in the solution. Because the distribution coefficient is easily measured and calculated, it is directly comparable under similar experimental conditions. For most radionuclides, including uranium, sorption onto soil is influenced by time, temperature, pH, ionic strength, and different coexisting ions [15, 16].

Batch tests and column experiments are the laboratory methods most commonly-used to examine uranium adsorption on soil [6, 9]. Batch tests are the main method employed to obtain the distribution coefficient for assessing the influence of different factors on the sorption process [9]. The results from batch tests and batch-derived parameters can be used to represent environmental conditions, observe chemical equilibrium processes through a full contact reaction between nuclear and soil media, and to describe surface complexation under different conditions. Research in recent years has made considerable progress, with more attention focused on the effects of experimental conditions. Kim *et al*. [17] used batch tests to investigate the influence of environmental parameters on U(VI) sorption in the presence of different kinds of saprolite derived from interbedded shale, and the results showed that the process was strongly dependent on pH. Bruno *et al*. [18] used breakthrough curves to study uranium sorption onto kaolinite, montmorillonite, HA, and composite clay material, and found that pH and ionic strength had a significant influence on the sorption of uranium ions. Kohler *et al*. [19] used batch tests to study U(VI) transport under variable chemical conditions and found that U(VI) could complex with metal ions in porous media, and that surface complexation changed as the pH and U(VI) pulse concentrations changed. Similarly, column experiments could provide an important means for observing the retention and migration of radionuclides [6, 20]. For example, Nagasaki [21] used column experiments to investigate the migration of U(VI) ions in montmorillonite colloids in the presence and absence of HA, while Khalili *et al*. [22] used column experiments to examine the sorption of U(VI) and Th(IV), and to determine the metal ion loading capacity.

In this study, samples of natural groundwater and soil were collected from a candidate very low level radioactive waste (VLLW) disposal site [23] in southwest China. We conducted batch tests to examine U(VI) adsorption as a function of equilibrium time, U(VI) concentration, soil particle size, pH, temperature, and carbanion. The goal of the study was to examine the kinetic and equilibrium adsorption of U(VI) onto natural soil, which would be a geological barrier of the repository, to determine the influence of various parameters on U(VI) sorption, and to investigate whether it is possible to artificially change these conditions to develop an optimum adsorption effect during the construction and operation of the repository.

MATERIALS AND METHODS

Batch sorption tests of U(VI) using groundwater and soil samples from a VLLW disposal site were conducted, and the thermodynamic parameters of U(VI) sorption behavior in soil were examined based on sorption tests, equilibrium time, and isotherms of U(VI) sorption in soil. In addition, the effects of particle size, temperature, pH, and ionic concentrations of the sorption solution on the K_d value of U(VI) were examined.

Description of the sample site

The VLLW disposal site was in the northern part of Longmen Mountain in southwest of China, on narrow, elongated river terraces at the confluence of the main river and one of its tributaries. The repository, which covered an area of 125 80 (10,000) m^2 and was 20 m deep, was in the center of the site. The majority of the area is dominated by Silurian strata, but a Quaternary stratum is clearly visible along the river valley. Three boreholes were constructed through the rock layer on the river terraces to facilitate collection of the groundwater and soil samples. The stratigraphic column, which had a columnar cross-section, spanned the lithological formations and the depth of the Quaternary and Silurian layers. Only the unconfined aquifer in the shallow Quaternary layer was considered for the disposal of VLLW. This aquifer is mainly composed of clay, sand, and gravel, and has a maximum thickness of about 31 m [23]. The physicochemical properties of the soil samples extracted from the three boreholes are shown in tab. 1.

Soil samples were collected in the candidate VLLW disposal site, and the particle size distribution

Table 1. Properties of the groundwater and soil samples

Groundwater [mgL^{-1}]		Soil [ug/g or %]	
Ca^{2+}	66.53	Cu	28.7
Mg^{2+}	5.59	Pb	34.2
K^+/Na^+	6.67	Zn	86.3
CO_3^{2-}	0	Ti	4657
HCO_{3-}	220.88	V	88.7
Cl^-	6.03	Co	15
SO_4^{2-}	13.45	Ni	33.2
Total hardness	189.17	As	10.1
Alkalinity	181.16	Cd	0.25
General acidity	4.5	Cr	73.1
Total salinity	319.15	Hg	0.062
		Sc	12.2
		Zr	289
		Mn	667
		Al_2O_3 (%)	13.85
		CaO (%)	0.46
		Na_2O (%)	0.69
		SiO_2 (%)	67.55
pH	7.8 (no unit)	MgO (%)	1.05

was analyzed based on size class. Taking borehole zk3 as an example, drilling has indicated the thickness of the unsaturated zone with 6.5 m, and one sample was collected every 1 meter (numbered zk3-1, zk3-2, … , zk3-7). *In-situ* observation revealed strong soil heterogeneity. The particle size distribution of all of the soil samples was analyzed using the stepwise screening method with sieves of 20, 10, 5, 2, 0.83, 0.38, 0.25, 0.18, 0.15, 0.12, 0.11, 0.075, and 0.02 mm. A grading curve was then drawn based on the screening results (fig. 1). As shown in fig. 1, particles larger than 0.83 mm comprised about 70-80 % of the media, being mainly composed of coarse particles, sand and gravel, which have weak adsorption of uranium. The ratio of the particle size between 0.83 and 0.075 mm was 20-30 %, and this fraction primarily consisted of fine sand, very fine sand or silt sand. This fraction would play an important role in the sorption and retardation of nuclides, including uranium, and was therefore considered an important parameter. Finally, the 0.075 mm particle fraction accounted for less than 0.7 %. Although this fraction strongly adsorbs radionuclides, because of its very low content, it could not be thoroughly investigated.

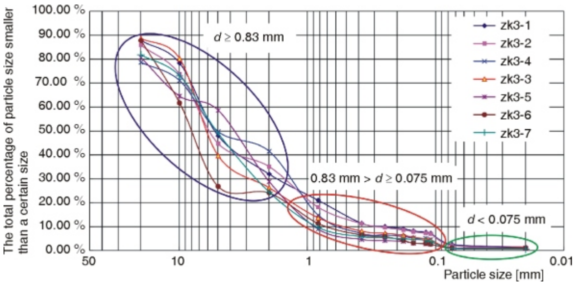

Figure 1. Distribution of the particle size of soil in the zk3 borehole. The thickness of the unsaturated zone from borehole zk3 was 6.5 m, one sample was collected every 1 meter and numbered zk3-1, zk3-2, …, zk3-7

All of the groundwater samples were collected from discharges of underground water at the experimental field site (tab. 1).

Principles and methodology

Static thermodynamic parameters of radionuclide sorption form the basis of investigations of sorption mechanisms and related experimental models in studies of radionuclide sorption processes in a medium.

Distribution coefficient (K_d)

The K_d is an important parameter for assessing the retention and migration of radionuclides. This value is derived from the rate equation of Henry's linear adsorption isotherm [24]

$$\frac{\partial S}{\partial t} \quad K_1 C \quad K_2 S \tag{1}$$

In an equilibrium state, the following relationship can be obtained [24]

$$K_d \quad \frac{S}{C} \tag{2}$$

where K_d is the distribution coefficient, and S and C are the equilibrium constants in the solid and liquid phases, respectively. K_d reflects the ratio of the concentration of a reagent adsorbed on the solid phase to the concentration of the reagent retained in the liquid phase, and is called the distribution coefficient.

The K_d value of uranium can be calculated using eq. 3 [25]

$$K_d \quad \frac{(A_0 \quad A_t)V}{A_t M} \tag{3}$$

where A_0 [g] is the mass of uranium added to the solution, A_t [g] – the mass of uranium retained in the solution after sorption equilibrium , V [mL] – the total volume of the solution , and M [g] – the mass of the soil.

Sorption isotherm

The characteristics of the sorption process, including the sorption capacity, sorption strength, and sorption state, can be described macroscopically with sorption isotherms. Adsorption isotherms commonly include the Freundlich and Langmuir isotherms, among others. A sorption isotherm is the equation describing the relationship between the solute concentration in the two phases (solid and liquid) when the solute molecules reach an equilibrium state of sorption at the interface of the two phases at a certain temperature.

The empirical formula of the Freundlich isotherm is expressed in an exponential form [25]

$$Q \quad KC^{1/n} \tag{4}$$

where Q [Bqg^{-1}] is the unit sorption capacity of the solid, C [BqmL^{-1}] – the equilibrium radionuclide concentration in the solution, K – the sorption equilibrium constant, and n is a constant. It is generally thought that when $1/n = 0.1$~0.5, the sorption occurs relatively easily, while if $1/n > 2$, it is relatively difficult for sorption to occur.

Apparatus, reagents, and experimental conditions

Apparatus

The experimental set-up comprised the following equipment:

- DDA-3 six-channel low-level α measuring instrument: Instrument background 0-8 c/24 h (China Institute for Radiation Protection),

- MUA trace uranium analyzer: measuring range 0.03 10^{-9} – 20 10^{-9} g/mL (Beijing Yulun Technology Co., Ltd., China),
- THZ-312 rotary shaker (Shanghai Jinghong Laboratory Instrument Co., Ltd., China),
- Electrodeposition cell (custom made), and
- PHSJ-4A pH meter: accuracy 0.01 (Yidian Analytical Instrument Co., Ltd., Shanghai, China).

Materials and reagents

A standard solution of ^{238}U(VI) (1.0 mg/ml) was provided by the China Institute of Meteorology for the experiments. Groundwater samples were collected from water seepage points at the VLLW disposal site. The groundwater was hydrocarbonate type, with a pH of approximately 7.8. The properties of the test groundwater are shown in tab. 2. Near-surface soil was collected at the VLLW disposal site. A 2 kg composite soil sample was collected in a rose flower pattern from a depth of 0 to 50 cm. The gravel and plant roots were removed, after which the soil was oven-dried, ground, and sieved into different particle size grades. Information regarding the chemical properties of the test soil is shown in tab. 2. The batch tests were conducted at an ambient temperature of 25 °C.

Experimental process and controlled conditions

The near-surface soil from the disposal site was used as the adsorbent in the U(VI) sorption tests. Triplicate samples were prepared for the tests under different controlled conditions (shown below), and the results represent the average from the three tests. The soil samples, which had a particle size of less than 0.15 mm, were weighed (0.5 g) into 100 mL polyethylene bottles and 30 mL of test groundwater were added. The soil suspensions were then allowed to stand for a week, after which 0.1 mL of ^{238}U(VI) solution (1 10^{-6} mol/L, 1/4000 of the U(VI) standard solution) was added. The bottle was subsequently capped and placed on an oscillator for intermittent oscillation followed by centrifugation (15 min at 3000 rpm). The supernatant was then collected and fluorescence enhancer was added as outlined in test method GB6768-86 [26] for the determination of U(VI) in water. The K_d value was calculated using eq. (3).

The following experiments were applied to examine the influence of various factors on U(VI) adsorption.

RESULTS AND DISCUSSION

Equilibrium time

The U(VI) sorption test was conducted using 0.5 g of 100 mesh (particle size 0.15 mm) soil at a 1:6 (g/mL) solid-liquid ratio. The initial concentration of ^{238}U(VI) in the aqueous phase was 300 g/L.

By definition, K_d is the ratio of the sorbate concentration associated with the solid to sorbate concentration in the surrounding aqueous solution when the system is at equilibrium. However, under non-equilibrium conditions, the adsorption process was still increasing relatively linearly, and the distribution coefficient could be used as a reference value to express the adsorption characteristics. As the sorption time increased, the K_d value of U(VI) increased substantially from 17 to 360 mL/g between 15 and 20 days of sorption (fig. 2). When the contact time exceeded 15 days,

Table 2. Controlled and various factors of experiments

Various Factor	Equilibrium time (d)	Initial U(VI) concentration [mol/L]	Particle size [mm]	pH	Temperature [°C]	Carbonate ions [mol/L]
Equilibrium time	3, 5, 7, 9, 11 ,13, 15, 17, 19, 21	1 10^{-5}	0.15	6.8-7.2	20	–
Initial concentration	15	1 10^{-5} 2 10^{-5} 3 10^{-5} 7 10^{-5} 1 10^{-4}	0.15	6.8-7.2	20	–
Soil particle size	15	1 10^{-5}	0.83 > *d* 0.38 0.38 > *d* 0.25 0.25 > *d* 0.18 0.18 > *d* 0.15 0.15 > *d* 0.12 0.12 > *d* 0.11 0.11 > *d* 0.075	6.8-7.2	20	–
pH	15	1 10^{-5}	0.15	4.2; 4.8 6.2; 7.3 7.8; 8.5 8.9; 9.1	20	–
Temperature	15	1 10^{-5}	0.15	6.8-7.2	20, 30, 40, 50, 60	–
Coexisting ions	15	1 10^{-5}	0.15	6.8-7.2	20	0.02, 0.04, 0.06, 0.08, 0.1

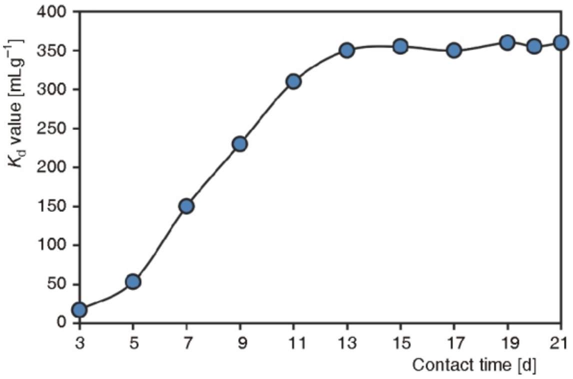

Figure 2. Relationship between sorption time and the K_d of U(VI) in soil

the K_d value fluctuated and stabilized between 355 and 360 mL/g, then approached a state of equilibrium. When the sorption equilibrium was reached, the K_d value of U(VI) in the soil was 360 35 mL/g. Therefore, we concluded that as the sorption time increased, the K_d value of U(VI) in soil gradually increased and finally reached a state of equilibrium.

Other studies have investigated the adsorption kinetics of uranium sorbed by adsorbents including zeolite [27], bentonite [28], diatomite [10], magnetic Fe_3O_4 particles [2], clays [29], natural aerated zone soil [30], and weathered saprolite [17] and shown that their adsorptive equilibrium times were 3, 4, 5, 6, 10, 1, and 7 days, respectively. The equilibrium time for this study differed from those reported by other studies because the other studies reported information about U(VI) sorption by adsorbent materials, while this study reported sorption by natural soil.

Sorption isotherms and the effects of the initial radionuclide concentration

Once the sorption equilibrium was reached, there was a significant linear relationship between the log-transformed U(VI) concentrations of the aqueous and solid phases (fig. 3). The isotherm plot (Q_e *vs*. Ce) is shown in fig. 3(a), while fig. 3(b) shows the linear fitting of isotherm data. This relationship fitted the Freundlich isotherm, $Q = KC^{1/n}$ [24], and the fitting results were

$$Q \quad 20.1C^{1.4} \, (r \quad 0.997)$$

As above-mentioned, when 1/n = 0.1-0.5, sorption occurred very easily, while when 1/n > 2, sorption was difficult. We obtained a 1/n value of 1.4, which indicates that the test soil had capacity for U(VI) sorption, and that U(VI) sorption occurred easily in the test soil.

Previous researchers have reported similar results. For example, Niu *et al*. [14], who studied the adsorption of U(VI) onto attapulgite, concluded that attapulgite sorption fit the Freundlich model well. Similar conclusions have been drawn by Setzer [31], who studied thermodynamic and kinetic investigations of uranium adsorption on soil. Furthermore, Kushwaha *et al*. [32] used palm-shell-based adsorbents to study sorption of U(VI) from aqueous solutions and found that their adsorption model fit all of the isotherms, including the Freundlich isotherm. A comparable conclusion was drawn by Mishra [33], who investigated the sorption behavior of uranium in agricultural soils. Gartman *et al*. [34] studied U(VI) fate in Hanford sediment and found that sediment sorption fit the Freundlich isotherm in the absence of air experiments.

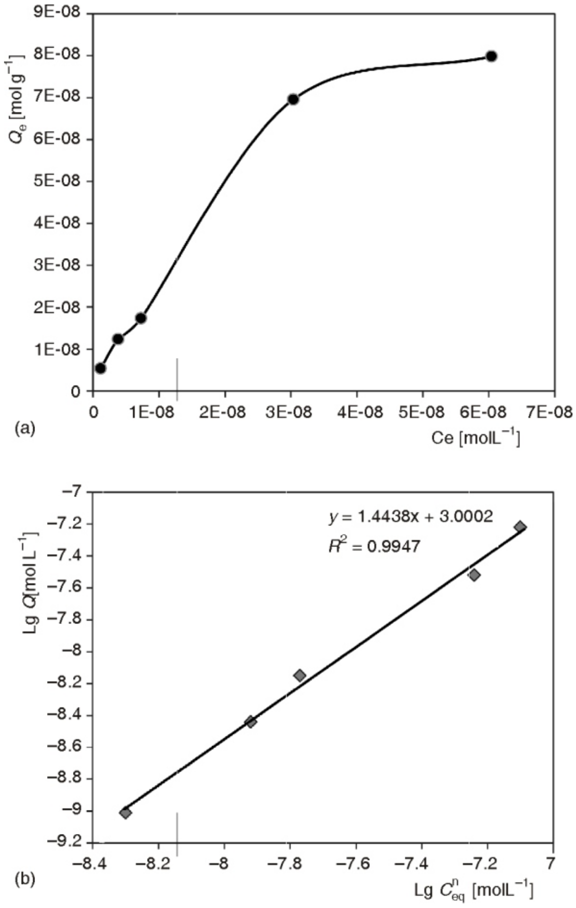

Figure 3. Isotherm plot (Q_e *vs*. C_e and linear fitting of the isotherm of U(VI) in the soil

The U(VI) adsorptive capacity increased as the initial radionuclide concentration increased (fig. 3), which is consistent with the results from other studies of U(VI) adsorption by soil [10, 35]. In this study, the U(VI) adsorption capacity in the natural soil was confirmed to be 14.2 μg/g, which followed a similar pattern. As the initial uranium concentration in solution increased, the adsorption capacity of U(VI) initially increased quickly, then slowly until a balanced state was obtained.

Effect of soil particle size

Figure 4 shows the relationship between the K_d value of U(VI) and soil particle size. As the soil particle

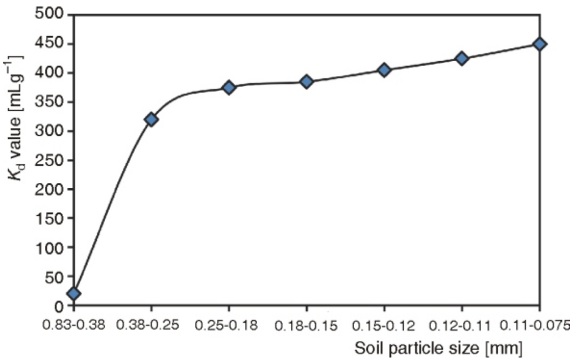

Figure 4. Influence of particle size on U(VI) sorption to soil

size decreased, the K_d value of U(VI) gradually increased. Further, when the soil particle size was less than 60-80 mesh, the rate of change of the K_d value gradually slowed. These findings indicate that the soil particle size had a considerable influence on the soil U(VI) sorption capacity. Increases in the surface area of the particles were conducive to the sorption process, and vice versa. Moreover, finer soil particles were associated with a higher U(VI) sorption capacity of the soil. Our experimental data demonstrated that, as the soil particle size decreased, the radionuclide U(VI) sorption capacity of the soil was enhanced, and this tendency was more evident for relatively large particles.

These results are similar to those reported by other researchers. For example, Zou *et al.* [35] used natural zeolite coated with manganese oxide to remove U(VI) in a fixed bed ion-exchange column and found that, as the particle size of the zeolite increased, the value of K_d decreased. Michard *et al.* [36] investigated the sorption and desorption of uranyl ions by silica gel and observed a similar decreasing trend for grain sizes that were an order of magnitude smaller (<800 m). Based on these findings, they concluded that particle size had a limited effect on the equilibrium concentration, but greatly influenced the sorption kinetics.

Effect of solution pH

The relationship between solution pH and the K_d value of U(VI) in the soil is shown in fig. 5. As the pH of the aqueous phase increased, the K_d value of U(VI) in the soil also increased; specifically, the U(VI) sorption capacity of the soil was enhanced. The K_d value increased slowly when the pH was less than 8, and increased rapidly when the pH was greater than 8. These findings indicate that pH had a weak influence on U(VI) sorption in an acidic environment, but had a much greater influence on the U(VI) sorption capacity of soil in an alkaline environment. For these reasons, the main species at low pH are UO_2^{2+}, $UO_2(OH)^+$, $(UO_2)_3(OH)^{5+}$, $UO_2(OH)_2^0$, and UO_2CO_3, while the prominent species are UO_2CO_3, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ at pH > 7 [37]. However, soil includes multifarious organic matter and hydrous oxide minerals that possess surface hydroxyl groups. The protons can be donated to the surrounding solution and take up cations in return [30]. Therefore, it is possible that, under by acidic conditions, U(VI) precipitates onto the solid phase in either colloid or chelate form as the sorption equilibrium develops, resulting in increased K_d value. However, in an alkaline environment, various absorption and complex interactions result in minerals-U(VI)-carbonate complexes predominating [38], causing a sharp increase in the K_d value.

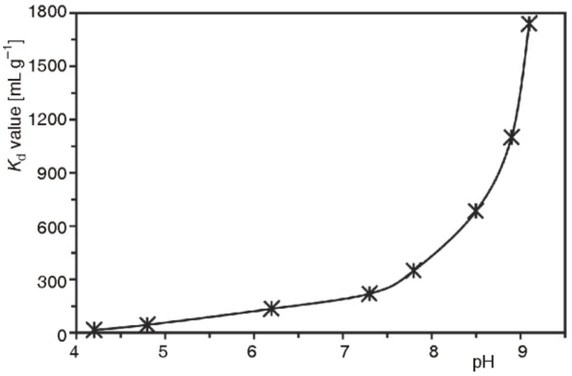

Figure 5. Influence of solution pH on U(VI) sorption to soil

Various studies have reported the influence of pH on uranium adsorption by an adsorbent. In their review of uranium adsorption of minerals, organic and inorganic components, and clays, Payne *et al.* [39] found that the K_d values were large at neutral pH, and that the influence of pH on K_d increased, then decreased [39]. Joseph *et al.* [40] examined the adsorption of U(VI) in Turkish soil and found that U(VI) uptake was low when the pH was between 4 and 6, and that the distribution ratio showed a gradual increase with increases in pH [40]. Yet another study of the effect of pH on the sorption of U(VI) reported that U(VI) sorption increased quickly when the pH was between 3 and 6, peaked at a pH of approximately 6.5, and then decreased as the pH increased beyond 6.5 [14]. These findings contrast with those of our study because each soil has a unique structure and properties, and therefore unique adsorption performance. In this study, we primarily report the uranium adsorption performance of soil under alkaline conditions.

Effect of solution temperature

Temperature plays a critical role in sorption because thermal modifications of compounds change their structure, composition and sorption ability. The relationship between the solution temperature and the K_d value of U(VI) in the soil are presented in fig. 6. At ambient temperature (25°C) or higher, the K_d value of U(VI) fluctuated between 340 and 365 mL/g, with an average of 351 mL/g and a maximum relative rate of change of 3 %. The relatively low rate of change indi-

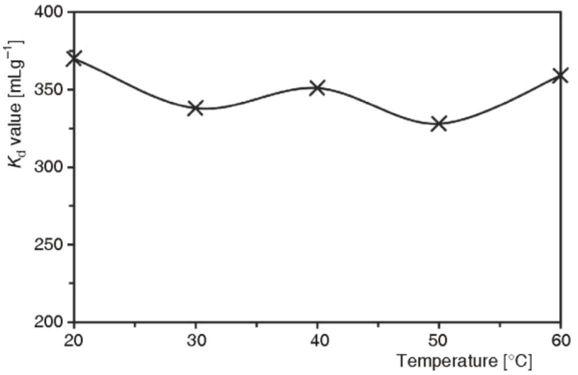

Figure 6. Influence of temperature on U(VI) sorption to soil

cates that temperature did not have a significant effect on U(VI) sorption in the soil.

Previous studies have reported the influence of temperature on the adsorption of uranium. For example, Kushwaha *et al*. [32] studied the rate of adsorption of U(VI) to palm shells and found that it decreased as the temperature increased between 30 °C and 70 °C. Moreover, Joseph *et al*. [40] studied U(VI) adsorption by clay and found that the effective diffusion and distribution coefficients, D_e and K_d, increased at two different temperatures (25 °C and 60 °C). Xiao *et al*. [28] studied adsorption of U(VI) by bentonite and found that it increased as the temperature increased from 25 °C to 65 °C. Under these selected temperatures, the adsorption of uranium presented relatively little fluctuation, without substantial changes. This may be related to the selected experimental temperature range, for the fine-grained soil medium, 20-60 degrees of temperature has not yet reached the substantial changes in the adsorption properties of excitation conditions.

Effect of carbonate concentration

The relationship between the concentration of carbonate ions and the K_d value of U(VI) in the soil is shown in fig. 7. When the carbonate ion concentration was lower than 0.01 mol/L, the K_d value declined rapidly as the carbonate ion concentration increased. When the carbonate ion concentration was greater than 0.01 mol/L, the K_d value declined slowly as the concentration of the carbonate ion increased. This trend indicates that changes in low-level carbonate ion concentrations had more influence on U(VI) sorption than changes in high-level carbonate ion concentrations. Overall, the K_d value of U(VI) consistently declined with increasing concentrations of carbonate ion. Groundwater carbonate ions may react with U(VI), and the resulting complexes could influence U(VI) sorption in the soil. Previous studies examining high levels of U(VI) in shallow groundwater revealed that U(VI) was preferentially complexed with carbonate in alkaline groundwater [41]. Liu *et al*. [42] studied adsorption of U(VI) by titanate and pointed out that the presence of CO_3^{2-} inhibited U(VI) sorption, which is consistent with our results.

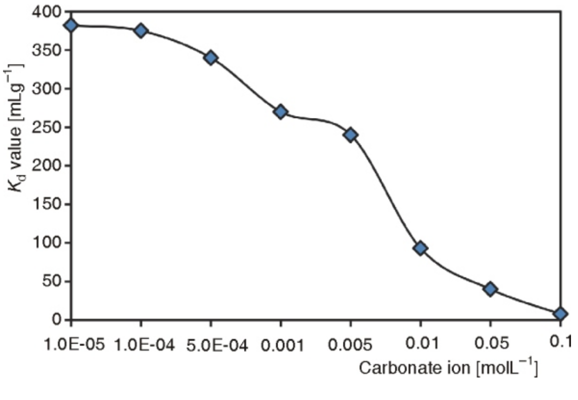

Figure 7. Influence of carbonate ion concentration on U(VI) sorption to soil

CONCLUSIONS

Sorption characteristics of uranium in soil (*d* > 0.83 mm) from a Chinese VLLW disposal site were investigated using batch tests to conduct a comprehensive examination of the capacity of soil to form a geological barrier. The key factors considered were equilibrium time, initial concentration, soil particle, pH, temperature, and carbonate. Based on the experimental results, the following conclusions could be made. (1) U(VI) was adsorbed by natural soil, and the adsorption equilibrium time in natural soil at the candidate VLLW disposal site was between 15 and 20 days. (2) The sorption behavior of U(VI) in the soil solution could be expressed by the Freundlich sorption isotherm ($Q = KC^{1/n}$). (3) Adsorption was greatest when the pH was high, at low carbanion concentrations, and for soil particles. (4) Carbonate ions have a strong influence on the Kd value, which suggests that the ion exchange capacity may be the main sorption mechanism. (5) While changes in temperature had some influence on the sorption capacity, the influence was relatively limited. The values of partition coefficients under site-specific soil conditions for U(VI) adsorption would form a useful and reliable basis for evaluating the characteristics of the adsorption of uranium in soil media.

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AUTHORS' CONTRIBUTIONS

R. Zuo and J. Wang conceived and designed the study. All samples were collected and prepared by R. Zuo, Y. Teng, and J. Wang. R. Zui, L. Liu, X. Guan and J. Yang contributed to the measurement, experiment, analysis and discussion of results. The manuscript was written and figures prepared by R. Zuo, L. Liu, F. Ding, and X. Jiang. All authors read and approved the manuscript.

REFERENCES

[1] Oliveira, L., *et al*., Distribution of ^{238}U, ^{232}Th, ^{40}K, and ^{137}Cs Concentrations in Soil Samples Nearby a Nuclear Laboratory, Capao Island, Brazil, *Nucl Technol Radiat*, *30* (2015), 2, pp. 149-153
[2] Tan, L., *et al*., Facile Preparation of Oxine Functionalized Magnetic Fe_3O_4 Particles for Enhanced Uranium (VI) Adsorption, *Colloid Surf. A., 466* (2015), 12, pp. 85-91
[3] Korichi, S., Bensmaili, A., Sorption of Uranium (VI) on Homoionic Sodium Smectite Experimental Study and Surface Complexation Modeling, *J. Hazard. Mater., 169* (2009), 1-3, pp. 780-793
[4] Salama, A., *et al*., Numerical Investigation of High Level Nuclear Waste Disposal in Deep Anisotropic Geologic Repositories, *Prog. Nucl. Energ., 85* (2015), 11, pp. 747-755
[5] Kautsky, U., *et al*., The Impact of Low and Intermediate-Level Radioactive Waste on Humans and the Environment over the Next One Hundred Thousand Years, *J. Environ. Radioact., 151* (2016), 2, pp. 395-403
[6] Mibus, J., *et al*., Migration of Uranium(IV)/(VI) in the Presence of Humic Acids in Quartz Sand: A Laboratory Column Study, *J. Contam. Hydrol., 89* (2007), 3-4, pp. 199-217
[7] Vukašinović, I., *et al*., Radioactivity Measurements in Soils Surrounding Four Coal-Fired Power Plants in Serbia by Gamma-Ray Spectrometry and Estimated Dose, *Nucl Technol Radiat, 29* (2014), 4, pp. 296-306
[8] Harguindeguy, S., *et al*., Isotopic Investigation of the Colloidal Mobility of Depleted Uranium in a Podzolic Soil, *Chemosphere, 103* (2014), 5, pp. 343-348
[9] Arnold, T., *et al*., Sorption of Uranium(VI) Onto Phyllite, *Chem. Geol., 151* (1998), 1-4, pp. 129-141
[10] Sprynskyy, M., *et al*., The Separation of Uranium Ions by Natural and Modified Diatomite from Aqueous Solution, *J. Hazard. Mater., 181* (2010), 1-3, pp. 700-707
[11] Majdan, M., *et al*., Uranium Sorption on Bentonite Modified by Octadecyltri Methyl Ammonium Bromide, *J. Hazard. Mater., 184* (2010), 1-3, pp. 662-670
[12] Ivanova, B., Spiteller, M., Adsorption of Uranium Composites onto saltrock Oxides – Experimental and Theoretical Study, *J. Environ. Radioact., 135* (2014), 9, pp. 75-83
[13] Yusan, S., Erenturk, S., Sorption Behaviors of Uranium(VI) Ions on α-FeOOH, *Desalination, 269* (2011), 1-3, pp. 58-66
[14] Niu, Z., *et al*., Effect of pH, Ionic Strength and Humic Acid on the Sorption of Uranium (VI) to Attapulgite, *Appl. Radiat. Isot., 67* (2009), 9, pp. 1582-1590
[15] Lesher, E., *et al*., Detection and Characterization of Uranium-Humic Complexes during 1D Transport Studies, *Geochim. Cosmochim. Acta, 109* (2013), 3, pp. 127-142
[16] Katsoyiannis, I., *et al*., The Effect of Groundwater Composition on Uranium(VI) Sorption onto Bacteriogenic Iron Oxides, *Water Res., 40* (2006), 19, pp. 3646-3652
[17] Kim, Y., *et al*., Fate and Transport of Uranium (VI) in Weathered Saprolite, *J. Environ. Radioact., 139* (2015), 1, pp. 154-162
[18] Bruno, C., *et al*., Adsorption of Uranyl Ions on Kaolinite, Montmorillonite, Humic Acid and Composite Clay Material, *Appl. Clay Sci., 85* (2013), 1, pp. 53-63
[19] Kohler, M., *et al*., Experimental Investigation and Modeling of Uranium (VI) Transport under Variable Chemical Conditions, *Water Resour. Res., 32* (1996), 12, pp. 3539-3551
[20] Artinger, R., *et al*., Humic Colloid-Borne Migration of Uranium in Sand Columns, *J. Contam. Hydrol., 58* (2002), 1-2, pp. 1-12
[21] Nagasaki, S., Sorption of Uranium (VI) on Na-Montmorillonite Colloids: Effect of Humic Acid and Its Migration, *Stud. Surf. Sci. Catal., 132* (2001), pp. 829-832
[22] Khalili, F., Al-Banna, G., Adsorption of Uranium (VI) and Thorium (IV) by Insolubilized Humic Acid from Ajloun Soil – Jordan, *J. Environ. Radioact., 146* (2015), 8, pp. 16-26
[23] Zuo, R., *et al*., Modeling Migration of Strontium in Sand and Gravel Aquifer in the Candidate VLLW Disposal Site, *J. Radioanal. Nucl. Chem., 281* (2009), 3, pp. 653-662
[24] Zuo, R., *et al*., Factors Influencing Plutonium Sorption in Shale Media, *Radiochim. Acta., 98* (2010), 1, pp. 27-34
[25] Teng, Y., *et al*., Detection of Tritium Sorption on Four Soil Materials, *J. Environ. Radioctiv., 102* (2010), 2, pp. 212-216
[26] ***, Methods of Analyzing Microquantity of Uranium in Water, Ministry of Environmental Protection of the Peopole's Republic of China (in Chinese), GB6768-86, 1987
[27] Singer, D., *et al*., U(VI) and Sr(II) Batch Sorption and Diffusion Kinetics Into Mesoporous Silica (MCM-41), *Chem. Geol., 390* (2014), 12, pp. 152-163
[28] Xiao, J., *et al*., Sorption Behavior of U(VI) onto Chinese Bentonite: Effect of pH, Ionic Strength, Temperature and Humic Acid, *J. Mol. Liq., 188* (2013), 12, pp. 178-185
[29] Akcay, H., Kurtulmus, F., Study of Uranium Sorption and Desorption on Some Turkish Clays, *J. Radioanal. Nucl. Chem., 200* (1995), 6, pp. 529-544
[30] Li, X., *et al*., Adsorption and Desorption of Uranium (VI) in Aerated Zone Soil, *J. Environ. Radioactiv., 115* (2013), 1, pp. 143-150
[31] Setzer, S., *et al*., Sorption Behavior of Uranium in Agricultural Soils, The New Uranium Mining Boom, 2012, pp, 579-584
[32] Kushwaha, S., Sudhakar, P., Sorption of Uranium From Aqueous Solutions Using Palm-Shell-Based Adsorbents: a Kinetic and Equilibrium Study, *J. Environ. Radioact., 126* (2013), 4, pp. 115-124
[33] Mishra, S., *et al*., Thermodynamic and Kinetic Investigations of Uranium Adsorption on Soil, *J. Radioanal. Nucl. Chem., 294* (2012), 1, pp. 97-102
[34] Gartman, B., *et al*., Uranium Fate in Hanford Sediment Altered by Simulated Acid Waste Solutions, *Appl. Geochem., 63* (2015), 12, pp, 1-9
[35] Zou, W., *et al*., Removal of Uranium (VI) by Fixed Bed Ion-Exchange Column Using Natural Zeolite Coated with Manganese Oxide, *Chin. J. Chem. Eng., 17* (2009), 4, pp. 585-593

[36] Michard, P., *et al*., Sorption and Desorption of Uranyl Ions by Silica Gel: pH, Particle Size and Porosity Effects, *Micropor. Mat., 5* (1996), 5, pp. 309-324

[37] Xiao, J., *et al*., Sorption Behavior of U(VI) Onto Chinese Bentonite: Effect of pH, Ionic Strength, Temperature and Humic Acid, *J. Mol. Liq., 188* (2013), 12, pp. 178-185

[38] Gustafsson, J., *et al*., Towards a Consistent Geochemical Model for Prediction of Uranium (VI) Removal from Groundwater by Ferrihydrite, *Appl. Geochem., 24* (2009), 3, pp. 454-462

[39] Payne, T., et al., Assessment of Surface Area Normalisation for Interpreting Distribution Coefficients (Kd) for Uranium Sorption, *J. Environ. Radioact., 102* (2011), 10, pp. 888-895

[40] Joseph, C., *et al*., Diffusion of U(VI) in Opalinus Clay: Influence of Temperature and Humic Acid, *Geochim. Cosmochim. Acta., 109* (2013), 3, pp. 74-89

[41] Wu, Y., *et al*., Occurrence, Behavior and Distribution of High Levels of Uranium in Shallow Groundwater at Datong Basin, Northern China, *Sci. Total Environ., 472* (2014), 2, pp. 809-817

[42] Liu, W., *et al*., Adsorption of U(VI) by Multilayer Titanate Nanotubes: Effects of Inorganic Cations, Carbonate and Natural Organic Matter, *Chem. Eng. J., 286* (2016), 2, pp. 427-435

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ФАКТОРИ КОЈИ УТИЧУ НА АДСОРПЦИЈУ U(VI) У ЗЕМЉИШТУ ПОТЕНЦИЈАЛНОГ ОДЛАГАЛИШТА ОТПАДА ВЕОМА НИСКЕ РАДИОАКТИВНОСТИ У КИНИ

У погледу U(VI), за геолошко одлагање отпада веома ниског нивоа радиоактивности веома су важна својства земљишта. У овом раду испитан је капацитет за сорпцију уранијума земљишта са потенцијалног места за одлагање отпада веома ниског нивоа радиоактивности у Кини. Посебно су процењени време еквилибријума, почетна концентрација, честице земљишта, pH, температура и карбонати. Резултати указују да је после 15 до 20 дана сорпције, K_d вредност флуктуирала и стабилизовала се на 355-360 mL/g. Адсорптивни капацитет уранијума повећавао се услед повећања почетне концентрације уранијума, да би се смањивао са порастом величине честице земљишта. pH вредност игра важну улогу у сорпцији U(VI) у земљишту, нарочито при алкалним условима, и има значајан утицај на капацитет сорпције уранијума у земљишту. Шта више, присуство карбоната смањује сорпцију U(VI) у земљишту због јаке комплексације карбоната са U(VI) у подземним водама. У целини, процењено је понашање сорпције U(VI) у природном земљишту, што може бити важан фактор за геолошку баријеру одлагалишта и доприноси овладавању карактеристикама адсорпције уранијума у одређеној врсти земљишта током процеса одлагања отпада веома ниског нивоа.

Кључне речи: уранијум, земљиште, адсорпција, фактор утицаја, тест серије, радиоактивни отпад веома ниског нивоа