pH effect on Re(VII) and Se(IV) diffusion in compacted GMZ bentonite

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Abstract

In a high-level radioactive waste (HLW) repository, pH has an impact on the solubility, migration, and adsorption of radionuclides. Thus, understanding the effects of pH on the diffusion of radionuclides is essential for long-term disposal of HLW. In this work, the diffusion behaviors of Re(VII) and Se(IV) in compacted Gaomiaozi (GMZ) bentonite at different pH have been investigated by a through-diffusion method. The effective diffusion coefficient, i.e., D_e values of Re(VII) and Se(IV) were in the range of $(1.0 - 2.4) \times 10^{-11} \text{ m}^2/\text{s}$ at pH 3.0 - 10.0 and $(0.38 - 2.3) \times 10^{-11} \text{ m}^2/\text{s}$ at pH 3.0 - 9.0. In the case of Re(VII), the D_e values remained almost unchanged probably because ReO_4^- was the dominant species in the pH range of 3.0 to 10.0. In the case of Se(IV), whose predominant species were HSeO_3^- at pH < 9.0 and SeO_3^{2-} at pH ≥ 9.0 , the D_e values decreased by a factor of 3 - 6 at pH 9.0, i.e., $D_e(\text{pH} < 9.0)/D_e(\text{pH} 9.0) \approx 3 \sim 6$, implying that the species with a higher valence state had a stronger

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anion exclusion effect. The decrease in D_e values can be explained by the diffusion species of Se(IV). Additionally, the rock capacity factor α decreased with the increase of pH. HSeO_3^- was absorbed on GMZ bentonite with distribution coefficient K_d values in the range of $(1.0 - 2.5) \times 10^{-4} \text{ m}^3/\text{kg}$ at $\text{pH} \leq 8.0$, whereas SeO_3^{2-} was negligibly sorbed at $\text{pH} > 8.0$.

Keywords

Diffusion; Se(IV); Re(VII); pH; GMZ bentonite

1. Introduction

In China, GMZ bentonite is selected as a potential backfill material for high-level radioactive waste (HLW) repositories due to its high cation exchange capacity, low permeability and good sealing effect. Safety analysis of the repository, which involves modeling of the radionuclide transport from the repository to the geosphere, requires an understanding of the diffusion process of radionuclides in compacted bentonite (Wang and Tao, 2004).

^{79}Se and ^{99}Tc are critical fission products in HLW due to their long half-lives and low retention abilities. To avoid radioactivity, stable species such as rhenium and selenium are often used as surrogates for ^{99}Tc and ^{79}Se (Wu et al., 2014). The valence states of ^{99}Tc and Re can change from VII to III (Boggs et al., 2011; Li et al., 2012b; Rard, 2005). Both ^{99}Tc and Re exist mainly as two stable oxidation states, i.e.,

Tc(IV)/Tc(VII) or Re(IV)/Re(VII), in the environment. pH has an insignificant effect on the effective/apparent diffusion coefficient (D_e/D_a) of ^{99}Tc in bentonite, probably because $^{99}\text{TcO}_4^-$ is the most stable species in natural environments (Wang and Tao, 2004) and granite (Li et al., 2012a). For example, Wang et al. (2004) and Zhao et al. (2012) used a capillary method and reported that the D_a values were in the range of $(1.6 - 3.3) \times 10^{-10} \text{ m}^2/\text{s}$ and $(2.1 - 3.3) \times 10^{-10} \text{ m}^2/\text{s}$ in compacted bentonite with a dry density of 800 kg/m^3 at pH of 4.0 - 10.0, respectively. The difference was less than two-fold. Li et al. (2012) observed that the D_e values of $^{99}\text{TcO}_4^-$ in Beishan granite were $(0.973 - 1.31) \times 10^{-12} \text{ m}^2/\text{s}$ at pH 3.0 - 10.0. $^{99}\text{TcO}_4^-$ has been observed to be a non-sorbing species in bentonite (Li et al., 2012b). However, weak sorption of $^{99}\text{TcO}_4^-$ was found by Zhao et al. (2012) and Li et al. (2012), which may be related to uncertainties arising from the different experimental set-up and data processing in bentonite and granite. The diffusion behavior of Re(VII) is similar to that of $^{99}\text{Tc(VII)}$. The D_e values of Re(VII) decreased from 5.30×10^{-11} to $0.3 \times 10^{-11} \text{ m}^2/\text{s}$ as dry density increased from 1300 to 1800 kg/m^3 (Wu et al., 2014). The E_a of Re(VII) diffusion was 25 kJ/mol, indicating that it followed a pore diffusion model (Wu et al., 2016).

Thermodynamically stable species of ^{79}Se are Se(-II), Se(0), Se(IV) and Se(VI) according to the pH-Eh conditions. Selenite (Se(IV)) and selenate (Se(VI)) received more attention due to their higher mobility compared to other species. Compared to selenite, selenate (Se(VI)), i.e., HSeO_4^- and SeO_4^{2-} , shows lower adsorption under the

same conditions (Jang et al., 2015). The D_a value of 1.7×10^{-11} m²/s in Boom clay was an order of magnitude lower than that of HTO (Beauwens et al., 2005). Selenate is predominantly the most stable species under strongly oxidizing conditions. Therefore, selenate is temporarily not considered in this paper. Se(IV) is identified as one of the largest contributors (Descostes et al., 2008) for gauging the performance assessment of HLW disposal. Most studies have focused on the adsorption of Se(IV) on solid phases such as illite, smectite (Missana et al., 2009a), pyrite (Bruggeman et al., 2005; Kang et al., 2011), or siderite (Scheinost et al., 2008). As is well known, the speciation of Se(IV) is highly dependent on pH (Montavon et al., 2009; Sato and Miyamoto, 2004). At low pH values, the main species are H₂SeO₃ and HSeO₃⁻. SeO₃²⁻ is the dominant form at higher pH values. Most studies on the migration behavior of Se(IV) focus on the behavior of SeO₃²⁻ in clay minerals, such as in bentonite (Idemitsu et al., 2015; Sato et al., 1995), tuff (Tachi et al., 1998), and limestone (Descostes et al., 2008). For instance, Wu et al. (2014) measured the D_e values of HSeO₃⁻ in GMZ bentonite, and found that they were in the range of $(0.45 - 54) \times 10^{-11}$ m²/s at compacted dry densities of 1300 - 1800 kg/m³. Idemitsu et al. (2015) found that the D_e values of SeO₃²⁻ in Kunipia-F bentonite were in the range of $(0.19 - 25.0) \times 10^{-12}$ m²/s at compacted dry densities of 800 - 1600 kg/m³. Sato et al. (1995) measured D_a values of $(3.2 - 46) \times 10^{-11}$ m²/s at compacted dry densities of 400 - 1800 kg/m³ at pH 9.0 in Na-bentonite. Tachi et al. (1998) found that the diffusion of Se(IV) was unaltered at the pH values of 8.0 and 11.0. The D_e values were $(6.6 - 6.8) \times$

10^{-12} m²/s in tuff. However, Descostes et al. (2008) measured D_e values of (0.1 - 1.5) $\times 10^{-13}$ m²/s for $^{75}\text{SeO}_3^{2-}$ in Callovo-oxfordian argillites and 0.6×10^{-13} m²/s in Oxfordian limestones. They could not explain their low diffusion coefficients compared to other anions.

Many researchers have reported that Se(IV) shows high adsorption on montmorillonite (Charlet et al., 2007; Peak et al., 2006), Fe-Mn oxides (Chubar et al., 2014), and natural iron oxides (Missana et al., 2009b), by considering the formation of both inner- and/or outer-sphere surface complexes. For instance, extended X-Ray absorption fine structure (EXAFS) measurements and record X-ray absorption near-edge structure spectroscopy (XANES) have been used to show that Se(IV) adsorbed on montmorillonite forms only bidentate, binuclear inner-sphere complexes at pH 4.5 (Peak et al., 2006). Goldberg (2013) found that Se(IV) and oxide minerals, such as amorphous Al oxide and amorphous Fe oxide, formed inner-sphere surface complexes at low pH and outer-sphere surface complexes at high pH. However, Se(IV) is adsorbed less strongly on clay minerals than on metal oxides, for unclear reasons. In general, HSeO_3^- shows higher adsorption than SeO_3^{2-} on the surface of clays. For example, Boulton et al. (1998) found that Se(IV) was strongly sorbed on sodium bentonite below pH 7.0. Montavon et al. (2009) observed that the adsorption on MX-80 bentonite was governed by ligand exchange reaction with H_2SeO_3 and the formation of a surface complex with HSeO_3^- under acidic conditions. Under alkaline conditions, SeO_3^{2-} was sorbed on Ca and Mg-rich systems to form ternary surface

complexes involving Ca and Mg. Missana et al. (2009b) showed that SeO_3^{2-} could be absorbed on the surface of Na-smectite and Na-Illite. However, Bar-Yosef and Meek (1987) observed that SeO_3^{2-} could not be absorbed on the surface of montmorillonite and kaolinite at pH in the range of 7.0 to 9.0.

Radionuclide diffusion is closely related to the pore water chemistry, and pH is an important factor in this process. Therefore, it is necessary to understand the effect of pH on the diffusion of radionuclides. For instance, Re(VII) and Se(IV) have different adsorption properties. Re(VII) shows no sorption, whereas Se(IV) can be adsorbed on the surface of bentonite under acidic conditions. In this paper, the diffusion behaviors of Re(VII) and Se(IV) (as surrogates of $^{99}\text{Tc(VII)}$ and $^{79}\text{Se(IV)}$, respectively) in GMZ bentonite were investigated by the through-diffusion method in the pH range of 3.0 -10.0 and 3.0 - 9.0, respectively. We quantified the impact of pH on the diffusion of Re(VII) and Se(IV), and on sorption of Se(IV), under ambient conditions. The D_e values and the accessible porosity (ε_{acc}) were obtained.

2. Materials and Methods

2.1 Materials

GMZ bentonite (75.4 wt.% montmorillonite) used in the experiments was obtained from Beijing Research Institute of Uranium Geology without any pretreatment. The bulk dry density was 1600 kg/m^3 . Experiments on Re(VII) and Se(IV) diffusion were carried out in synthetic pore water from Beishan in the Gansu

province and 0.05 mol/L NaClO₄, respectively. The composition of the synthetic pore water of Beishan is listed in Table 1. The pH of the synthetic pore water was adjusted by the addition of < 0.01 mol/L HCl or NaOH. To avoid bacterial growth, 0.003 mol/L NaN₃ was added to the solution. SeO₂ (Sinopharm Reagent, China, AR) and NH₄ReO₄ (Alfa Aesar, 99.997%) were dissolved in distilled water.

Table 1 Composition of the synthetic pore water (Wu et al., 2014)

Elemental composition	Mass (mol/L)
Na ⁺	0.0475
K ⁺	0.00038
Ca ²⁺	0.0121
Mg ²⁺	0.00425
N ₃ ⁺	0.00308
HCO ₃ ⁻	0.0008
Cl ⁻	0.0206
SO ₄ ²⁻	0.02325
F ⁻	0.00012
NO ₃ ⁻	0.00031

2.2 Diffusion experiments

The diffusion experiments were conducted by a through-diffusion method. The diffusion set-up and experimental procedure can be found elsewhere (Van Loon et al., 2003). The diameter and thickness of the cylinder were 2.54 cm and 0.90 cm, respectively. Two stainless steel filters were placed in the samples (thickness: 0.157 cm, diameter: 2.54 cm, and porosity: 0.3 cm). The error produced by the diffusive

resistance of the confining filters was ignored because the ratio of the diffusion lengths in the filter and in clay was sufficiently small, i.e., ~ 0.17 . The 10% uncertainty in the D_e value became tolerable in view of other sources of error, such as measurement errors (Glaus et al., 2008). Table 2 shows the experimental conditions. The experiment on Se(IV) was conducted in 0.05 mol/L NaClO₄ to avoid the influence of ions from the synthetic pore water. In the case of Re(VII) with fast transportation, the experiment was conducted at 10 ± 2 °C to decrease the diffusion rate, because it was difficult to obtain the data at the transient-state stage, which is used for calculating the rock capacity α . On the other hand, the experiment of Se(IV) was conducted at 40 ± 2 °C to accelerate the diffusion. After the bentonite samples had been equilibrated for 4 - 5 weeks to reach full saturation, 0.8×10^{-3} mol NH₄ReO₄ and 6.0×10^{-3} mol SeO₂ were added to the source reservoirs. The Eh and pH were in the ranges of -0.1 - 0.4 mV and 3.0 - 10.0, respectively. The oxidation states of Re and Se were Re(VII) and Se(IV), respectively. At different time intervals (1 - 2 days), the solution in the target reservoir was replaced by a fresh one to maintain the lowest possible concentration of tracers. The concentrations of Re(VII) and Se(IV) in both source and target reservoirs were obtained from ICP-OES (PerkinElmer Optima 2100DV) measurements.

Table 2 Experimental conditions for diffusion experiments

Item	Condition/method	
Temperature	$10 \pm 2^\circ\text{C}$	$40 \pm 2^\circ\text{C}$
Tracer solution	Re(VII)	Se(IV)

Saturated solution	Beishan pore water	0.05 mol/L NaClO ₄
pH of solution	3.0, 4.0, 6.0, 9.0, 10.0	3.0, 5.0, 6.0, 8.0, 9.0
Atmosphere		Atmosphere
Dry density		1600 kg/m ³
V _{high}		200 mL
V _{low}		10 mL

2.3 Data processing

The diffusion behaviors of Re(VII) and Se(IV) followed the one-dimensional diffusion process. Fick's second law was employed:

$$\frac{\partial C(x,t)}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 C(x,t)}{\partial x^2} \quad (1)$$

where, $C(x,t)$ (g/L) is the mass concentration of Re(VII) or Se(IV) in water, t (s) is the diffusion time, D_e (m²/s) is the effective diffusion coefficient, α (-) is the rock capacity factor, and x (m) is the diffusion distance.

The experimental and theoretical data processing in the through-diffusion method has been described previously (Van Loon et al., 2003). The calculation of uncertainty for the experimental data of accumulated mass and flux can be found elsewhere (Van Loon and Soler, 2004). The D_e and α values were obtained by fitting the breakthrough curve with the transient and steady-state phases by least square fitting. Based on the following initial and boundary conditions, the analytical solution of the total amount of diffused radionuclides species A_{cum} was obtained as follows:

$$\begin{aligned}
c(x,t) &= 0, t = 0; \forall x, \\
c(0,t) &= C_0, x = 0; t > 0, \\
c(L,t) &= 0, x = L; t > 0
\end{aligned}$$

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

where L (m) is the sample thickness, C_0 (g/m³) is the initial concentration of the diffusing species, and S (m²) is the cross-sectional area of the clay.

The flux at the low-concentration boundary ($x = L$) $J(L,t)$ is calculated by the following equation:

$$J(L,t) = \frac{1}{S} \cdot \frac{\partial A}{\partial t} \quad (3)$$

2.4 Species analysis

Fig. 1 Visual MINTEQ-predicted Se(IV) species distribution vs. pH

Selenite has a complex chemical behavior in aqueous solutions because of its several oxidation states, such as H₂SeO₃, HSeO₃⁻ and SeO₃²⁻ (Qin et al., 2012). The

effect of pH on the Se(IV) species was observed by Visual MINTEQ, the results for which are shown in Figure 1. The predominant species were H_2SeO_3 , HSeO_3^- , and SeO_3^{2-} . Based on the model, these curves show that H_2SeO_3 , HSeO_3^- , and SeO_3^{2-} were the main species in the pH ranges of 0 - 2.0, 4.0 - 7.0, and 9.0 - 12.0, respectively. A mixture of H_2SeO_3 and HSeO_3^- was observed at pH 3.0 - 4.0. HSeO_3^- and SeO_3^{2-} were observed in the pH range of 7.0 to 8.0. On the contrary, rhenium was relatively stable. ReO_4^- was the predominant species under ambient conditions.

3. Results and discussion

3.1 Re(VII) diffusion

Figure 2 shows the plots of $J(L,t)$ and A_{cum} vs. time for Re(VII) diffusion in compacted GMZ bentonite only at pH 4.0 because both A_{cum} and $J(L,t)$ showed no significant change with increased pH. The symbols represent the experimental results, while the solid and dashed lines represent the fitting and expected results, respectively. The error bars represent the uncertainties of the calculated curve and experimental data. The time to reach the steady state was ~ 2 days.

Fig. 2 $J(L,t)$ and A_{cum} vs. time for Re(VII) diffusion in compacted GMZ bentonite at pH 4.0 by the through-diffusion method.

Table 3 lists the diffusion parameters of Re(VII), such as D_e , D_a , and ε_{acc} . In the case of an anion without adsorbing ability, like Re(VII), the ε_{acc} is less than the total porosity, i.e., $\varepsilon = 0.44 \pm 0.02$, which was obtained by measuring tritiated water (HTO) diffusion in GMZ bentonite at 1600 kg/m^3 (Wu et al., 2012a). The α value corresponds to the ε_{acc} for non-sorbing species. (Van Loon et al., 2007; Van Loon and Soler, 2004). The uncertainty of α includes the uncertainties of the measurement, the dead volume, and the pipetting and weighing procedures. D_a is calculated by the following equation:

$$D_a = \frac{D_e}{\alpha} \quad (4)$$

Table 3 Diffusion parameters for Re(VII) in compacted bentonite (1600 kg/m^3)

Anion	Condition	C_0	D_e	D_a	ε_{acc}
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		$\times 10^{-3} \text{ mol/L}$	$\times 10^{-11} \text{ m}^2/\text{s}$	$\times 10^{-11} \text{ m}^2/\text{s}$	-
ReO_4^-	pH 3.0	4.0 ± 0.4	2.4 ± 0.1	16.7 ± 0.1	0.15 ± 0.01
ReO_4^-	pH 4.0	4.0 ± 0.2	1.7 ± 0.1	-	< 0.1
ReO_4^-	pH 6.0	3.6 ± 0.2	2.2 ± 0.1	14.0 ± 0.1	0.15 ± 0.01
ReO_4^-	pH 9.0	3.6 ± 0.2	1.0 ± 0.1	-	< 0.1
ReO_4^-	pH 10.0	3.6 ± 0.2	1.5 ± 0.1	-	< 0.1
ReO_4^- ^a	pH 4.0	7.6 ± 0.6	1.8 ± 0.1	10 ± 2	0.18 ± 0.01
$^{99}\text{TcO}_4^-$ ^b	pH 7.6	3.9×10^{-2}	2.8 ± 0.2	14.7 ± 0.5	0.19 ± 0.01
$^{125}\text{I}^-$ ^c	pH 7.6	4.0×10^{-8}	2.04 ± 0.08	18.5 ± 0.6	0.11 ± 0.02
$^{36}\text{Cl}^-$ ^d	pH 8.2	-	1.5	10	0.15
$^{36}\text{Cl}^-$ ^f	-	2.35×10^{-8}	0.11 ± 0.01	-	0.016 ± 0.002

a Data from (Wu et al., 2014)

b Data from (Li et al., 2012b)

c Data from (Wu et al., 2012b)

d Data from (Molera et al., 2003)

f Data from (Van Loon et al., 2007)

For ReO_4^- , whose predominant species was ReO_4^- in the pH range of 3.0 - 10.0, the D_e values of $(1.0 - 2.4) \times 10^{-11} \text{ m}^2/\text{s}$ and D_a values of $(1.40 - 1.67) \times 10^{-10} \text{ m}^2/\text{s}$ were almost unchanged with increasing pH. This was in good agreement with the diffusion of $^{99}\text{TcO}_4^-$ in compacted bentonite (Wang and Tao, 2004; Zhao et al., 2013) and granite (Li et al., 2012a). To reveal the relationship between D_e values and pH in bentonite, the D_e values of Re(VII) were compared with those of Tc(VII) and Se(IV), as shown in Figure 4. Compared to the other anionic species at 1600 kg/m^3 -compacted bentonite, such as $^{99}\text{TcO}_4^-$, $^{125}\text{I}^-$ and $^{36}\text{Cl}^-$, the D_e value was similar to that of $^{99}\text{TcO}_4^-$ (Wu et al., 2012b), $^{125}\text{I}^-$ (Wu et al., 2012b) and $^{36}\text{Cl}^-$ (Molera et al., 2003), whereas it was an order of magnitude higher than that of $^{36}\text{Cl}^-$ (Van Loon et al., 2007). This can be explained that the diffusion of $^{36}\text{Cl}^-$ was driven by Brownian motion because the experiments were operated in 0.05 mol/L NaCl solution, unlike

the diffusion of Re(VII), $^{99}\text{TcO}_4^-$, $^{125}\text{I}^-$ and $^{36}\text{Cl}^-$, which were driven by the concentration gradient. The ε_{acc} value ≤ 0.15 rely on the first two data of A_{cum} vs. time, so that the values smaller than 0.1 are not reliable. The ε_{acc} values were less than the total porosity, indicating that ReO_4^- exhibited negative adsorption due to anion exclusion (Molera et al., 2003; Van Loon et al., 2007). However, Wang et al. (2004) and Zhao et al. (2012) obtained K_d values of $^{99}\text{Tc(VII)}$ in the range of $(0.9 - 2.9) \times 10^{-3} \text{ m}^3/\text{kg}$ and $(1.6 - 2.3) \times 10^{-3} \text{ m}^3/\text{kg}$ in MX-80 and GMZ bentonite, respectively, by capillary methods. It is still unclear whether the non-zero K_d values of $^{99}\text{Tc(VII)}$ were caused by the diffusion method, chemical species, or data processing.

3.2 Se(IV) diffusion

Figure 3 shows the plots of $J(L,t)$ and A_{cum} vs. time for Se(IV)-diffusion in compacted GMZ bentonite at pH 3.0 - 9.0. The diffusion time required to reach the steady state was ~ 13 days. Table 4 shows the diffusion parameters for Se(IV) in compacted GMZ Bentonite. The K_d and uncertainty of K_d values were derived by the following equation (Molera et al., 2003; Van Loon et al., 2007):

$$K_d = \frac{\alpha - \varepsilon}{\rho} \quad (5)$$

$$uK_d = K_d \cdot \sqrt{\left(\frac{uD_e}{D_e}\right)^2 + \left(\frac{u\rho}{\rho}\right)^2 + \left(\frac{u\varepsilon}{\varepsilon}\right)^2} \quad (6)$$

where, uD_e , $u\rho$ and $u\varepsilon$ are the uncertainties of D_e , ρ and ε , respectively. The widths of diffusion paths of Re(VII) and Se(IV) can be considered as almost identical at all pH

values due to similar ionic radii of 0.053 and 0.050 nm, respectively, when ignoring the possible effect of the higher electric charge of SeO_3^{2-} at high pH. The ε_{acc} of Re(VII) was used to calculate the K_d value of Se(IV), i.e., $\varepsilon_{acc}(\text{Se(IV)}) = 0.15$. The D_e values were in the range of $(0.38 - 2.3) \times 10^{-11} \text{ m}^2/\text{s}$. They decreased with the increase of pH, which can be explained by considering that the Se(IV) species are transformed from H_2SeO_3 through HSeO_3^- to SeO_3^{2-} . At pH 3.0, the D_e value was the highest because the predominant species were H_2SeO_3 and HSeO_3^- . The D_e value remained unchanged at pH 5.0 - 8.0. Thus, it can be concluded that the predominant species, HSeO_3^- , governs the diffusion. However, the D_e values decreased at pH 9.0, i.e., $D_e(\text{pH} < 9.0)/D_e(\text{pH} 9.0) \approx 3 \sim 6$. This can be explained by considering that more negatively charged species show stronger anion exclusion (Appelo et al., 2010), leading to lower accessible porosity. This makes it increasingly difficult for the species to pass through, due to their narrower diffusion path (Van Loon et al., 2003). The α values decreased with increasing pH. This is not only because the Se(IV) species changes to more negatively charged species, i.e., H_2SeO_3 at $\text{pH} < 3.0$, HSeO_3^- at $\text{pH} 4.0 - 7.0$ and SeO_3^{2-} at $\text{pH} \geq 9.0$, but it is also because the surface becomes more negatively charged, i.e., functional Al-OH and Si-OH groups on the surface become deprotonated at high pH, resulting in an increased negative charge at the surface.

Fig. 3 $J(L,t)$ and A_{cum} vs. time for Se(IV) diffusion in compacted GMZ bentonite at pH 3.0 - 9.0 by through-diffusion method

Table 4 Diffusion parameters for Se(IV) in compacted GMZ bentonite

Condition	C_0 $\times 10^{-2}$ mol/L	D_e $\times 10^{-11}$ m ² /s	D_a $\times 10^{-11}$ m ² /s	α -	K_d $\times 10^{-4}$ m ³ /kg
pH 3.0	2.8 ± 0.8	2.3 ± 0.1	4.2 ± 0.2	0.55 ± 0.02	2.5 ± 0.19
pH 5.0	2.8 ± 0.8	1.7 ± 0.1	4.1 ± 0.3	0.41 ± 0.02	1.6 ± 0.38
pH 6.0	2.8 ± 0.8	1.6 ± 0.1	3.4 ± 0.3	0.47 ± 0.02	2.0 ± 0.48
pH 8.0	2.7 ± 0.8	1.2 ± 0.1	3.9 ± 0.3	0.31 ± 0.01	1.0 ± 0.25
pH 9.0	2.6 ± 0.8	0.38 ± 0.01	2.9 ± 0.2	0.13 ± 0.01	-

The D_a values of $(2.9 - 4.2) \times 10^{-11}$ m²/s showed no significant change because both of D_e and α values increased. At pH ≤ 8.0 , the α value was higher than the ε_{acc} of ReO_4^- , indicating that Se(IV) was adsorbed on the bentonite by the formation of a surface complex between selenite (HSeO_3^-) and the surface of montmorillonite (Montavon et al., 2009). The K_d values were $(1.0 - 2.5) \times 10^{-4}$ m³/kg for HSeO_3^- , in good agreement with the previously published results in Kunigel-V1Na-bentonite (Sato and Miyamoto, 2004). The Se(IV) uptakes on GMZ bentonite varied with the pH of the solution. Similar pH-dependent adsorption behavior has been previously observed for selenite on Fe oxide (Duc et al., 2006) and Al oxide (Goldberg, 2013). Selenite adsorption on oxide minerals increases under acidic conditions and decreases

under alkaline conditions. Under acidic conditions, the Si-OH (or Al-OH) of montmorillonite changes to Si-(OH)₂⁺ (or Al-(OH)₂⁺) (Kim, 2003), leading to the adsorption of Se(IV) on the surface and subsequent of surface complexation. Se(IV) is absorbed on the surface to form inner-sphere and outer-sphere complexes on Al-(OH)₂⁺ (Bourg et al., 2003; Goldberg, 2013).

3.3 Comparison of diffusion parameters

Table 5 the diffusion parameters of Re(VII), ⁹⁹Tc(VII) and Se(IV) in clays

Anion	Clay	Experiment condition	D_e $\times 10^{-11} \text{ m}^2/\text{s}$	D_a $\times 10^{-11} \text{ m}^2/\text{s}$	K_d $\times 10^{-4} \text{ m}^3/\text{kg}$	Reference
ReO ₄ ⁻	GMZ bentonite	1600 kg/m ³ pH3.0-10.0	1.0 - 2.4	14 - 16.7	-	This work
Se(IV)	GMZ bentonite	1600 kg/m ³ pH3.0-9.0	0.38 - 2.3	2.9 - 4.2	≤ 2.5	This work
⁹⁹ TcO ₄ ⁻	MX-80 bentonite	1020 kg/m ³ pH4.0-10.0	39 - 51	16 - 33	9 - 29	(Wang and Tao, 2004)
⁹⁹ TcO ₄ ⁻	GMZ bentonite	800 kg/m ³ pH4.0-10.0	-	21 - 33	16 - 23	(Zhao et al., 2013)
⁹⁹ TcO ₄ ⁻	Beishan granite	2700 kg/m ³ pH 3.0-9.0	0.0973 -0.131	-	3.84× 10 ⁻³ -1.37	(Li et al., 2012a)
SeO ₃ ²⁻	Kunipia-F bentonite	(800 - 1600) kg/m ³	0.019 - 2.5	-	-	(Idemitsu et al., 2015)
SeO ₃ ²⁻	Tuff	1780 kg/m ³ pH 8.0-11.0	0.66 - 0.68	-	1.5 - 13	(Tachi et al., 1998)

Table 5 summarizes the diffusion parameters of Re(VII), ⁹⁹Tc(VII) and Se(IV) in clays. Depending on the experimental conditions, the D_e values of Re(VII) and ⁹⁹Tc(VII) were in the range of 10⁻¹² - 10⁻¹⁰ m²/s, whereas the D_e values of Se(IV) were in the range of 10⁻¹³ - 10⁻¹¹ m²/s.

Fig. 4 D_e values vs. pH for ReO_4^- , Se(IV) and TcO_4^- in compacted clays

Figure 4 shows the plots of D_e values vs. pH for Re(VII) and Se(IV) in bentonite, and $^{99}\text{TcO}_4^-$ in bentonite (Wang and Tao, 2004) and granite (Li et al., 2012a). For ReO_4^- and $^{99}\text{TcO}_4^-$, pH had a negligible influence on the D_e values in compacted bentonite and granite. In contrast, the D_e values of Se(IV) decreased at $\text{pH} > 8.0$. There was no clear difference in the D_e values of Se(IV) and Re(VII) up to $\text{pH} 9.0$. This may be explained by considering that the dominating species were HSeO_3^- and ReO_4^- , respectively. On the other hand, the predominant species of Se(IV) at $\text{pH} 9.0$ was SeO_3^{2-} , leading to a smaller effective diffusion coefficient due to stronger anion exclusion under higher-pH conditions.

Fig. 5 Illustration of the possible diffusion paths of Re(VII) and Se(IV) in GMZ bentonite

Figure 5 shows an illustration of the possible diffusion paths of Re(VII) and Se(IV) in GMZ bentonite. According to Van Loon et al. (Van Loon et al., 2007), the pore space includes the interlayer space (TOT-layers) and the interparticle space. The interparticle space can further be subdivided into free water space and diffusive double layer (DDL) space. Only water and cations can enter the TOT-layers. The diffusion of anions mainly occurs through the interparticle space, or more accurately, in free water space. In the case of ReO_4^- , the effective diffusion coefficient was negligibly altered in pH 3.0 - 10.0 probably because pH had a limited impact on the interparticle space. On the other hand, Se(IV) was adsorbed on the surface of GMZ

bentonite at pH below 9.0, by the formation of a surface complex such as AlHSeO_3 , which is an inner-sphere complex at low pH (Goldberg, 2013). However, SeO_3^{2-} was hardly sorbed on the surface of bentonite at pH 9.0, because the equilibrium constant of 0.369 for the outer-sphere complex $\text{AlOH}_2^+-\text{SeO}_3^{2-}$ was small, based on the triple layer model (Goldberg, 2013). Thus, the decreasing of D_e values of SeO_3^{2-} at pH 9.0, owed to the larger anion exclusion because of double charge of the anion species.

4. Conclusion

The effect of pH on the diffusion behaviors of Re(VII) and Se(IV) was studied on compacted GMZ bentonite. The results show that the diffusion of anions depends mainly on the species. In the case of Re(VII), ReO_4^- was the only species in the solution. The D_e values of $(1.0 - 2.4) \times 10^{-11} \text{ m}^2/\text{s}$ at pH 3.0 - 10.0 decreased by less than a factor of 3 with the increase in pH, indicating that pH had an insignificant impact on the surface charge of montmorillonite, and no significant influence on the diffusion paths of the species. In addition, Re(VII) was negligibly adsorbed on the surface of bentonite at pH 3.0 - 10.0. On the contrary, the D_e value of Se(IV) was in the range of $(0.38 - 2.3) \times 10^{-11} \text{ m}^2/\text{s}$ at pH 3.0 - 9.0. It decreased by a factor of 3 - 6 times at pH > 8.0, i.e., $D_e(\text{pH} < 9.0)/D_e(\text{pH} 9.0) \approx 3 \sim 6$. As well as we know now, pH has no significant influence on the width of diffusive double layer. The major difference between Re(VII) and Se(IV) is that Se(IV) has more species, i.e., H_2SeO_3 , HSeO_3^- , and SeO_3^{2-} . SeO_3^{2-} shows stronger anion exclusion, leading to lower effective

diffusion coefficient. Moreover, Se(IV) was adsorbed on bentonite with K_d values of $(1.0 - 2.5) \times 10^{-4} \text{ m}^3/\text{kg}$ at $\text{pH} \leq 8.0$, indicating the formation of a surface complex between selenite (HSeO_3^-) and the surface of montmorillonite.

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