Journal of Radioanalytical and Nuclear Chemistry (2021) 329:149–158
https://doi.org/10.1007/s10967-021-07780-2

Diffusion behavior of Se(IV) in Tamusu clayrock core by through-diffusion method

Yuzhen Sun[1,2] · **Hui Zhang**[1] · **Chuan-Pin Lee**[3] · **Mingbiao Luo**[1] · **Rong Hua**[3] · **Weigang Liu**[3] · **Jie Kong**[3] · **Yanqin Hu**[3]

Received: 19 January 2021 / Accepted: 10 May 2021 / Published online: 5 June 2021

Abstract

For the first time in laboratory, the diffusion behavior of Se(IV) in Tamusu clayrock core was studied by means of through-diffusion method. The effects of pH, ionic strength and humic acid on the diffusion behavior of Se(IV) in clayrock were studied. The effective diffusion coefficient, distribution coefficient and rock capacity factor value were obtained. The diffusion mechanism of radionuclide in Tamusu clayrock is discussed, which can provide experimental data support and theoretical references for the pre-selection of clayrock sites and safety assessment in China's high-level radioactive waste deep geological repository.

Keywords Se(IV) · Tamusu clayrock · Through-diffusion · Diffusion coefficient · Distribution coefficient

Introduction

Tamusu area is the primary pre-selection site of clayrock disposal repository for high-level radioactive waste (HLW). It is very urgent to carry out its safety assessment. The retardation behavior of nuclides is an important part of the safety assessment of the host rock of the repository. Clayrock is characterized by high self-closure, low permeability and low porosity. It is significant to evaluate the diffusion behavior of key nuclides in Tamusu clayrock. Through-diffusion method is considered to be the most accurate and reliable method for radionuclide migration research, which is widely adopted by researchers. Over the past several decades, the researchers have completed the migration behavior of HTO, ^{129}I, ^{36}Cl [1], ^{99}Tc [2], ^{79}Se [3] and other major radionuclides in granite, bentonite, kaolinite, montmorillonite, Opalinus clay and other geological samples. However, the research on the migration behavior of radionuclides in Tamusu clayrock has just begun. ^{79}Se is a long-lived fission product with half-life of 2.95×10^5 years. It is a pure beta radiator with a maximum radiation energy 150.7 keV. The fission yield induced by ^{235}U thermal neutron is 0.044% [4]. Because of its various speciation, long life, high radioactivity and high mobility, it has become one of the most concerned radionuclides in safety assessment [5, 6].

There are many valence species of selenium, which mainly exist in the form of + 4 and + 6 anions in oxic aqueous solution. These anions are easily soluble in water, highly mobile, highly bioavailable and toxic [7, 8]. Se(IV) mainly exists in the form of selenium oxide (SeO_2) and SeO_3^{2-}. SeO_2 is a stable oxide of selenium, soluble in water and can combine with water to form $SeO_3^{2-}$and $HSeO_3^{-}$ [9]. The diffusion behavior of Se(IV) in Tamusu clayrock core and the effects of pH, ionic strength and humic acid on the diffusion behavior were systematically studied by through-diffusion of nuclides in Tamusu clayrock core. The diffusion of Se(IV) is discussed, the diffusion mechanism is analyzed, to provide basic information and decision-making basis for the safety assessment of Tamusu clayrock geological repository in China.

✉ Mingbiao Luo
luomingbiao_ecut@126.com

✉ Rong Hua
huarong80@126.com

[1] State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, Jiangxi, China

[2] Jiangxi College of Traditional Chinese Medicine, Fuzhou 344000, Jiangxi, China

[3] College of Nuclear Science and Engineering, East China University of Technology, Nanchang 330013, Jiangxi, China

Theory

In this experiment, through diffusion method is used. For one-dimensional diffusion process, nuclide diffusion follows one-dimensional diffusion equation:

$$\frac{\partial C}{\partial t} = D_a \cdot \frac{\partial^2 C}{\partial x^2} \tag{1}$$

where c is the concentration of the species in solution (mol L^{-1}); t is the diffusion time (s); D_a is the apparent diffusion coefficient in the compacted Tamusu clayrock ($m^2\ s^{-1}$); x is the diffusion distance (m).

D_a can be replaced by D_e. The relationship between them is as follows:

$$D_a = \frac{D_e}{\alpha} \tag{2}$$

where D_e is the effective diffusion coefficient ($m^2\ s^{-1}$); α is the rock capacity factor, defined as follows:

$$\alpha = \varepsilon + \rho \cdot K_d \tag{3}$$

where K_d is the equilibrium distribution coefficient of Se(IV) ($m^3\ kg^{-1}$); ε is the porosity of clayrock; ρ is the dry density of compacted clay ($kg\ m^{-3}$). For the non-adsorbed tracer ($K_d = 0$), the rock capacity factor is equal to porosity.

The initial and boundary conditions are as follows:

$$C(x > 0, t = 0) = 0$$
$$C(x = 0, t > 0) = C_0$$
$$C(x = d, t > 0) = 0$$

The equation can be expressed as a function of t(diffusion time) and x(diffusion distance)—as follows:

$$C(x,t) = \left(1 - \frac{x}{L}\right)C_0 - \frac{2C_0}{\pi}\sum_{n=1}^{\infty}\left\{\frac{1}{n}\sin\left(\frac{n\pi x}{L}\right)exp\left(\frac{-n^2\pi^2 D_a t}{L^2}\right)\right\} \tag{4}$$

where L represents the thickness of clay sample (m); C_0 is the initial concentration of Se(IV) (m).

By using Fick's first law and according to the conservation of mass, the formula (1–4) is integrated to obtain the analytical solution of the total amount of accumulated nuclides:

$$A_{cum} = S \cdot L \cdot C_0\left(\left\{\frac{D_e \cdot t}{L^2} - \frac{\alpha}{6} - \frac{2 \cdot \alpha}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2} \cdot exp\left\{-\frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{L^2 \cdot \alpha}\right\}\right\}\right) \tag{5}$$

where A_{cum} is the total amount of nuclides passing through the boundary of $x = L$ in time t (μg); L is the thickness of the clay sample (m); S is the cross-sectional area of the clay sample (m^2).

The flux J of the collection bottle is calculated by the following equation:

$$J(L,t) = \frac{A_{cum}}{S \cdot \Delta t} \tag{6}$$

Here J(L,t) is the flux at the low-concentration boundary($x = L$) ($\mu g\ cm^{-2}\ d^{-1}$)).

Experimental

Materials and methods

Tamusu area is located in the north central part of Alxa League Right Banner, Inner Mongolia Autonomous Region. It is located in the western part of the southern margin of Bayingobi Basin and the northern margin of zongnai mountain and salazha mountain. In this work, the clayrock used was derived from TZK-2 core with a depth of 543.7–543.8 m.

Sample preparation The Tamusu clayrock sample was cut into thin sections with a thickness of 3 mm and a diameter of 45 mm (Jiangxi geological survey and Research Institute), as shown in Fig. 1a.

Sodium chloride, sodium hydroxide and hydrochloric acid were purchased from Ningbo Zhongxing Chemical Reagent Co., Ltd. Selenium dioxide and humic acid were

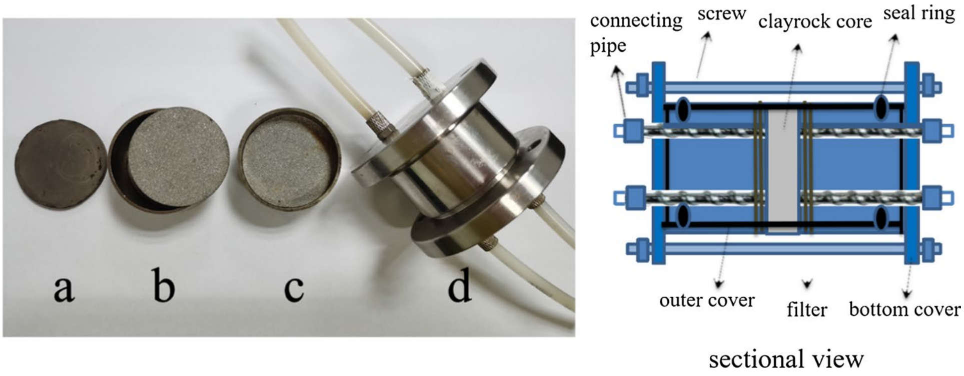


Fig. 1 Clayrock core, diffusion cell (left) and the component of diffusion cell (right)

purchased from Shanghai Aladdin Co., Ltd. The pH buffer reagent was purchased from Sinopharm Chemical Reagent Co., Ltd. The selenium standard solution was purchased from Shanghai Bestway Chemical Technology Co., Ltd. All the reagents were analytically pure. Distilled water is made in the laboratory.

Diffusion Cell (stainless steel, made by ourselves), Electronic Balance (BSA124S, Sartorius Scientific Instruments Co.,), pH meter (PB10, Sartorius Scientific Instruments Co.,), Ltd Inductively Coupled Plasma Optical Emission Spectrometer (ICAP-7400, Thermo Fisher Technology (China) Co., Ltd), Scanning Electron Microscope (NNS-450, Philips FEI Company of the Netherlands), X-Ray Diffraction (D8 Advance, Brooke Analytical Instruments Co., Ltd), X-Ray Fluorescence (S8 Tiger, Brooke Analytical Instruments Co., Ltd).

Through-diffusion method

Compared with compacted powder clay, clayrock core has higher density and more compact structure, which can more truly reflect the diffusion of radionuclides. The inner diameter of the outer cover of the diffusion cell is 45 mm, and the thickness of the sample is 3 mm (as shown in Fig. 1 sectional view). The cut slice of Tamusu clayrock was placed in the middle of the outer cover of the diffusion pool and fixed with glue (as shown in Fig. 1c), so that the contact interface between the core and the diffusion pool was completely closed, and the water test was carried out. The thickness of a stainless steel filter (diameter 45 mm, thickness 1.57 mm, porosity 0.3 (as shown in Fig. 1b) is placed on both sides of the core, and the bottom cover, screw and pipeline are installed on both sides (as shown in Fig. 1d). Connect the pipeline and peristaltic pump according to Fig. 2. Start the peristaltic pump and equilibrium the core with equilibrium solution for 30 days to make the core completely soaked with equilibrium solution. At the beginning of the through-diffusion experiment, the equilibrium solution of the two sections of the diffusion cell was replaced by the diffusion source liquid at one end, and the other end was connected with the collection solution to start the nuclide diffusion. The collection solution was replaced every 3–7 days. The concentration of nuclide diffusion source liquid and collection solution was determined by ICP-OES, and the diffusion coefficient was calculated.

Experimental condition

Tamusu clayrock cores (3 mm thick, 45 mm in diameter) were equilibrated with NaCl solutions of different pH and concentrations for 30 days. The diffusion source solution was 500 mL 3000 mg L^{-1} selenium solution with the same pH and ionic strength as the equilibrium solution. The collecting solution was 10 mL NaCl solution with different pH and concentration. The temperature was 20(±5) ℃ and the diffusion time was 135 days. Other conditions are as follows:

(1) The influence of solution pH. The ionic strength of the equilibrium solution is 0.05 mol L^{-1} and the pH is adjusted to 4.0, 7.0 and 8.0 respectively, the pH of the diffusion source solution is adjusted to 4.0, 7.0 and 8.0 respectively. The collected solution was 10 mL of equilibrium solution of corresponding diffusion cell.

(2) The influence of ionic strength of solution. The equilibrium solution is 0.05 mol L^{-1} and 0.7 mol L^{-1} NaCl solution whose pH value is 7.0, and the corresponding diffusion source solution is 0.05 mol L^{-1} and 0.7 mol L^{-1} NaCl solution whose pH value is 7.0. The collected solution was 10 mL of equilibrium solution of corresponding diffusion cell.

(3) The influence of humic acid. The equilibrium solution was 0.05 mol L^{-1} NaCl solution, and the pH was adjusted to 7.0. In the equilibrium test, 10 mg L^{-1} humic acid was added to the equilibrium solution

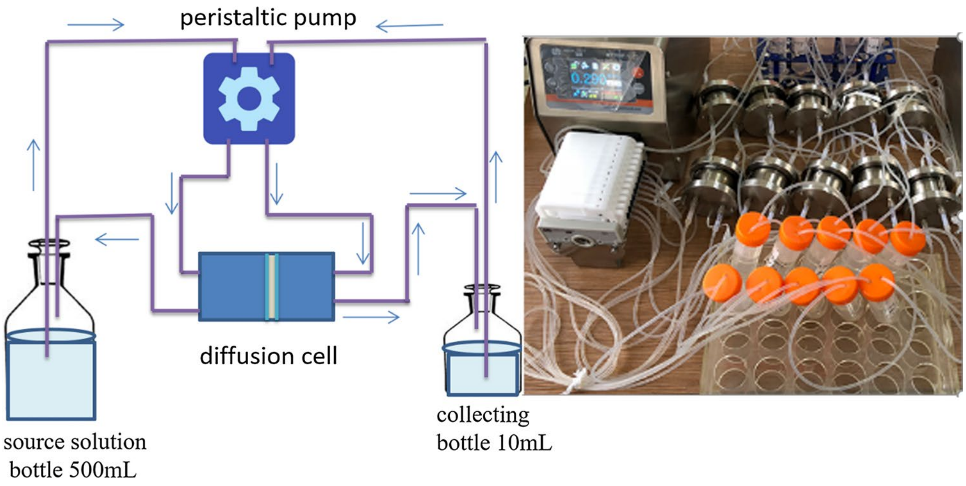


Fig. 2 Schematic diagram of diffusion device in through-diffusion cell

when the core water was in equilibrium. After 30 days of equilibrium, no humic acid but only 3000 mg L^{-1} selenium solution was added to the diffusion source solution when the nuclide was diffused. In the contact test, 10 mg L^{-1} humic acid was added to the clayrock for 30 days, and then 3000 mg L^{-1} selenium solution and 10 mg L^{-1} humic acid were added to the diffusion solution. The contact time was 0 days at pH = 7.0, 45 days at pH = 7.0 and 45 days at pH = 10.0, respectively. The collected solution was 0.05 mol L^{-1} NaCl solution, and the pH was adjusted to 7.0 and 10.0, respectively.

Results and discussion

Physicochemical properties and microstructure of Tamusu clay

The specific surface area of clayrock is 3.58 $m^2\ g^{-1}$, the average pore size is 19.7 nm, and the average particle size is 4.15 μm. Clayrock contains a small amount of Ca, Fe, Al and other element oxides, the compositions of Tamusu clayrock in XRF analysis are shown in Table 1.

Figure 3 is the XRD pattern of clay. It can be seen that in 2θ the diffraction angle is 2.00°, 15.84°, 26.00°, 26.64°, 30.77°, there are obvious characteristic peaks at these places. Compared with Standard picture card, clay contains dolomite, wairakite, quartz and ankerite. The results show that the main mineral composition of Tamusu area is dolomite, albite and zeolite, the average content of the three minerals is 70–80%, and the others are orthoclase, illite and kaolinite [10]. Zeolites have special silica cavity structure and unique pipe space arrangement. Like diodes, zeolites can allow molecules or atoms which smaller than the diameter of the pipe to pass through, forming a unique molecular sieve function [11]. The content of zeolite in Tamusu clayrock is as high as 52.3%, so it has strong adsorption and retardation ability for Se migration [10].

In this experiment, the zero-potential point of clayrock was measured in NaCl system. Plot ΔpH with the original pH of the solution (ΔpH is the change of pH value of the suspension after shaking for 48 h). The results are shown in Fig. 4. According to the curve equation, the zero-potential point of clayrock is 7.75. When the solution pH is less than 7.75, the clay surface is electropositive, which blocks the diffusion of $HSeO_3^-$ and SeO_3^{2-}. When the solution pH is more than 7.75, the clay surface is electronegativity, which accelerates the diffusion of anion. He et al. [12] determined that the zero-potential point of Tamusu clayrock in KNO_3 system is 8.45. When the pH value of the solution is less than 8.45, the clay surface is positively charged, which weakens the diffusion of $HSeO_3^-$ and SeO_3^{2-}. When the pH value is greater than 8.45, the clay surface is negatively charged, which accelerates the diffusion of $HSeO_3^-$ and SeO_3^{2-}. Similarly, minerals with high zero-potential point have better retardation performance for selenium diffusion, while minerals with low zero-potential point, such as quartz, have slightly worse retardation performance for selenium diffusion [13].

Figure 5 is the SEM image of clayrock before and after diffusion 135 days of selenium solution. It can be seen that

Table 1 XRF analysis of Tamusu clayrock

Molecular formula	Wt%	Molecular formula	Wt%
Na_2O	4.21	CO_2	14.61
MgO	5.07	K_2O	2.07
Al_2O_3	14.30	CaO	9.18
SiO_2	43.00	Fe_2O_3	6.25

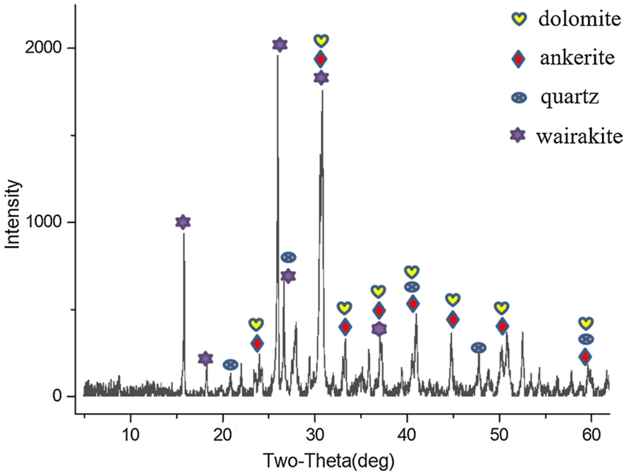


Fig. 3 XRD diffraction pattern of Tamusu clay

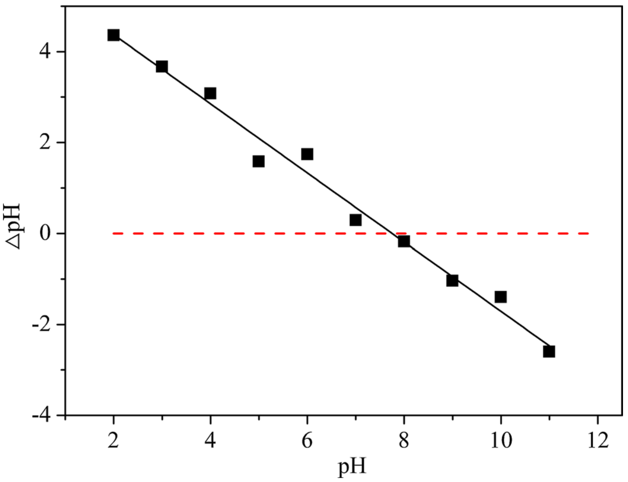


Fig. 4 Zero potential plot of clay

there are a large number of flakes and pores of variable sizes on the surface of clayrock particles before diffusion, which increases the specific surface area of clay. After diffusion, a large number of particles adhere to some apertures and particle surface of clayrock, which indicates that clayrock has blocking effect on the diffusion of selenium solution.

Effect of pH

In the geological environment of Tamusu in Inner Mongolia, the pH range of groundwater is 7.75–9.86, with an average value of 8.3. However, with the passage of time and the change of specific location and depth, the pH will change. In the case of water equilibrium, the diffusion of nuclides in clay can be regarded as diffusion in saturated rock pores. The pH of solution will affect the chemical form of nuclides and the surface properties of clay, thus affecting the diffusion behavior of nuclides. The zero-potential point of Tamusu clay is 7.75, which indicates that the surface of the clay is electropositive when pH is less than 7.75, and electronegative when pH is higher than 7.75. In view of the groundwater pH is greater than 7.75, it is concluded that the surface of Tamusu clay is mostly electronegative in the environment.

The main forms of Se(IV) in aqueous solution are H_2SeO_3, $HSeO_3^-$ and SeO_3^{2-}. As shown in Fig. 6, H_2SeO_3, $HSeO_3^-$ and SeO_3^{2-} are the main forms at pH 0–2.0, 4.0–7.0 and 9.0–12.0. In Se(IV) aqueous solution, when the pH value of the solution is less than 7.2, Se(IV) mainly exists in the form of $HSeO_3^-$. When the pH value of the solution is between 7.2 and 14.0, Se(IV) mainly exists in the form of SeO_3^{2-} [9]. Therefore, when pH is 4.0 and 7.0, Se(IV) diffuses in the form of $HSeO_3^-$ in clay. When pH is 8.0, Se(IV) diffuses in the form of SeO_3^{2-} in clay.

The diffusion flux J(L,t) and total amount A_{cum} of Se(IV) in clayrock are shown in Fig. 7 in NaCl solution with different pH values at 15 ℃. The diffusion process is divided into transition state and steady state. The experimental values of diffusion flux show that the time to steady state is 100, 80 and 60 days at pH = 4.0, 7.0 and 8.0, respectively. With the increase of pH, the time to steady state shortens. According to the fitting curve, the time of nuclide diffusion to 135 days can be obtained the J(L,t) of Se(IV) at pH 4.0, 7.0 and 8.0 were (0.161, 0.333 and 0.564) μg cm^{-2} d^{-1} and A_{cum} were (145, 584 and 879) μg, respectively. With the increase of pH, J(L,t) and A_{cum} increased.

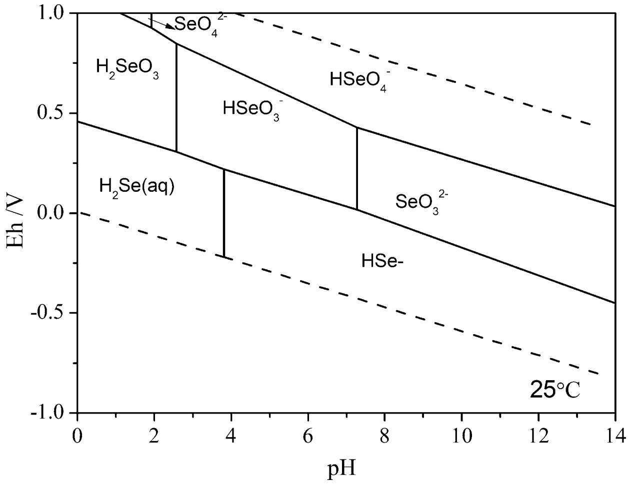


Fig. 6 Redox potential diagram of Se [9]

The diffusion coefficients calculated by the formula are shown in Table 2. Under the conditions of pH 4.0, 7.0 and 8.0, the D_e values obtained were (2.34, 3.06 and 4.93) × 10^{-14} m^2 s^{-1}, respectively, with the increase of pH, D_e values also increased. α was 0.159, 0.0632 and 0.081, K_d was (0.390, 0.0200 and 0.0872) mL g^{-1}, D_a was (1.47, 4.84 and 6.12) × 10^{-12} m^2 s^{-1}, respectively, which increased with the increase of pH. Compared with the Se(IV) internal diffusion method [14], the variation law is consistent, but the D_a value of the through-diffusion is 1–2 orders of magnitude smaller. The distribution coefficient is also reduced, the rock core density is larger and the particles are more compact, which is conducive to block the diffusion of nuclides.

When the pH of the solution is in the range of 4.0–8.0, increasing the pH is conducive to the diffusion of Se(IV)

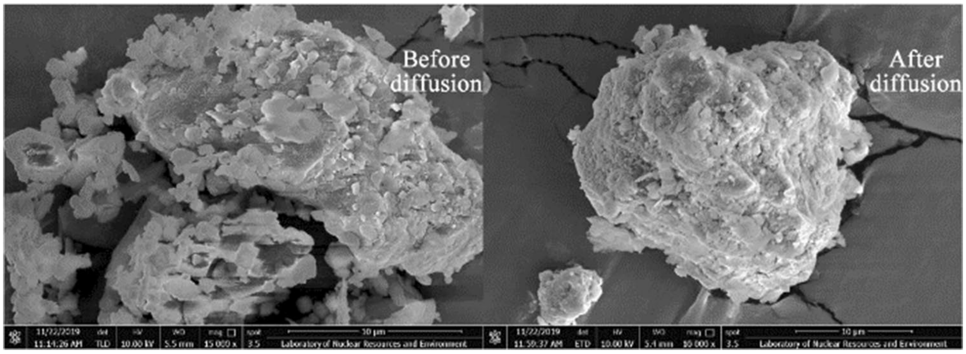


Fig. 5 SEM image of clayrock before (left) and after (right) diffusion 135 days of selenium solution

in the rock core. With the increase of pH, the content of $HSeO_3^-$ decreases in the solution, but SeO_3^{2-} increases. The experimental results also show that the migration of $HSeO_3^-$ is slower than that of SeO_3^{2-}. At the same time, because the zero-potential point of clayrock is 7.75, affected by the surface charge of clay, it has a strong attraction to anions under acidic conditions. With the increase of pH value of solution, this attraction decreases. When pH value is higher than 7.75, the negative charge of clay surface will exclude anions, so the corresponding diffusion speed will be accelerated.

The diffusion coefficients of Se in different geological samples at different pH values of solution in some references are listed in the Table 3. It can be concluded that the D_e values obtained by Se(IV) diffusion in the Tamusu claytock are less than those obtained from other geological samples. In Table 3, the D_e value obtained by Se(IV) diffusion in Beishan granite core ranges from $(0.86–4.81)\times10^{-13}$ m^2 s^{-1}, and K_d value is 10^{-3} mL g^{-1} [19]. The D_e values obtained by diffusion in other granites and limestones are 10^{-13} m^2 s^{-1}, those obtained by diffusion in Japanese tuff are 10^{-12} m^2 s^{-1} [3, 13], and those obtained by diffusion in GMZ bentonite and MX-80 bentonite are 10^{-12}–10^{-11} m^2 s^{-1} [15–18], which are all larger than the D_e values of Se(IV) in Tamusu clayrock in this experiment. Compared with Beishan granite, the diffusion of Se(IV) in Tamusu clayrock has smaller D_e value and larger K_d value. Tamusu clayrock has less adsorption of selenium, resulting in lower diffusion coefficient.

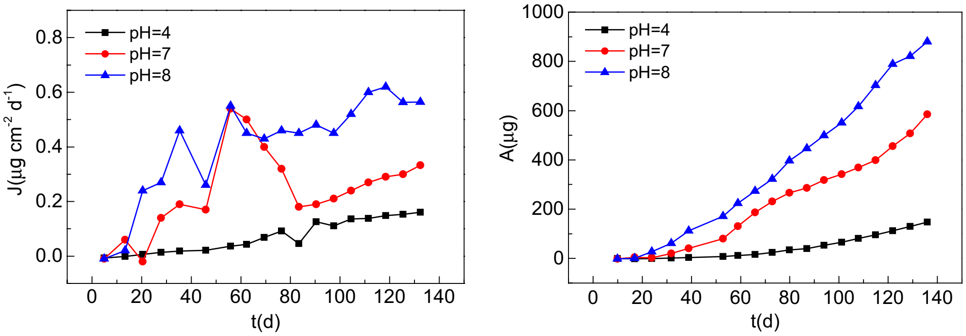


Fig. 7 Diffusion flux (left) and total amount (right) of Se(IV) in different pH solutions

Table 2 Diffusion parameters of Se(IV) under different pH

pH	C_0 (mg L^{-1})	$D_e\times10^{-14}$ (m^2 s^{-1})	α	K_d (mL g^{-1})	$D_a\times10^{-13}$ (m^2 s^{-1})
4.0	3500 ± 50	2.34 ± 0.01	0.159 ± 0.003	0.390 ± 0.002	1.47 ± 0.07
7.0	3750 ± 50	3.06 ± 0.12	0.0632 ± 0.013	0.0200 ± 0.0009	4.84 ± 0.21
8.0	3800 ± 50	4.93 ± 0.19	0.081 ± 0.002	0.0872 ± 0.0039	6.12 ± 0.27

Table 3 Diffusion parameters of Se in different pH solutions and geological samples

Sample	Diffusion condition	D_e (m^2 s^{-1})	K_d (mL g^{-1})	References
Tamusu clay	pH = 4,7,8	$(2.34–4.93)\times10^{-14}$	0.39–0.08	this article
GMZ bentonite	groundwater	0.77×10^{-11}		[15]
Montmorillonite	pH = 9.0	2.13×10^{-12}		[16]
GMZ bentonite	pH = 3.0–10.0	$(0.38–2.3)\times10^{-11}$	0.1–0.25	[17]
Granite	pH = 7.85	7.53×10^{-13}	0.0619	[3]
Limestone	pH = 9.46	4.53×10^{-13}	0.184	
Tuff in Japan	pH = 8,11	$(6.8, 6.6)\times10^{-12}$	1.1, 0.23	[13]
MX-80	pH = 7.9	$(0.125–1.54)\times10^{-11}$	4.7–6.97	[18]
Beishan granite core	pH = 2–8.5	$(0.86–4.81)\times10^{-13}$	0.0006–0.002	[19]

Effect of ion strength

The salinity of groundwater in Tamusu area is in the range of (693–38200) mg L^{-1}, with an average of 13974 mg L^{-1}. The internal diffusion experiment shows that the diffusion coefficient increases with the increase of solution ionic strength [14]. Therefore, only 0.05 and 0.7 mol L^{-1} NaCl solutions are selected for rock core diffusion experiment to explore the influence of salinity on diffusion. In NaCl solutions with different ionic strength values, the diffusion flux $J(L,t)$ and total diffusion A_{cum} of Se(IV) in clay core under the experimental temperature of 15 ℃ are shown in Fig. 8. The diffusion process is divided into transition state and steady state. From the experimental values in Fig. 8, it can be seen that Se(IV) is in equilibrium at 90 days when the ionic strength is 0.05 mol L^{-1}, and reaches equilibrium at 75 days when the ionic strength is 0.7 mol L^{-1}. The time to reach equilibrium is shortened with the increase of ionic strength. At 135 days, the $J(L,t)$ of Se(IV) at the ionic strength of 0.05 and 0.7 mol L^{-1} were (0.57 and 2.39 μg cm^{-2} d^{-1}), respectively, while A_{cum} were (634 and 3658) μg, respectively, which increased more than 5 times. It indicated that the diffusion flux and total amount of Se(IV) in clay increased with the increase of ionic strength.

The diffusion coefficient calculated by the formula is shown in Table 4. When the ionic strength is 0.05 mol L^{-1} and 0.7 mol L^{-1}, the D_e values of Se(IV) diffusion in clay core are (3.06 and 32.9) × 10^{-14} m^2 s^{-1}, respectively. With the increase of ionic strength, D_e increases obviously, indicating that increasing the ionic strength of diffusion solution is conducive to the migration of Se(IV) in clayrock. Meanwhile, α was 0.0632 and 0.749, K_d was (0.266 and 0.020) mL g^{-1}, D_a was (4.84 and 4.39) × 10^{-13} m^2 s^{-1}, respectively. In the internal diffusion method, when the ionic strength is 0.5 mol L^{-1}, the D_a value of Se(IV) diffusion is 3.19 × 10^{-10} m^2 s^{-1} [14], which is larger than that of the through diffusion method under similar conditions.

According to the Gouy–Chapman–Stern electric double layer model [20], the thickness of the diffusion electric double layer is related to the ionic strength of solution and the charge of the ions. However, in low salt solution ($I < 0.7$ mol L^{-1}), the thickness of diffusion electric double layer decreases with the decrease of ionic strength, while in high salt solution ($I > 0.7$ mol L^{-1}), the thickness of diffusion electric double layer is basically unchanged [21]. The pore size of clay particles is composed of free water layer and diffusive electric double layer (DDL) [22]. When the surface of clay particles is electronegative, the effect of ionic strength on diffusion is shown in Fig. 9, and the effect of ionic strength is the same when the surface of clay particles is electronegative. Ionic strength does not change the pore size of clay, but it will affect the thickness of the diffusion electric double layer on the particle surface. With the increase of ionic strength, the diffusion electric double layer becomes narrower, the free water layer becomes wider, and the ion channel becomes wider. Therefore, the α value obtained by diffusion increases. The diffusion channel of anions in clayrock is free water layer between particles, so the diffusion speed increases with the increase of ionic strength. The main existing form of Se(IV) in solution is $HSeO_3^-$, which has electrostatic attraction with the surface of clay particles. It is easy to form complex with the surface of clay, and a small amount of $HSeO_3^-$ will be adsorbed on the surface of clay, thus slowing down the diffusion speed.

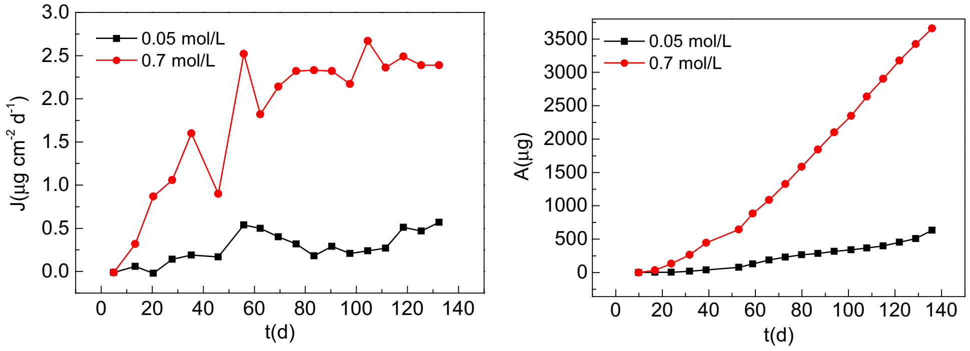


Fig. 8 Diffusion flux (left) and total amount (right) of Se(IV) in different ionic strength conditions

Table 4 Diffusion parameters of Se(IV) under different ionic strength conditions

C_{NaCl} (mol L^{-1})	C_0 (mg L^{-1})	$D_e \times 10^{-14}$ (m^2 s^{-1})	α	K_d (mL g^{-1})	$D_a \times 10^{-13}$ (m^2 s^{-1})
0.05	3750 ± 50	3.06 ± 0.118	0.0632 ± 0.013	0.266 ± 0.015	4.84 ± 0.21
0.7	3400 ± 50	32.9 ± 1.1	0.749 ± 0.031	0.0200 ± 0.0009	4.39 ± 0.23

Table 5 shows D_e values of Se(IV) by through-diffusion method in different geological samples with different ionic strength. It can be concluded that the D_e values obtained by Se (IV) diffusion in Tamusu clayrock are less than those obtained in other geological samples. The D_e value of Se(IV) is 10^{-13} m^2 s^{-1} in Beishan granite and 10^{-12}–10^{-11} m^2 s^{-1} in GMZ bentonite. Se(IV) in GMZ bentonite has weak adsorption, D_e value increases with the increase of ionic strength, α value increases with the increase of ionic strength [23, 24], the change rule is similar to this experiment.

Effect of humic acid

Humic acid is a ubiquitous organic acid in nature, which can affect nuclide migration through redox reaction and complexation [25]. The equilibration solution was 0.05 mol L^{-1} NaCl solution, pH = 7 and 10 mg L^{-1} humic acid was added to the equilibration solution when the rock core water was in equilibration. After 30 days of equilibration, humic acid was not added to the diffusion source solution during Se(IV) diffusion. The J(L,t) and A_{cum} obtained by diffusion are shown in Fig. 10. It can be concluded from the experimental values in the figure that the flux obtained from $C_{HA} = 10$ mg L^{-1} equilibration test is basically consistent with $C_{HA} = 0$, the time of reaching steady state about 60 days, and J(L,t) and A_{cum} at 120 days are 0.320 μg cm^{-2} d^{-1} and 327 μg, respectively. There is less different from $C_{HA} = 0$. This indicates that the interaction between clayrock and humic acid has little effect on the diffusion of Se(IV).

In the contact to humic acid test, 10 mg L^{-1} humic acid was added to the clayrock for 30 days, and then 3000 mg L^{-1} Se(IV) and 10 mg L^{-1} humic acid were added to the diffusion source solution. The contact time was 0 day at pH = 7, 45 days at pH = 7 and 45 days at pH = 10, respectively. The contact test is shown in Fig. 10. The time of steady state is about 60 days when the contact time is 0 days, and about 75 days when the contact time is 45 days. At 120 days, the J(L,t) and A_{cum} values of contact 0 day were 1.54 μg cm^{-2} d^{-1} and 1765 μg. When Se(IV)

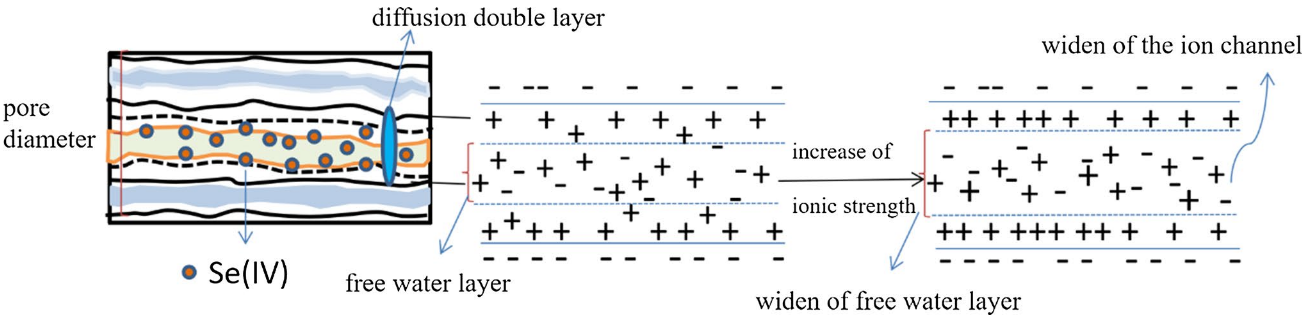
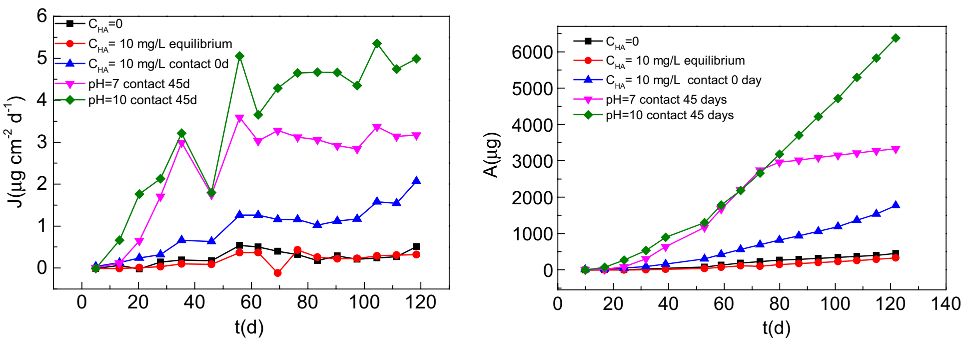


Fig. 9 Schematic diagram of the effect of ionic strength in solution on Se(IV) diffusion

Table 5 Diffusion parameters of Se in different ionic strength solutions and geological samples

Sample	Condition	D_e (m^2 s^{-1})	K_d (mL g^{-1})	α	References
Tamusu clay	0.05–0.7 M NaCl	$(3.06–32.9) \times 10^{-14}$	0.27–0.02	0.06–0.75	This article
Granite core	0.1 $NaClO_4$	2.14×10^{-13}			[19]
GMZ bentonite	0.13–1.0 M NaCl	$(1.60–4.69) \times 10^{-11}$	0.18–0.16	0.55–0.65	[23]
GMZ bentonite	0.05–0.5 M NaCl	$(0.53–3.5) \times 10^{-11}$			[24]

Fig. 10 Effect of humic acid on diffusion flux (left) and total amount (right) of Se(IV)



was contacted to humic acid for 45 days, the $J(\mathrm{L},t)$ and A_{cum} values were 3.17 μg cm^{-2} d^{-1} and 3329 μg at pH = 7 and 4.99 μg cm^{-2} d^{-1} and 6380 μg at pH = 10. The order of diffusion flux and diffusion total amount are: pH = 7, 0 day < pH = 7, 45 days < pH = 10, 45 days. The longer the contact time is, the larger the diffusion flux and total amount of diffused Se(IV) are. The alkaline condition is more conducive to the diffusion of Se-HA complex. Combined with the equilibrium test, it can be inferred that the effect of Se(IV) and humic acid on the diffusion is greater than that of humic acid on clay.

The diffusion coefficients calculated by the formula are shown in Table 6. The D_e value of Se(IV) diffusion in clayrock in equilibrium experiment is 3.24×10^{-14} m^2 s^{-1}, α value is 0.116, K_d value is 0.0224 mL g^{-1}, D_a value is 2.79×10^{-13} m^2 s^{-1}. Due to the influence of humic acid, the diffusion coefficient increases, because there is a small amount of Se-HA complex between humic acid and Se(IV) in this time. At the same time, humic acid changes the surface of clay, making α value increase and effective diffusion coefficient increase.

Calculated by software, the D_e values of Se(IV) diffusion in clayrock for contacting 0 day, contacting 45 days at pH = 7 and pH = 10 were $(15.2, 32.1 \text{ and } 55.9)\times10^{-14}$ m^2 s^{-1}, α values were 0.425, 0.163 and 1.29, K_d values were (0.141, 0.041 and 0.472) mL g^{-1}, D_a values were $(3.56, 1.97 \text{ and } 4.35)\times10^{-13}$ m^2 s^{-1}, respectively. With the increase of contact time, the diffusion coefficient increases obviously, which indicates that the interaction time between Se(IV) and humic acid is slow and takes a long time. The diffusion coefficient increased with the increase of pH value, which indicates that the alkaline condition is conducive to the formation of Se-HA complex. Compared with the equilibrium test, the diffusion of Se(IV) increased more obviously in the contact test, which indicates that the diffusion of Se(IV) was more affected by the contact time of Se(IV) and humic acid. That is to say, the formation of Se-HA complex had a greater impact on the diffusion of Se(IV) in clayrock than the change of clay surface properties by humic acid. Under the influence of humic acid in internal diffusion, the D_a value of Se(IV) diffusion in clay increases with the increase of pH value, which is similar to that of through-diffusion method.

Maybe the diffusion coefficient increases in the presence of HA compared to the absence of HA. It may be that humic acid forms a complex with Se(IV), and the migration rate of the complex is faster. At the same time, the value of α increased because humic acid changed the surface characteristics of clay, which was conducive to the diffusion of Se. The K_d value in the presence of humic acid is higher than that in the absence of humic acid, which is due to the interaction between humic acid and clay, which improves the adsorption of Se(IV) by clay.

It can be seen from Table 7 that the presence of humic acid increases the diffusion coefficient of Se(IV) in different geological samples, and the increase is obvious. Se(IV) in montmorillonite is affected by humic acid, the D_e value

Table 6 Diffusion parameters of Se(IV) under the influence of humic acid

Condition	C_0 (mg L^{-1})	$D_e\times10^{-14}$ (m^2 s^{-1})	α	K_d (mL g^{-1})	$D_a\times10^{-13}$ (m^2 s^{-1})
HA = 0	3750 ± 50	3.06 ± 0.12	0.0632 ± 0.001	0.0020 ± 0.0001	4.84 ± 0.21
HA = 10 Equilibrium	3500 ± 50	3.24 ± 0.13	0.116 ± 0.023	0.0224 ± 0.0001	2.79 ± 0.13
HA = 10 Contact 0 day	3300 ± 50	15.2 ± 0.6	0.425 ± 0.088	0.141 ± 0.006	3.56 ± 0.17
pH = 7 Contact 45d	3920 ± 50	32.1 ± 0.1	0.163 ± 0.016	0.041 ± 0.0042	1.97 ± 0.63
pH = 10 Contact 45d	3920 ± 50	55.9 ± 2.4	1.29 ± 0.11	0.472 ± 0.045	4.35 ± 0.42

Table7 Diffusion parameters of Se in the presence of organic acids and geological samples

Sample	Method	Condition	D_e (m^2 s^{-1})	K_d (mL g^{-1})	α	References
Tamusu clay	Through-diffusion	HA = 0	3.06×10^{-14}	0.002	0.0632	this article
		HA = 10 mg L^{-1}	32.1×10^{-14}	0.041	0.163	
Montmorillonite	Through-diffusion	HA = 0	2.13×10^{-12}		0.12	[16]
		HA = 10 mg L^{-1}	18.5×10^{-12}		1.45	
		Formic acid	20.8×10^{-12}	0.630	1.19	
		Oxalate	6.22×10^{-12}	0.468	0.34	
		Citric acid	4.25×10^{-12}		0.31	

increases 9 times, K_d and α also increase, and the influence of other organic acids is the same [16], and the change rule is similar to this experiment. Therefore, the addition of humic acid is beneficial to the retardation effect on nuclides.

Conclusions

In this article, the through-diffusion method was used to study the diffusion behavior of Se(IV) in the Tamusu clayrock core of Inner Mongolia. The effective diffusion coefficient, rock capacity factor and apparent diffusion coefficient under different pH, ionic strength and humic acid conditions were obtained. The diffusion of Se(IV) in the clayrock core under different conditions were analyzed. The results show that: ① The diffusion of Se(IV) in the rock core, D_e value increases with the increase of pH value, K_d value decreases with the increase of pH value. ② D_e value of Se(IV) diffusion in the rock core increases with the increase of ionic strength, K_d value decreases with the increase of ionic strength. ③ After adding humic acid, the D_e value of Se(IV) diffusion in the rock core increases, which indicates that humic acid and Se form complex and increase the diffusion rate of Se, and the α value also increases, which indicates that humic acid changed the surface properties of clay and widened the diffusion accessible porosity. After contact with humic acid for 45 days at pH = 7 and pH = 10, the time of reaching steady state was prolonged, and the D_e value of Se(IV) diffusion was increased. The results show that it takes time for Se(IV) to form complex with humic acid, and the increase of pH is beneficial to the formation of complex.

Acknowledgements This research was supported by grants from National Natural Science Foundation of China (Grant No.21761002).

References

1. Aurélie C, Christophe T, Carl I, Ian C, Stephane G, Imene E, Tomas K, Francis C, Thorsten S (2015) Complete restriction of $^{36}Cl^-$ diffusion by celestite precipitation in densely compacted illite. Environ Sci Technol Lett 2:139–143
2. Li C, Liu XY, Chen T, Tian WY, Zheng Z, Wang LH, Liu CL (2012) The influence of pH on the sorption and diffusion of $^{99}TcO_4^-$ in Beishan granite. Int J Chem Aspects Nucl Sci Technol 100(7):449–456
3. Wen RY, Gao HC, Jiang C, Liu YF (1991) Migration studies of the fission product nuclides in rocks -1-Diffusion behavior of radionuclide ^{79}Se in granite and limestones samples. J Nucl Radiochem 13(4):213–217
4. Guo JR (2008) Fission product analysis technology. Atomic Energy Press, Beijing
5. Wang ZF, Wu T, Ren P, Hua R, Wu H, Xu MH, Tong YH (2019) Through-diffusion study of Se(IV) in γ-irradiated bentonite and bentonite-magnetite. J Radioanal Nucl Chem 322:801–808
6. Wang H, Wu T, Chen J, Zheng Q, He CH, Zhao YL (2015) Sorption of Se(IV) on Fe- and Al-modified bentonite. J Radioanal Nucl Chem 303:107–113
7. Fordyce F (2007) Selenium geochemistry and health. Ambio 36(1):94–97
8. Tinggi U (2003) Essentiality and toxicity of selenium and its status in Australia: a review. Toxicol Lett 137(1–2):103–110
9. Séby F, Potin Gautier M, Giffaut E, Borge G, Donard OFX (2001) A critical review of thermodynamic data for selenium species at 25°C. Chem Geol 171(3–4):173–194
10. Rao GW (2018) Study on characteristic of surrounding rock of high-level radioactive waste geological disposal reservoir: a case study of mudstone in the upper part of the BayinGobi formation in the preselected area if Tamusu in Inner Mongolia. East China Institute of Technology, China, Nanchang
11. Feng WL (2009) Characteristics and origin of clay minerals in the sandstone of Taiyuan Formation, Northeastern Ordos Basin. Chengdu University of Technology, China, Chengdu
12. He HY, Liu J, Dong Y, Li HH, Zhao SW, Wang J, Jia ML, Zhang H, Liao JL, Yang JJ, Yang YY, Liu N (2019) Sorption of selenite on Tamusu clay in simulated groundwater with highsalinity under aerobic/anaerobic conditions. J Environ Radioactiv 203:210–219
13. Tachi Y, Shibutani T, Sato H, Yui M (1998) Sorption and diffusion behavior of selenium in tuff. J Contam Hydrol 35(1):77–89
14. Wu H, Huang W, Duan ZQ, Luo MB, Wang ZF, Hua R (2020) Investigation of Se(IV) diffusion in compacted Tamusu clay by capillary method. J Radioanal Nucl Chem 324:903–911
15. Wang H, Wu T, Chen J, Zhao YL, He CH, Li JY (2014) Through- and out- diffusion of Se(IV) and Re(VII) in compacted bentonite. Adv Mater Res 953:614–620
16. Li QM (2015) Effect of organic matter and illite on the Se(IV) and Re(VII) diffusion in compacted montmorillonite. East China Institute of Technology, China, Nanchang
17. Wang ZF, Wang H, Li QM, Xu MH, Guo YH, Li JY, Wu T (2016) pH effect on Re(VII) and Se(IV) diffusion in compacted GMZ bentonite. Appl Geochem 73:1–7
18. Wu MC, Lee CP, Tsai SC, Liu CY, Pan CH, Tsai TL, Wei HJ, Men LC (2013) Evaluation of HTO and selenium diffusion behavior in compacted bentonite with different lengths. Successful university conference paper, China, Taiwan
19. Wang CL, Yang XY, Wei FX (2019) The influence of pH on diffusion of ^{75}Se(IV) in Beishan granite. J Radioanal Nucl Chem 319:365–377
20. Russel WB, Saville DA, Schowalter WR (1989) Colloidal dispersions. Cambridge University Press, Cambridge
21. Tian WY, Li C, Liu XY, Wang LH, Zheng Z, Wang XY, Liu CL (2013) The effect of ionic strength on the diffusion of ^{125}I in GMZ bentonite. J Radioanal Nucl Chem 295(2):1423–1430
22. Peak D, Saha U, Huang P (2006) Selenite adsorption mechanisms on pure and coated montmorillonite: an EXAFS and XANES spectroscopic study. Soil Sci Soc Am J 70(1):192–203
23. Wu T, Wang ZF, Wang H, Zhang ZQ, Van Loon LR (2017) Salt effects on Re(VII) and Se(IV) diffusion in bentonite. Appl Clay Sci 141:104–110
24. Iida Y, Yamaguchi T, Tanaka T (2012) Experimental and modeling study on diffusion of selenium under variable bentonite content and porewater salinity. J Nucl Sci Technol 48(8):1170–1183
25. Zhao YL, Wang H, Luo Y, Fu BF, Wu T, He CH (2015) Effect of humic acid on Re(VII) diffusion in GMZ bentonite. At Energ Sci Technol 49(6):979–983