Re(VII) diffusion in bentonite:

Effect of organic compounds, pH and temperature

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Abstract: In order to understand the diffusion properties of anionic radionuclides (RN) in bentonite in the presence of organic compounds with chelating and reducing properties, the effect of humic acid (HA), citrate, oxalate and formate on Re(VII) diffusion were investigated by a through-diffusion method under different pH (pH 7.0 and 10.0) and temperature conditions (10 ~ 65 °C). When the molar ratio of oxalate to Re(VII) was higher than 1:1, the accumulated mass and flux were observed to decrease drastically as a function of time. It can be explained by photocatalytic impact of Fe(III) on the reduction of Re(VII) to insoluble Re(IV) by oxalate. Thus, the diffusion of Re(VII) was also observed to decrease in the presence of minor citrate, oxalate and formate. Effective diffusion coefficient (D_e) values decreased from $8.7 \times 10^{-11} \text{ m}^2/\text{s}$ to $(5.1 \sim 5.9) \times 10^{-11} \text{ m}^2/\text{s}$. In contrast, HA had no significant impact on Re(VII) diffusion. The D_e values of 1.54×10^{-11} and $6.5 \times 10^{-12} \text{ m}^2/\text{s}$ were obtained at pH 7.0 and 10.0, respectively. HA thus neither

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has an effect on the speciation of Re(VII) nor does it change the charge of the surface. The latter is probably due to the fact that HA preferentially interacts with the aluminol sites of the montmorillonite edges without changing the zeta potential of the surface. The dependence of D_e of Re(VII) on temperature in the absence and presence of citrate or formate was described by the Arrhenius equation. The activation energy, E_a , was in the range of (20.7 ~ 25.1) kJ/mol, demonstrating that Re(VII) diffusion followed a pore water diffusion model.

Keywords: diffusion, perrhenate, bentonite, organic compounds, temperature

1. Introduction

Technetium-99 is of great concern in the disposal of high-level radioactive waste (HLW) because of its long half-life of 2.1×10^5 years and its low retention/adsorption on the backfilling material (e.g. bentonite) and surrounding host rock. Under oxic conditions, the pertechnetate (TcO_4^-) anion is the dominant species. It has a high mobility because of its high solubility in water and its low adsorption properties on mineral surfaces. Earlier work showed that the effective diffusion coefficient (D_e) in bentonite was in the range of $10^{-10} \sim 10^{-12} \text{ m}^2/\text{s}$ (Li et al., 2012b) and in the case of granite $10^{-12} \sim 10^{-13} \text{ m}^2/\text{s}$ (Li et al., 2012). However, TcO_4^- can be reduced in the environment to relatively sparingly soluble and immobile Tc(IV) species under anaerobic conditions by Fe-bearing clay minerals (Bishop et al., 2011; Um et al., 2011), reducing bacteria (Plymale et al., 2011) and redox active organic molecules (Reinoso Maset et al., 2006). The apparent diffusion coefficient (D_a) of Tc in compacted bentonite decreased from 10^{-10} to $10^{-12} \text{ m}^2/\text{s}$ under reducing condition (Sawatsky and Oscarson, 1991).

1 Organic compounds such as humic acids (HA), acetate, citrate, etc., which are ubiquitous in
2 the environment, can enter a repository and coexist with radioactive waste. Significant
3 concentrations of organic compounds including citrate and oxalic acid are also found in several of
4 the tanks at Hanford (Xia et al., 2006). They could have an important effect on the migration of
5 radionuclides (RN) by forming water soluble complexes (Boggs et al., 2011; Wall et al., 2013),
6 enhancing their solubility (Gu et al., 2011; Reinoso Maset et al., 2006) and modifying the surface
7 properties of clays (Ramos et al., 2014; Ramos and Huertas, 2014). For example, reduced Tc,
8 Tc(IV), can be complexed with citrate (Wall et al., 2013), ethylenediaminetetraacetic acid (EDTA)
9 (Boggs et al., 2013; Gu et al., 2011), oxalate (Xia et al., 2006), acetate (Boggs et al., 2010) and
10 humic substances (Boggs et al., 2011; Gu et al., 2011), increasing the solubility of TcO₂(s) (Gu et
11 al., 2011). The solubility of Re(IV)-EDTA complexes was also found to be higher than that of
12 Re(VII) (Corkhill et al., 2013). Hence, these studies thus question whether reduction of Tc(VII) to
13 Tc(IV) indeed leads to an immobilization of Tc.

14 Interestingly, it has been widely reported that addition of small molecular weight organic
15 acids such as oxalate and citrate can significantly accelerate the photoreduction of Cr(VI) in the
16 presence of semiconductor materials (Meichtry et al., 2007), mineral clays (Jiang et al., 2012; Lan
17 et al., 2008; Shao et al., 2009) and soils (Tian et al., 2010; Yang et al., 2008). For instance, Lan et
18 al. (2008) found that montmorillonite and illite greatly accelerate the Cr(VI) reduction reactions
19 by citrate at pH 4.0 and 4.5. Hug et al. (1997) reported that oxalate and citrate accelerated the
20 photoreduction of Cr(VI) catalyzed by Fe(III) as organic ligands. Rhenium, could be used as an
21 analogue for technetium in diffusion experiment in order to avoid complications of working with
22 radioactive material (Wu et al., 2014b) In case of “organic matter effects”, EDTA enhanced the

1 diffusion of Tc(VII), i.e. the D_e values of Tc(VII) were 4 times larger in the presence of EDTA,
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5 Many researchers focused on the interaction between organic compounds and Tc(IV) or
6 Re(IV). Knowledge on the chemical behavior of Tc(VII) and Re(VII) are very important for safety
7 assessment of HLW because of their high mobilities. The goals of this study are to better
8 understand the effect of organic compounds on Re(VII) diffusion, which can provide insight on
9 the diffusion behavior of Tc-organic complexes, and might contribute to a better prediction of their
10 migration behavior in backfilling material of a HLW repository. The following organic compounds
11 with chelating and partially reducing properties were used: humic acids (HA), citrate, oxalate and
12 formate. Effect of pH (7.0 and 10.0) and temperature (10 ~ 65) °C were investigated under
13 ambient conditions. Activation energies (E_a) were calculated using the Arrhenius equation.

15 **2. Materials and Methods**

16 **2.1 Materials**

17 Montmorillonite is the main component of Gaomiaozi (GMZ) bentonite, which is chosen as
18 the backfilling material for HLW repository in China (Ye et al., 2010). It was formed by fusing
19 two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide in
20 tetrahedral–octahedral–tetrahedral (TOT) coordination. Montmorillonite K-10, which was
21 originally designed for catalytic purposes, was used in this study to investigate the photocatalytic
22 reduction of Re(VII) by organic acids. The montmorillonite K-10 with a specific surface area of

240 m²/g was purchased from Aladdin. The molecular weight is 282.20 g/mol. The chemical composition was as follows: SiO₂ (73.0%), Al₂O₃ (14.0%), Fe₂O₃ (2.7%), CaO (0.2%), MgO (1.1%), Na₂O (0.6%), K₂O (1.9%). GMZ bentonite with a specific surface area of 570 m²/g was obtained from the Beijing Research Institute of Uranium Geology without further processing. The chemical composition was as follows: SiO₂ (67.43%), Al₂O₃ (14.2%), TFe₂O₃ (2.4%), CaO (1.13%), MgO (0.10%), Na₂O (1.75%), K₂O (0.73%), P₂O₅(0.02%), TiO₂(0.12%), FeO(0.29%), MnO(0.02%) (Ye et al., 2010), HA were purchased from Aldrich Co. Ltd. They were dissolved in a 0.01 mol/L NaOH solution. Solutions of organics were prepared by dissolving given amounts of analytical grade citric, oxalic and formic acid in 0.05 mol/L NaCl. The pH of the solutions was adjusted to 7.0 and 10.0 with NaOH. 0.003 mol/L NaN₃ was added to the solutions to suppress bacterial growth.

Re(VII) was prepared in distilled water using NH₄ReO₄ (Alfa Aesar, 99.997%). The dominant species is predicted to be ReO₄⁻. The effective ionic radii is 0.053 nm (Shannon, 1976). The concentration of Re was determined by ICP-OES (PerkinElmer Optima 2100DV).

2.2 Diffusion experiments

Fig. 1. Schematic experimental set-up used in the through-diffusion experiments (Van Loon et al., 2003).

The through-diffusion set-up and experimental procedures have been described elsewhere (Van Loon et al., 2003). A schematic drawing of the experimental set-up is shown in Figure 1. All

experiments were operated under ambient condition. The bentonite and montmorillonite samples were directly compacted to a bulk dry density of 1300 ~ 1600 kg/m³ in a cylindrical cell of Ø25.4 × 10.0 mm, respectively. The sample was sandwiched between two stainless steel filter plates (Stainless steel: 316 L, pore diameter: 10 µm, diameter: 2.54 cm, thickness: 0.78 mm, Ligacon AG, Switzerland). The source reservoir had a volume of 200 mL and was filled with 0.05 mol/L NaCl whereas the target one (V_{low}) had a volume 10 mL. After saturating the montmorillonite sample for 5 weeks, the source reservoir was spiked with ~3.0 g NH₄ReO₄. The solution in the target reservoir was replaced by a fresh one periodically (every 1 ~ 2 days) to maintain the Re(VII) concentration near to zero.

The diffusion cells were put in an incubator to maintain the temperature in the range of 10 ~ 65 °C. The diffusion experiment was started at a given temperature. As soon as the steady state phase was reached, the temperature was increased. For each temperature the steady state phase was used to calculate the D_e value (Van Loon et al., 2005).

2.3 Data processing

The through-diffusion experiments followed one-dimensional non-steady-state diffusion process. Fick's second law was applied.

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2}. \quad (1)$$

Where D_a (m²/s) is the apparent diffusion coefficient in the compacted clay, C (mol/L) is the concentration of the diffusing species, t (s) is the diffusion time, and x (m) is the diffusion distance.

If instantaneous linear sorption is considered, α is defined as:

$$\alpha = \varepsilon + \rho \cdot K_d \cdot \quad (2)$$

Where ε (-) is the porosity of the clay sample, ρ (kg/m³) is the bulk dry density of the compacted clay sample, and K_d (m³/kg) is the distribution coefficient. The relationship between D_a and D_e is given by the following equation:

$$D_a = \frac{D_e}{\alpha} \quad (3)$$

In the experimental set-up, the initial and boundary conditions are:

$$c(x, t) = 0, \quad t = 0; \quad \forall x,$$

$$c(0, t) = C_0, \quad x = 0; \quad t > 0,$$

$$c(L, t) = 0, \quad x = L; \quad t > 0.$$

The cumulative mass (A_{cum} , g) of the diffusing species as a function of the diffusion time t (s) is given by:

$$A_{cum} = S \cdot L \cdot C_0 \left(\frac{D_e \cdot t}{L^2} - \frac{\alpha}{6} - \frac{2 \cdot \alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cdot \exp \left\{ - \frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{L^2 \cdot \alpha} \right\} \right). \quad (4)$$

Here L (m) is thickness of the clay sample, C_0 (μg /m³) is the initial concentration of the diffusing species in the source reservoir, and S (m²) is the cross section area of the clay sample. The flux is calculated by the following equation:

$$J(L, t) = \frac{1}{S} \cdot \frac{\partial A}{\partial t}. \quad (5)$$

Where $J(L, t)$ is the flux at the low-concentration boundary ($x = L$).

3. Results and discussion

3.1 Effect of oxalate

Fig. 2. The accumulated mass (B) and diffusive flux (A) of Re(VII) in bentonite and montmorillonite as a function of diffusion time in the presence of oxalate. $T = 10 \pm 2$ °C, $I = 0.05$ mol/L, pH = 7.0, (-■-): $C_{\text{Re(VII)}} = 3.0 \times 10^{-3}$ mol/L, $C_{\text{oxalate}} = 0.1$ mol/L, 1300 kg/m³ compacted bentonite; (-○-): $C_{\text{Re(VII)}} = 3.0 \times 10^{-3}$ mol/L, $C_{\text{oxalate}} = 3.0 \times 10^{-3}$ mol/L, 1600 kg/m³ compacted bentonite; (-▲-): $C_{\text{Re(VII)}} = 6.0 \times 10^{-3}$ mol/L, $C_{\text{oxalate}} = 5.0 \times 10^{-2}$ mol/L, 1600 kg/m³ compacted montmorillonite.

In order to investigate the retardation effect of organic compounds on Re(VII) diffusion, oxalate was employed in the through-diffusion experiment. Figure 2 shows the effect of oxalate on the accumulated mass and diffusive flux of Re(VII) in bentonite and montmorillonite. The flux increases, reaches a maximum and decreases again with increasing diffusion time. The maximum flux was higher at a bulk dry density of 1300 kg/m³ than that of at 1600 kg/m³. Both bentonite and montmorillonite prevented Re(VII) from diffusing into the target reservoir. When the molar ratio of oxalate to Re(VII) was 1:1, the retardation effect became significant after 25 days. The retardation effect increased with increasing concentration of oxalate. It can be explained by photocatalytic impact of Fe(III) on the reduction of Re(VII) to insoluble Re(IV) by oxalate. Transition metal ions such as Fe(III) and Mn(II), which often coexist in clay minerals, can complex with citrate/oxalate. The Fe(III)-organic acids complexes with high photochemical activity led to a rapid reduction of Cr(VI) after absorption of sun light, whereas Mn(II)-organic acids accelerate the reduction in the dark (Jiang et al., 2012; Lan et al., 2008). Therefore, small molecular weight organic acids and Fe(III)/Mn(II) have a synergic action on the photocatalytic reduction reaction. Montmorillonite K10 contains free iron oxides and structural iron in the clay

octahedral lattice, Fe(III) was dissolved by oxalate to form Fe(III)-oxalate complexes with high photochemical activity due to the absorption of mimic solar light. Organic acid radicals such as $C_2O_4^{\bullet-}$, $CO_2^{\bullet-}$ and $O_2^{\bullet-}$ were generated through a metal-ligand-charge-transfer pathway, converting Re(VII) into Re(IV) rapidly according to following reaction scheme:

where "≡" is the surface of montmorillonite. Herein, montmorillonite accelerates the photocatalytic reduction of Re(VII) by oxalate, as previously reported under different conditions for Cr(VI) reduction (Jiang et al., 2012; Lan et al., 2008; Tian et al., 2010). Unfortunately, we were not able to identify Re(IV) in montmorillonite. Therefore it is not possible to verify the proposed mechanism of photocatalytic reduction of Re(VII). Hence, further studies are needed to investigate the interaction mechanism between them.

3.2 Effect of organic matter

Natural organic matter (NOM) is recognized as one of the largest input of organic

compounds into the repository. Depending on the host rock and location, the concentration of NOM can vary between 0.02 ~ 10 mg/L in granitic waters and 0.9 ~ 127 mg/L in salt dome ground waters (Stockdale and Bryan, 2013). In the case of Beishan HLW repository in China, the host rock is granite with a low NOM content. In contrast, the concentration of released Tc from nuclear waste glasses could reach values up to 10^{-4} mol/L (ca. 10 mg/L) as reported by Pirlet (2001) in the case of oxidized clay. The concentration of Tc is expected to be higher than that of organic compounds.

Fig. 3. The accumulated mass (A) and diffusive flux (B) of Re(VII) in montmorillonite as a function of diffusion time in the presence of citrate, oxalate and formate. $\rho = 1600 \text{ kg/m}^3$, $T = 10 \pm 2 \text{ }^\circ\text{C}$, $\text{pH} = 7.0$, $I = 0.05 \text{ mol/L}$, $C_{\text{citrate}} = 4.8 \times 10^{-5} \text{ mol/L}$, $C_{\text{oxalate}} = 1.1 \times 10^{-4} \text{ mol/L}$, $C_{\text{formate}} = 2.2 \times 10^{-4} \text{ mol/L}$, $C_{\text{HA}} = 3.5 \times 10^{-5} \text{ mol/L}$, $C_{\text{Re(VII)}} = 2.6 \sim 3.1 \times 10^{-2} \text{ mol/L}$.

Figure 3 shows A_{cum} and flux of Re(VII) diffusion in presence of 10 mg/L citrate, oxalate, formate and HA. In Fig. 3A, the A_{cum} of Re(VII) measured in the target reservoirs showed a good linear relationship with diffusion time. The D_e and α values were obtained by fitting the breakthrough curves in Fig. 3A with Eq. (4). In Fig. 3B, the flux initially increased for the first (~ 5) days in the transient phase, and then remained constant in the steady state phase. The data were the experimental results. The curves were calculated by Eq.(5) with the obtained D_e and α values as input data. The agreement of experimental and modeled data verified the correction of the D_e and α values. Fig. 3B showed that the organic compounds except HA reduce the amount of Re(VII) diffused from the source reservoir into the target reservoir, resulting in a lower flux

Re(VII), which confirms the results in Fig. 3A. In contrast, HA had no significant impact on A_{cum} and flux of Re(VII). Wang et al. (2015b) reported that Re(VII) diffusion increased in the presence of HA with increasing contact time. Majzik and Tombácz (2007a) reported that HA could sorb on the edges of montmorillonite by a ligand exchange reaction. However, no influence of HA on the zeta potential of montmorillonite was observed (Majzik and Tombácz, 2007b). HA thus neither has an effect on the speciation of Re(VII) nor does it change the charge of the surface. The latter is probably due to the fact that HA preferentially interacts with the aluminol sites of the montmorillonite edges without changing the zeta potential of the surface.

Table 1. The diffusion parameters of Re(VII) in montmorillonite in presence of organic compounds

Table 1 shows the fitting results of D_e , α and D_a values of Re(VII) in montmorillonite. In case of HA, the D_e values of $(8.3 \sim 8.7) \times 10^{-12} \text{ m}^2/\text{s}$ were almost equal, within the experimental error in absence and presence of HA. HA have no effect on the diffuse double layer and therefore HA have no significant effect on Re(VII) diffusion. Similar results were found for Re(VII) diffusion for a degree of compaction of 1600 (Wang et al., 2015a; Wu et al., 2014b) and 1800 kg/m^3 (Wang et al., 2015b). Compared to our recent work, the D_e values of $5.3 \times 10^{-11} \text{ m}^2/\text{s}$ for Re(VII) in Gaomiaozi bentonite remained unchanged in the absence and presence of EDTA. It could be explained by the fact that EDTA formed very stable compounds with Fe(III), markedly suppressing Fe(III) to participate in photocatalysis. Similar results were observed in montmorillonite and illite photocatalysis on the reduction of Cr(VI) by EDTA (Lan et al., 2008).

In the presence of citrate, oxalate and formate solutions, however, the D_e values of $(5.1 \sim 5.9) \times 10^{-12} \text{ m}^2/\text{s}$ were less than that of $8.7 \times 10^{-12} \text{ m}^2/\text{s}$ in the absence of them. We attributed this to the photocatalytic impact of montmorillonite on the reduction of Re(VII) to Re(IV) by organic acids.

3.3 Effect of pH

Fig. 4 The accumulated mass and flux of Re(VII) in montmorillonite as a function of diffusion time in presence of HA at pH 7.0 (A) and pH 10.0 (B). $\rho = 1600 \text{ kg/m}^3$, $T = 25 \text{ }^\circ\text{C}$, $C_{\text{HA}} = 10 \text{ mg/L}$, $I = 0.05 \text{ mol/L}$.

pH can alter not only the charge and therefore also the conformation and hydration of HA, but also the surface charge of the clay. Therefore, it might have an impact on the diffusivity of Re(VII). Figure 4 shows the breakthrough curves of Re(VII) diffusion in montmorillonite in presence of 10 mg/L HA at pH 7.0 and 10.0, respectively. Both accumulated mass and diffusive flux at pH 7.0 were higher than that at pH 10.0, indicating that more Re(VII) passed through bentonite at neutral condition.

Table 2. pH effect on the diffusion parameters of Re(VII) in montmorillonite in present of HA at a bulk dry density of 1600 kg/m^3

Li et al. (2012) revealed that K_d value decreased with increasing of pH, whereas, the D_e value of 9.7×10^{-13} to $1.3 \times 10^{-12} \text{ m}^2/\text{s}$ for $^{99}\text{TcO}_4^-$ remained almost unchanged in Beishan granite at pH

in the range of 3 to 10 because the dominant species was $^{99}\text{TcO}_4^-$. In this study, table 2 summarizes the diffusion parameters D_e , α and D_a of Re(VII) in the presence of HA at pH 7.0 and 10.0, respectively. The D_e value of $1.5 \times 10^{-11} \text{ m}^2/\text{s}$ at pH 7.0 was in agreement with that of $1.8 \times 10^{-11} \text{ m}^2/\text{s}$ in synthetic pore water at pH 7.6 (Wang et al., 2015a). These parameters were higher at pH 7.0 than that at pH 10.0. It seems that at higher pH the anion exclusion decreases which leads to a higher effective diffusion coefficient. However, this trend is insignificant, i.e. $D_e(\text{pH } 7.0)/D_e(\text{pH } 9.0) \approx 2$. Further investigations should be made to clarify the effect of pH on the effective diffusion coefficient of Re(VII).

3.4 Effect of temperature

Molecular diffusion depends on the temperature and this dependence can be described by the Arrhenius equation:

$$D_e = A \cdot e^{-E_a/RT}. \quad (15)$$

Here, A (m^2/s) is a pre-exponential factor, R ($8.314 \text{ J}/(\text{mol} \cdot \text{K})$) is the gas constant, and T (K) is the absolute temperature and E_a represents the activation energy. The E_a value is related to the diffusion mechanism of a species in the clay. For example, a pore water diffusion model was applied for $^{36}\text{Cl}^-$ diffusion in Na-montmorillonite with E_a values in the range of $15.0 \sim 25.1 \text{ kJ/mol}$. This value is almost the same as that in free water (Kozaki et al., 2001; Kozaki et al., 1998). Moreover, an interlayer diffusion model was suggested to explain the $^{134}\text{Cs}^+$ diffusion in Na- and Ca-montmorillonite with E_a values in the range of $34 \sim 52.6 \text{ kJ/mol}$ (Kozaki et al., 1996; Kozaki et al., 1999). Thus, the magnitude of the E_a value reveals the diffusion path of radionuclides in the clays.

Fig. 5. The accumulated mass and diffusive flux of Re(VII) in montmorillonite as a function of diffusion time and temperature in the absence (Fig. 5A and 5D) and presence of citrate (Fig. 5B and 5E) and formate (Fig. 5C and 5F). $\rho = 1600 \text{ kg/m}^3$, $C_{\text{org}} = 10 \text{ mg/L}$, $I = 0.05 \text{ mol/L NaCl}$.

Because the diffusion of Re(VII) was almost identical in the presence of citrate and oxalate, only citrate was used in the temperature experiments. Figure 5 shows the A_{cum} and flux results as a function of the absolute temperature. As expected, molecular diffusion increases with increasing temperature. The A_{cum} curves show different linear parts with increasing slope (Fig. 5A, B and C). Similarly, the flux curves increase fast in the transient state phase, and then evolve into a step-type increase with increasing temperature in the steady state phase (Fig. 5D, E and F).

According to the Arrhenius equation, D_e is temperature dependent, whereas α is independent on temperature (Van Loon et al., 2005). Only the steady state phase was employed at the higher temperatures. In this case, the short transient state phase in response to a change in temperature was neglected. At the start temperature (10 °C), both D_e and α values were calculated by fitting the experimental data with Eq.(4). After this initial phase only D_e was calculated by the following equation:

$$D_e = \frac{m \cdot L}{S \cdot C_0} \quad , \quad (16)$$

where m is the slope in Fig. 5A, B and C.

Fig. 6 Effective diffusion coefficients as a function of the reciprocal temperature for the diffusion of Re(VII), Re(VII)-citrate and Re(VII)-formate in montmorillonite. $\rho = 1600 \text{ kg/m}^3$, $T = 10 \pm 2$

1 °C, $C_{org} = 10 \text{ mg/L}$, $I = 0.05 \text{ mol/L NaCl}$.

3 Table 3. Temperature effect on the diffusion parameters of Re in montmorillonite

5 Figure 6 shows the relationship between D_e and temperature. The D_e values and E_a for
6 Re(VII), Re-citrate and Re-formate are summarized in Table 3. The E_a values were in the range of
7 (20.69 ~ 25.13) kJ/mol, indicating that Re(VII) diffusion followed a pore water diffusion model.
8 Van Loon et al. (2005) found that for the nonsorbing species HTO in Opalinus Clay E_a values
9 were in the range of (19.9 ~ 24.3) kJ/mol. For $^{36}\text{Cl}^-$ the E_a values were (18.3 ~ 21.6) kJ/mol, and
10 for $^{22}\text{Na}^+$ (18.8 ~ 26.1) kJ/mol. The activation energy of diffusion seems to be a non-sensitive
11 parameter.

13 4. Conclusions

14 The diffusion of Re(VII) in montmorillonite is a fast process. The measured D_e values were
15 in the range of $10^{-11} \text{ m}^2/\text{s}$. Macromolecular organic compounds (HA) had no significant effect
16 under neutral and slightly alkaline conditions. Unlike HA, small-molecular organic compounds
17 such as citrate, oxalate and formate with both chelating and reducing properties seem to retard
18 Re(VII) diffusion in montmorillonite under ambient conditions. The retardation effect became
19 more dramatically with increasing concentration of these organic acids. Because ^{99}Tc is more
20 reactive than Re, it might be possible that the presence of organic molecules might result in a
21 partial immobilisation of Tc.

22 Under slightly alkaline conditions ($\text{pH} = 10.0$), Re(VII) diffusion increased. However, this

1 trend is insignificant, i.e. D_e (pH 7.0)/ D_e (pH 9.0) $\approx$ 2. It probably because the predominant
2 species of Re(VII) was ReO_4^- at pH 7.0 and 9.0. The E_a values were in the range of (20.69 ~ 25.13)
3 kJ/mol in absence and in presence of minor amounts of citrate and formate, indicating that Re(VII)
4 diffusion follows a pore water diffusion model.

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Graphical abstract

Highlights

- The D_e values of ReO_4^- were decreased in present of citrate, oxalate and formate.
- HA had no significant impact on Re(VII) diffusion.
- The E_a values were in the range of (20.7 ~ 25.1) kJ/mol.
- Re(VII) diffusion in montmorillonite followed a pore water diffusion model

Table 1. The diffusion parameters of Re(VII) in montmorillonite in presence of organic compounds

Sample	$C_0 (\times 10^{-2} \text{ mol/L})$	$D_e (\times 10^{-12} \text{ m}^2/\text{s})$	$\alpha (-)$	$D_a (\times 10^{-10} \text{ m}^2/\text{s})$
Re(VII)	2.65 ± 0.04	8.7 ± 0.4	0.040 ± 0.002	2.20 ± 0.16
Re-HA	2.93 ± 0.04	8.3 ± 0.5	0.066 ± 0.004	1.26 ± 0.10
Re-citrate	2.91 ± 0.04	5.1 ± 0.3	0.024 ± 0.001	1.26 ± 0.10
Re-oxalate	2.91 ± 0.04	5.3 ± 0.3	0.044 ± 0.003	2.16 ± 0.18
Re-formate	2.93 ± 0.04	5.9 ± 0.3	0.044 ± 0.003	1.22 ± 0.10
Re(VII) ^a	0.22 ± 0.04	53.0 ± 2.0	0.29 ± 0.02	1.83 ± 0.14
Re-EDTA ^a	0.67 ± 0.20	54.0 ± 3.0	0.10 ± 0.01	5.40 ± 0.62

^a Measured data from (Wu et al., 2014a), artificial pore water, pH = 4.0, $\rho = 1300 \text{ kg/m}^3$.

Table 2. pH effect on the diffusion parameters of Re(VII) in montmorillonite in present of HA at a
bulk dry density of 1600 kg/m³

Sample	pH	C ₀ (× 10 ⁻³ mol/L)	D _e (× 10 ⁻¹² m ² /s)	α (-)	D _a (× 10 ⁻¹⁰ m ² /s)
Re(VII)-HA	7.0	3.7 ± 0.2	15.4 ± 0.5	0.043 ± 0.002	3.59 ± 0.27
Re(VII)-HA	10.0	3.7 ± 0.2	6.5 ± 0.4	0.036 ± 0.002	1.83 ± 0.14

Table 3. Temperature effect on the diffusion parameters of Re in montmorillonite

Sample	Condition	$D_e (\times 10^{-12} \text{ m}^2/\text{s})$	$\alpha (-)$	$E_a (\text{kJ/mol})$
Re	$10 \pm 2 \text{ }^\circ\text{C}$	0.87 ± 0.04	0.040 ± 0.002	25.13 ± 1.10
	$35 \pm 2 \text{ }^\circ\text{C}$	2.70 ± 0.04	-	
	$45 \pm 2 \text{ }^\circ\text{C}$	3.60 ± 0.04	-	
	$55 \pm 2 \text{ }^\circ\text{C}$	4.20 ± 0.04	-	
	$65 \pm 2 \text{ }^\circ\text{C}$	5.00 ± 0.04	-	
Re-citrate	$10 \pm 2 \text{ }^\circ\text{C}$	0.51 ± 0.03	0.024 ± 0.001	20.69 ± 1.76
	$35 \pm 2 \text{ }^\circ\text{C}$	1.00 ± 0.03	-	
	$45 \pm 2 \text{ }^\circ\text{C}$	1.50 ± 0.03	-	
	$55 \pm 2 \text{ }^\circ\text{C}$	1.80 ± 0.03	-	
	$65 \pm 2 \text{ }^\circ\text{C}$	2.00 ± 0.03	-	
Re-formate	$10 \pm 2 \text{ }^\circ\text{C}$	0.59 ± 0.03	0.043 ± 0.002	23.05 ± 1.69
	$35 \pm 2^\circ\text{C}$	1.27 ± 0.03	-	
	$45 \pm 2^\circ\text{C}$	1.82 ± 0.03	-	
	$55 \pm 2^\circ\text{C}$	2.23 ± 0.03	-	

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Abstract: In order to understand the diffusion properties of anionic radionuclides (RN) in bentonite in the presence of organic compounds with chelating and reducing properties, the effect of humic acid (HA), citrate, oxalate and formate on Re(VII) diffusion were investigated by a through-diffusion method under different pH (pH 7.0 and 10.0) and temperature conditions (10 ~ 65 °C). When the molar ratio of oxalate to Re(VII) was higher than 1:1, the accumulated mass and flux were observed to decrease drastically as a function of time. It can be explained by photocatalytic impact of Fe(III) on the reduction of Re(VII) to insoluble Re(IV) by oxalate. Thus, the diffusion of Re(VII) was also observed to decrease in the presence of minor citrate, oxalate and formate. Effective diffusion coefficient (D_e) values decreased from $8.7 \times 10^{-11} \text{ m}^2/\text{s}$ to $(5.1 \sim 5.9) \times 10^{-11} \text{ m}^2/\text{s}$. In contrast, HA had no significant impact on Re(VII) diffusion. The D_e values of 1.54×10^{-11} and $6.5 \times 10^{-12} \text{ m}^2/\text{s}$ were obtained at pH 7.0 and 10.0, respectively. HA thus neither has an effect on the speciation of Re(VII) nor does it change the charge of the surface. The latter is probably due to the fact that HA preferentially interacts with the aluminol sites of the montmorillonite edges without changing the zeta potential of the surface. The dependence of D_e of Re(VII) on temperature in the absence and presence of citrate or formate was described by the Arrhenius equation. The activation energy, E_a , was in the range of (20.7 ~ 25.1) kJ/mol, demonstrating that Re(VII) diffusion followed a pore water diffusion model.