Salt effects on Re(VII) and Se(IV) diffusion in bentonite

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Abstract:

The through-diffusion method was employed to investigate the effect of the salt concentration on the diffusion behaviour of Re(VII) and Se(IV) in compacted bentonite. The accessible porosity, ϵ_{acc} , of Re(VII) increased from 0.25 to 0.38 with an increase of the ionic strength from 0.1 to 1.0 mol/L. The dependency of the accessible porosity ϵ_{acc} on the salt concentration could be described approximately by a first-order decay exponential function. The interlayer porosity of GMZ bentonite was 21 % of the total porosity at a bulk dry density of 1600 kg/m³ at 12 °C. The D_e values of Re(VII) and Se(IV) increased from 2.6×10^{-11} to 6.1×10^{-11} m²/s and from 1.6×10^{-11} to 4.7×10^{-11} m²/s in GMZ bentonite with an increase of the ionic strength from 0.1 to 1.0 mol/L, respectively. In the case of Se(IV), the adsorption showed a different ionic strength dependency in GMZ bentonite and montmorillonite. The ionic strength has no significant effect on the sorption ($K_d = 1.8 \times 10^{-4}$ m³/kg) on GMZ bentonite, indicating the formation of inner-sphere surface complexes. In the case of synthetic montmorillonite, the K_d values increased with increasing ionic strength. This can be explained by the fact that the electric potential of surface sites becomes less negative with increasing ionic strength resulting in an increase in the adsorption of Se(IV) at a pH

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above the point of zero salt effect (PZSE). The D_e values of both Re(VII) and Se(IV) increased with increasing salt concentration. Both anions are totally excluded from the interlayer space and partially from the diffuse double layer. Ionic strength alters the effective diffusion coefficient of anions by controlling the thickness of the diffuse double layer. Anion diffusion data from the literature (effective and apparent diffusion coefficients) were satisfactorily evaluated by Archie's relation.

Key word: effective diffusion coefficient, diffusion, ionic strength, accessible porosity, bentonite

1. Introduction

In the disposal of high-level radioactive waste, radionuclides are retarded during their migration from the repository to the geosphere (Ding et al., 2015; Sun et al., 2016). Molecular diffusion is the predominant transport process of radionuclides in backfilling materials (i.e. bentonite) because of its low hydraulic conductivity (Glaus et al., 2007; Glaus et al., 2010; Manjanna et al., 2009). Anionic radionuclides with long half-lives such as ^{79}Se (Ikonen et al., 2016; Sato and Miyamoto, 2004), ^{99}Tc (Liu et al., 2015; Wang and Tao, 2004), ^{129}I (Tachi et al., 2011) and ^{36}Cl (Glaus et al., 2010; Van Loon et al., 2003) are hardly retarded in the geosphere and are therefore dose determining in safety assessment studies.

In general, radionuclide diffusion is governed by the pore water chemistry (Molera et al., 2003), the microstructure of the clays (Glaus et al., 2010; González Sánchez et al., 2008), the orientation of clay particles (Sato, 2005), and temperature (Higashihara et al., 2005; Joseph et al., 2013). In the case of pore water chemistry, the salt concentration is an important factor because it

will affect the diffusion of radionuclides in clays. The salt effect depends on the charge of the radionuclides. For example, the effective diffusion coefficient (D_e) for anions such as $^{36}\text{Cl}^-$ and $^{125}\text{I}^-$ in bentonite increases with increasing ionic strength (Glaus et al., 2010; Ishidera et al., 2008; Molera et al., 2003; Tachi and Yotsuji, 2014; Tian et al., 2013; Van Loon et al., 2007). D_e for cations such as Cs^+ , Na^+ , Sr^{2+} , Co^{2+} and Zn^{2+} , in bentonite and illite showed the opposite dependency (Glaus et al., 2015; Glaus et al., 2010; Tachi and Yotsuji, 2014; Tachi et al., 2011), and D_e for neutral species such as HTO showed no dependency at all (Glaus et al., 2010; González Sánchez et al., 2008; Tachi and Yotsuji, 2014; Tachi et al., 2011). Glaus et al. (2010) argued that the predominant diffusion path of cations is preferentially through the interlayer or the diffuse double-layer space, whereas these regions are almost inaccessible for anions. Tachi and Yotsuji (2014) proposed a diffusion model, which is based on the electrical double layer theory and a simplified pore structure, in order to describe the salt effect on Cs^+ , Na^+ , I^- and HTO diffusion in Na-montmorillonite. Tachi et al. (2011) explained the reduced cation and enhanced anion diffusivity caused by a higher salt concentration by a change of the tracer concentration gradient in the diffuse double layer. No salt effect was observed for the diffusion of HTO, Na^+ and Cl^- in kaolinite (Glaus et al., 2010). This could be explained by the fact that kaolinite has almost no charge so that the earlier mentioned phenomena are absent.

$^{79}\text{Selenium}$ ($t_{1/2} = 650,000$ yrs) is a radionuclide of interest due to its long half-life. The speciation of Se(IV) includes H_2SeO_3 , HSeO_3^- and SeO_3^{2-} , but under the typical E_h/pH conditions of clay pore water the oxyanion HSeO_3^- is predominant (Torres et al., 2011). It is the most important species for the safety assessment of a repository because of its low retention in clays and the resulting high mobility in the geosphere. Compared to anions, such as $^{36}\text{Cl}^-$, $^{129}\text{I}^-$ and

$^{99}\text{TcO}_4^-$, Se(IV) can adsorb on clays. The value of the distribution coefficient (K_d) is $(0.8 - 35) \times 10^{-3} \text{ m}^3/\text{kg}$ for MX-80 bentonite, $(0.5 - 100) \times 10^{-3} \text{ m}^3/\text{kg}$ for montmorillonite (Montavon et al., 2009) and $(50 - 500) \times 10^{-3} \text{ m}^3/\text{kg}$ for Na-smectite (Missana et al., 2009). Peak et al. (2006) observed an inner-sphere surface complexation for the sorption of Se(IV) on natural montmorillonite. However, Charlet et al. (2007) reported that Se(IV) was sorbed on synthetic montmorillonite by forming outer-sphere complexes. Nevertheless, Se(IV) shows a higher retention and a lower diffusivity than other oxyanions such as Re(VII) (Wu et al., 2014). Many researchers have reported that anions diffuse through the free pore space and cations diffuse through the interlayer space of bentonite (Tachi and Yotsuji, 2014; Tournassat and Appelo, 2011; Van Loon et al., 2007).

In this study, the effect of the salt concentration on the diffusion of Re(VII) (as surrogate to $^{99}\text{Tc(VII)}$) and Se(IV) (as surrogate to $^{79}\text{Se(IV)}$) was investigated using a through-diffusion method. Re(VII) and Se(IV) were chosen as a non-sorbing and sorbing anionic species, respectively. The objectives of this study were (i) to acquire their diffusion parameters such as D_e , D_a , α , and K_d values, (ii) to resolve the diffusion pathways of oxyanions, and (iii) to evaluate quantitatively the dependence of the effective diffusion coefficient on the ionic strength of the pore water.

2. Materials and Methods

2.1 Materials

Gaomiaozi (GMZ) bentonite was obtained from the Beijing Research Institute of Uranium Geology and was used without further purification or processing. The detailed physical

characteristics of the GMZ bentonite can be found elsewhere (Ye et al., 2010). The chemical composition was: SiO₂ (67.43 %), Al₂O₃ (14.2 %), Fe₂O₃ (2.40 %), FeO (0.29 %), TiO₂ (0.12 %), CaO (1.13%), K₂O (0.73 %), P₂O₅ (0.02%), MgO (0.10 %), Na₂O (1.75 %), MnO (0.02%) and loss on ignition (11.38 %). The mineral composition of the GMZ bentonite is similar to that of the Volclay KWK bentonite (Table 1). The synthetic montmorillonite (K-10) purchased from Aladdin was used without further processing. The bulk chemical composition was analyzed by X-ray fluorescence spectrometry (Shimadzu XRF-1800): SiO₂ (73.0%), Al₂O₃ (11.3%), Fe₂O₃ (2.03%), TiO₂ (0.33%), CaO (0.54%), K₂O (1.08%), P₂O₅ (0.03%), MgO (2.2%), Na₂O (0.29%) and loss on ignition (9.2%).

0.05 to 1.0 mol/L NaClO₄ was used as background electrolyte in all diffusion experiments. The ionic strength included the concentrations of Re(VII), Se(IV) and NaClO₄. In order to prevent bacterial growth, NaN₃ was added to both source and sampling reservoirs at a concentration of 0.003 M. The pH was adjusted to 7.0 with HCl or NaOH.

Table 1.

2.2 Through-diffusion experiment

The diffusion experiments in this investigation were carried out using the through-diffusion method described in detail in Van Loon et al. (2003). After the GMZ bentonite was compacted to a bulk dry density of 1600 kg/m³, it was placed between two stainless steel filter plates in a diffusion cell. The detailed diffusion set-up and the experimental procedure were described by Van

Loon et al. (2003). Table 2 lists the sizes of the bentonite plug and of the stainless steel filter.

Table 2.

After the bentonite plug was equilibrated with a NaClO_4 solution for 5 weeks, Re(VII) and Se(IV) were added by dissolving a given amount of SeO_2 (from Sinopharm Reagent) and NH_4ReO_4 (Alfa Aesar, 99.997%) in the source reservoir with 200 mL NaClO_4 solution. The concentration of Re(VII) and Se(IV) were ca. 8.0×10^{-3} and 2.5×10^{-2} mol/L, respectively. In the case of GMZ bentonite, both Re(VII) and Se(IV) were added simultaneously, whereas only Se(IV) was added in the solution connected with montmorillonite K-10. The high concentration was employed to make sure that they can be detected by ICP-OES (Perkin Elmer Optima 2100DV). According to Wang et al. (2004), the initial concentration had no significant impact on the effective diffusion coefficient of anionic radionuclides such as $^{99}\text{TcO}_4^-$, whose speciation did not change during the experiment. The solution in the sampling reservoir was replaced periodically to keep the concentration low (close to zero) to assure a constant concentration gradient until the diffusive flux of Re and Se reached a constant value. E_h , pH and the concentration of Re and Se in the source solution were monitored during the diffusion process. E_h was in the range of 0.2 to 0.5 V and pH was around 7.0, assuring that HSeO_3^- and ReO_4^- were the dominating species. The diffusion experiments with Re(VII) and Se(IV) in GMZ bentonite were performed at a temperature of 12 ± 3 °C and 25 ± 3 °C.

2.3 Data processing

D_e and α were calculated using Fick's second law that describes the one-dimensional non-steady-state diffusion process in a porous material by:

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

where c is the concentration of the species in solution (mol/L); t is the diffusion time (s); D_e is the effective diffusion coefficient in the compacted clay (m^2/s); α is the rock capacity factor (-) and x is the diffusion distance (m).

The cumulative mass of a given species, A_{cum} (μg), diffused through the bentonite specimen is calculated - with appropriate initial and boundary conditions - as follows:

$$\begin{aligned} c(x, t) &= 0; t = 0; \forall x, \\ c(0, t) &= C_0; x = 0; t > 0, \\ c(L, t) &= 0; x = L; t > 0, \\ A_{cum} &= S \cdot L \cdot C_0 \left(\frac{D_e \cdot t}{L^2} - \frac{\alpha}{6} - \frac{2 \cdot \alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cdot \exp \left\{ -\frac{D_e \cdot n^2 \cdot \pi^2 \cdot t}{L^2 \cdot \alpha} \right\} \right). \end{aligned} \quad (2)$$

L represents the thickness of the clay sample (m); C_0 is the initial concentration of species ($\mu\text{g}/\text{m}^3$) and S the cross section area of the clay sample (m^2). The flux, J (in $\mu\text{g}/(\text{cm}^2 \text{ d})$), at the low-concentration boundary ($x = L$) is calculated by the following equation:

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

3. Results and discussion

3.1. Effect of ionic strength on Re(VII) diffusion

Rhenium, which lies just below technetium in the periodic table of elements, has similar chemical properties as technetium, and is therefore often used as an analogue for the radioactive

⁹⁹Tc. Our recent work showed that Re(VII) is a good analogue to study the diffusion behaviour of ⁹⁹Tc(VII) in GMZ bentonite (Wu et al., 2014). The diffusion experiment in GMZ bentonite was conducted at 12 ± 3 °C to get more data in the transient state to obtain a reliable α value, especially for the non-sorbing Re(VII). Figure 1 shows the evolution of the accumulated diffused mass and flux with time for Re(VII) in the GMZ bentonite at different ionic strength values. Both A_{cum} and flux increased with increasing ionic strength up to 0.7 mol/l. For an ionic strength larger than 0.7, no further significant increase could be observed. D_e and α were obtained from the best fit of the breakthrough curves of A_{cum} vs. time (Fig. 1A) using Eq. (2) by a least square method. Lines in Fig.1B were calculated by Eq. (3) with obtained D_e and α values as the input parameter.

Fig. 1

Re(VII) is hardly sorbed on the surface of bentonite. Due to the anion exclusion effect, α is less than the total porosity, i.e. α equals ϵ_{acc} . ϵ_{acc} (-), is introduced to describe the transport of the anion through the pore connected from one side to the other side of the clay. Table 3 summarizes the diffusion parameters of Re(VII) in GMZ bentonite for different ionic strength values in the range from 0.1 to 1.0 mol/L. With increasing ionic strength, D_e increased from 2.6×10^{-11} to 6.1×10^{-11} m²/s, and ϵ_{acc} increased from 0.25 to 0.38. The apparent diffusion coefficient (D_a) was calculated by:

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

and changed from 1.0×10^{-10} to 1.7×10^{-10} m²/s. The higher D_e and ϵ_{acc} values in this study are in good agreement with the reported ones in GMZ bentonite at 0.05 mol/L NaClO₄ solution (Wang et

al., 2016) and at 0.088 mol/L synthetic pore water (Wu et al., 2014).

Table 3.

3.2. Effect of ionic strength on Se(IV) diffusion

The sorbing species Se(IV) can form inner- and outer-sphere complexes on the surface of bentonite, depending on the properties of the used bentonite (Charlet et al., 2007). In order to calculate K_d and to compare the results with those in our previous paper (Wu et al., 2014), the diffusion experiments of Se(IV) in the natural GMZ bentonite were performed at 12 ± 3 °C. Diffusion of Se(IV) in the synthetic montmorillonite was performed at 25 °C (Fig.2). The breakthrough curves were similar to that of Re(VII) except that a longer time was required to reach the steady state. The diffusion parameters D_e , α and K_d are summarized in Table 4. The distribution coefficient, K_d , is defined as:

$$K_d = \frac{\alpha - \varepsilon_{acc}}{\rho_d}, \quad (5)$$

where, ρ_d (kg/m³) is the bulk dry density of the compacted bentonite. All the diffusion and sorption parameters, i.e. D_e , D_a , α and K_d , increase with increasing ionic strength. Because the temperature of the montmorillonite experiments is higher than that of GMZ bentonite, the D_e , α and K_d are higher. The D_a values in montmorillonite ($(1.0 - 1.2) \times 10^{-11}$ m²/s) were lower than those in GMZ bentonite ($(3.4 - 7.2) \times 10^{-11}$ m²/s) due to the higher α values in montmorillonite.

Fig. 2

Table 4 shows that the diffusivity of Se(IV) increases with increasing ionic strength, indicating that its diffusion behaviour is that of an anion. Se(IV) can also hardly enter the interlayer space of bentonite. A lower D_e value was obtained in this work, compared to our previous results (Wang et al., 2016; Wu et al., 2014). This is probably caused by the lower experimental temperature and the different compositions of the pore water.

Choi and Oscarson (1996) reported that the pore diameter in bentonite was two orders of magnitude higher than the effective ionic radius of ReO_4^- and HSeO_3^- , which are 0.50 and 0.53 nm, respectively (Shannon, 1976). Therefore, the accessible porosity of Re(VII) was used to calculate the distribution coefficient of Se(IV) because of the similar effective ionic radius and identical charge. The ϵ_{acc} values of Re(VII) in GMZ bentonite at 12 °C were used to calculate the K_d values of Se(IV) in montmorillonite at 25 °C. Possible temperature effects were neglected because ϵ_{acc} had only a very small contribution to the rock capacity factor. The adsorption of Se(IV) showed a different ionic strength dependence for GMZ bentonite and montmorillonite, probably because of the mineral composition of clays, such as calcite, which had a strong affinity of Se(IV) to form a ternary surface complex on montmorillonite (Montavon et al., 2009). For the GMZ bentonite, the K_d value did not depend significantly on the ionic strength. This is in accordance with the adsorption of selenite on Na-smectite as described in Missana et al. (2009). It indicates that Se(IV) sorbs as an inner-sphere surface complex. This is also in good agreement with Peak et al. (2006), who showed by extended X-ray absorption fine structure spectroscopy (EXAFS) that Se(IV) formed bidentate binuclear inner-sphere complexes on the clay surface. In the case of montmorillonite, the K_d values increased with increasing ionic strength from $2.28 \times$

$10^{-3} \text{ m}^3/\text{kg}$ to $3.36 \times 10^{-3} \text{ m}^3/\text{kg}$. Similar results were observed for Se(IV) adsorption on montmorillonite (Montavon et al., 2009) and soils (Barrow and Whelan, 1989), and phosphate adsorption on γ -alumina and kaolinite (He et al., 1997). A crossover point, which is referred to as the point of zero salt effect (PZSE), was observed in the pH-dependency of ion adsorption. At high pH levels - $\text{pH} > \text{PZSE}$, which was typically below 3.0 for montmorillonite (Peak et al., 2006), an increasing of ionic strength increased anion sorption. The electric potential of surface sites becomes less negative with increasing the ionic strength and therefore increases the amount of Se(IV) adsorption. Moreover, the K_d values of $(2.28 - 3.36) \times 10^{-3} \text{ m}^3/\text{kg}$ in montmorillonite are in good agreement with the those given by Montavon et al. (2009). The K_d value was expected to be around $3 \times 10^{-3} \text{ m}^3/\text{kg}$ at Se(IV) concentration of $2.5 \times 10^{-2} \text{ mol/L}$. The K_d value on GMZ bentonite is more than one order of magnitude lower than those measured on synthetic montmorillonite. This is also in good agreement with Montavon et al. (2009). Charlet et al. (2007) observed prevalently outer-sphere complexes based on a structure-based MUSIC model and on X-ray absorption spectroscopy (XAS). This apparent contradiction can be explained by the fact that both outer-sphere and inner-sphere complexes can be formed simultaneously between selenite and the surface of montmorillonite, the partitioning of both species being controlled by the chemical composition of the aqueous solution (pH, ionic strength, etc.) and by the type and properties of the clay minerals.

Table 4.

3.3. The dependence of accessible porosity on ionic strength

In a water saturated bentonite, radionuclide diffusion is assumed to take place in the pore

space which comprises the interlayer and interparticle pore spaces (Tournassat and Appelo, 2011; Van Loon et al., 2007). The interlayer pore space, which is the space between individual TOT-layers, allows only water and cations to enter. The electric potential in the interlayer is so large that anions are completely excluded. The interparticle pore space can be subdivided in a diffuse double layer (DDL) pore space and a free water pore space. The DDL, which is located between the free pore water and the clay surface, contains water, anions and an excess of cations. The free pore water is a charge-balanced aqueous solution containing water and equal amounts of anions and cations (Fig. 3).

Fig. 3

Anions are assumed to diffuse almost solely through the free pore space because the anion exclusion effect totally excludes them from the interlayer and partially from the DDL (Appelo and Wersin, 2007). The ionic strength alters the thickness of the DDL, characterized by the Debye length. According to the Gouy-Chapman theory, the Debye length is inversely proportional to the square root of ionic strength (Russel et al., 1989). With increasing ionic strength, the DDL porosity decreases and the free porosity becomes larger. As a result, the width of diffusion path increases at higher salt concentration, leading to a higher D_e value for anions at higher salt concentrations. At high ionic strength conditions, i.e. $I > 1$ mol/L, the DDL space can be neglected because it is very thin and occupies only a very small part of the pore space (Van Loon et al., 2007). At these conditions the interparticle pore space equals almost the free water pore space. Under low ionic strength conditions, however, anions occupy only a small part of the pore space

of bentonite.

The accessible porosity ε_{acc} , which can be measured by the through-diffusion method, is introduced to describe the diffusion path of anions in compacted clay. Normally, ε_{acc} is related to the diffusing species (Van Loon et al., 2003), the type of clay mineral (Glaus et al., 2010), the bulk dry density of compacted clay (Van Loon et al., 2007; Wu et al., 2012) and the ionic strength of the pore water (Van Loon et al., 2007). In case of non-sorbing anions with a negative sorption, ε_{acc} equals α (Wu et al., 2014; Van Loon et al., 2003). ε_{acc} increases with increasing ionic strength due to the decrease of DDL, leaving more free pore water space available for anions to enter. At high ionic strength, i.e. $I \geq 1$ M, ε_{acc} is more or less equal to the interparticle pore space ε_{ip} . The relationship of ε_{acc} and ionic strength I (mol/L) can be expressed by a first-order decay exponential function (Van Loon et al., 2007):

$$\varepsilon_{acc} = \varepsilon_{max} - A \cdot e^{-B \cdot I}. \quad (6)$$

Where ε_{max} is the interparticle porosity. A and B are dimensionless fitting constants related to the bulk dry density.

Fig.4

Figure 4 shows the relationship between ε_{acc} and I for Re(VII), ^{125}I (Tian et al., 2013) and ^{36}Cl (Glaus et al., 2010; Van Loon et al., 2007) in compacted bentonite. Lines represent the fitting curves obtained by Eq. (6). It shows that ε_{acc} decreases in the sequence of $\text{ReO}_4 > ^{125}\text{I} > ^{36}\text{Cl}$. The detailed fitting parameters can be found in Table 5. The results of ^{36}Cl from Glaus et al. (2010) were fitted by this method. The percentage of interlayer porosity (ε_{il} %) is calculated as follows:

$$\varepsilon_{it} \% = (1 - \frac{\varepsilon_{\max}}{\varepsilon_{tot}}) \times 100\% , \quad (7)$$

where ε_{tot} is the total porosity, which can be measured by diffusion of tritiated (HTO) (Glaus et al., 2010; Wu et al., 2012) or calculated from the bulk and grain density ($\varepsilon_{tot} = 1 - \rho_d / \rho_s$, where ρ_s is the grain density) (Van Loon et al., 2007). In GMZ bentonite, the fraction of interlayer porosity calculated from the Re(VII) data was much lower than that calculated from the ^{125}I data. This is probably caused by the different temperatures at which diffusion was measured, i.e. 12 °C in this study and 25 °C in the study of Tian et al. (2013). This would mean that the interlayer pore space depends on temperature what is very unlikely. Holmboe et al. (2012) reported that the percentage of interlayer porosity was more than 97 % for saturated bentonite in the range of 1400 to 1800 kg/m³ based on XRD profile modelling. Suzuki et al. (2004) estimated that the fraction of ε_{it} was 39 % for Na-bentonite at 900 kg/m³ and 78 % at 1350 kg/m³. Bourg et al. (2003) proposed that the interlayer porosity was 0.16 times dry density, and then $\varepsilon_{it} \%$ was ca. 60 % at 1600 kg/m³. Different investigation methods and approaches, and different experimental conditions employed to obtain the percentage of interlayer porosity, might be responsible for the discrepancy. Further investigations are necessary to clarify this discrepancy.

Table 5.

3.4 The relationship between D_e and ionic strength

The dependency of the effective diffusion coefficient on the accessible porosity can be expressed by Archie's law:

$$D_e = D_w \cdot \varepsilon_{acc}^n \quad (8)$$

Where D_w (m^2/s) is the diffusion coefficient in bulk water and n is the cementation factor related to the chemicophysical properties of both the clay and diffusing species. The salt effect on D_e can be described by substituting the relations for ε_{acc} from Eq.(6) in Eq.(8), yielding the following expression:

$$D_e / D_w = (\varepsilon_{max} - A \cdot e^{-B \cdot I})^n \quad (9)$$

Figure 5 shows the salt effect on D_e of Re(VII), Se(IV) and ^{36}Cl . The data of ^{36}Cl in Fig. 5 were obtained from Glaus et al. (2010) and Van Loon et al. (2007). Lines represent the fitting results by Eq. (9) in Fig. 5 with values of ε_{max} , A and B summarized in Table 5. In the case of Se(IV), the fitted values (A and B) of Re(VII) were used to calculate the cementation factor by Eq. (8). Equation (9) follows the trend of the experimental results of D_e vs. I for Re(IV), Se(IV) and ^{36}Cl . The D_e values increase in the sequence of $^{36}\text{Cl} < \text{Se(IV)} < \text{Re(VII)}$ at a bulk dry density of 1600 kg/m^3 , which corresponds with the sequence of their ε_{acc} . Considering the similar mineral composition of GMZ and Volclay KWK bentonites, the discrepancy of tortuosity and constrictivity of monovalent anions could be neglected. D_e of Re(VII) is mainly dependent on the accessible porosity.

Fig. 5

Table 6 lists the cementation factor used in Eq. (8) and (9) to describe the dependency of D_e on the ionic strength for different bentonites at bulk dry densities ranging from 1300 to 1900 kg/m^3 . All the n values calculated by this method were identical to that of reported results except

that the n value of Se(IV) in GMZ bentonite was higher than that reported by Wu et al. (2014), whose n value was 2.6 as measured by through-diffusion at different bulk dry density values. The discrepancy might contribute to the uncertainties of fitted parameters ($\varepsilon_{\max}$, A and B) of Re(VII), which was used to fit the data of Se(IV). In addition, the n value of ^{36}Cl from Glaus et al. (2010) was also higher than the reported one ($n=1.8$). The correlation coefficients R^2 were less than 0.80. Generally speaking, the effective diffusion coefficient can be predicted by using the accessible porosity, which can be done using information on the composition of the pore water and the bulk dry density of the compacted clay.

Table 6.

4 Conclusion

The anion accessible porosity represents the pore space in compacted bentonite available for diffusion of anions. Anions are totally excluded from the interlayer pore space and partially excluded from the DDL space. High salt concentrations reduce the DDL space by screening the charge, leading to an increase of ε_{acc} and an increase of the D_e .

The effect of salt concentration on the diffusion of Re(VII) and Se(IV) in compacted bentonite were investigated. The D_e , ε_{acc} and K_d values were obtained by a through-diffusion method. Both D_e of the non-sorbing ReO_4^- and the sorbing HSeO_3^- increased with increasing ionic strength. In the case of Se(IV), the variable ionic strength dependence was observed in GMZ bentonite and in montmorillonite. The ionic strength had no significant effect on the adsorption of

Se(IV) on GMZ bentonite, whereas increasing ionic strength increased its adsorption on K-10 montmorillonite.

The relationship of ε_{acc} and ionic strength can be described approximately by a first-order decay exponential function. The percentage of interlayer porosity (as a fraction of the total porosity) was 21 % at 12 °C. Combining the equation relating ε_{acc} to the ionic strength with Archie's relation successfully described the dependency of the D_e value of Re(IV), Se(IV) and ^{36}Cl on the ionic strength of the pore solution. Diffusion coefficients, which are important input parameters in the safety analyses of radioactive waste repositories, can thus be evaluated using information on the composition of the pore water (ionic strength), the type of anionic species, and characteristics of the porous material.

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Table 1. Mineral composition (as wt. %) of bentonites

Mineral composition	GMZ (%) [*]	Volclay KWK [#]
montmorillonite	75.4	71
quartz	11.7	4
cristobalite	7.3	-
feldspar	4.3	11
calcite	0.5	3
kaolinite	0.8	-
Albite	-	10
pyrite	-	0.7
Dolomite/Ankerite	-	< 2
Siderite	-	< 2

^{*} data from Ye et al. (2010)

[#] data from Van Loon et al. (2007)

Table 2. Dimensions of the bentonite plug and stainless steel filters used in the through-diffusion experiments

Item	value
Diameter of bentonite (cm)	2.54
Thickness of bentonite (cm)	0.90
Diameter of stainless steel filter (cm)	2.54
Thickness of stainless steel filter (cm)	0.157
Pore diameter of stainless steel filter (μm)	10
Dead volume of diffusion cell (V_{dead}) (cm^3)	1.8 ~ 2.0

Table 3. Ionic strength effect on diffusion parameters for Re(VII) in GMZ bentonite

Ionic strength	C_0	D_e	D_a	ε_{acc}
mol/L	$\times 10^{-3}$ mol/L	$\times 10^{-11}$ m ² /s	$\times 10^{-10}$ m ² /s	-
0.133	7.6 ± 0.4	2.56 ± 0.14	1.03 ± 0.09	0.25 ± 0.01
0.233	7.6 ± 0.4	3.31 ± 0.19	1.10 ± 0.09	0.30 ± 0.01
0.433	8.3 ± 0.4	4.01 ± 0.20	1.25 ± 0.10	0.32 ± 0.02
0.732	7.2 ± 0.4	5.93 ± 0.34	1.65 ± 0.17	0.36 ± 0.03
1.032	7.2 ± 0.4	6.12 ± 0.35	1.61 ± 0.17	0.38 ± 0.03
0.096 [*]	$7.6 \pm 0.6^*$	$1.8 \pm 0.1^*$	$1.0 \pm 0.2^*$	$0.18 \pm 0.01^*$
0.054 [#]	$3.6 \pm 0.2^{\#}$	$2.2 \pm 0.1^{\#}$	$1.4 \pm 0.01^{\#}$	$0.15 \pm 0.03^{\#}$

^{*} Measured data from Wu et al. (2014) at bulk dry density of 1600 kg/m³ in synthetic pore water at

10°C, the ionic strength of the solution was calculated by Visual MINTEQ 3.1

[#] Measured data from Wang et al. (2016). The ionic strength includes the concentration of Re and

NaClO₄.

Table 4. Ionic strength effect on diffusion parameters for Se(IV) in bentonite

Ionic strength mol/L	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
GMZ bentonite, T = 12 ± 3 °C					
0.233	2.5 ± 0.1	1.60 ± 0.05	2.91 ± 0.10	0.55 ± 0.01	1.81 ± 0.10
0.433	2.5 ± 0.1	2.56 ± 0.09	4.39 ± 0.21	0.58 ± 0.02	1.63 ± 0.18
0.728	2.0 ± 0.1	4.37 ± 0.18	6.52 ± 0.47	0.67 ± 0.04	1.81 ± 0.25
1.028	2.0 ± 0.1	4.69 ± 0.19	7.24 ± 0.42	0.65 ± 0.03	1.56 ± 0.21
0.15 [*]	6.2 ± 0.2	2.3 ± 0.2	3.4 ± 0.4	0.68 ± 0.05	1.8
0.08 [#]	2.8 ± 0.8	1.6 ± 0.1	3.4 ± 0.3	0.47 ± 0.02	1.0 ± 0.25
Montmorillonite, T = 25 ± 3 °C					
0.08	2.7 ± 0.8	4.06 ± 0.13	1.06 ± 0.05	3.82 ± 0.15	22.8 ± 1.7
0.13	2.9 ± 0.8	4.33 ± 0.13	0.97 ± 0.04	4.45 ± 0.12	26.5 ± 1.7
0.43	3.1 ± 0.8	6.30 ± 0.18	1.15 ± 0.05	5.48 ± 0.18	32.2 ± 2.5
0.73	3.1 ± 0.8	6.72 ± 0.19	1.16 ± 0.04	5.78 ± 0.15	33.6 ± 2.8

^{*} Measured data from Wu et al. (2014) at compacted dry density of 1600 kg/m³ in synthetic pore water at 10 °C

[#] Measured data from Wang et al. (2016) in NaClO₄ at 40 °C

Table 5. Overview of the fitting values used in Eq. (6)

Species	Dry density kg/m ³	$\varepsilon_{\max}$ -	A -	B -	ε_{tot}	ε_{it} %	Reference
Re(VII)	1600	0.35 ± 0.02	0.27 ± 0.02	4.69 ± 0.40	0.44*	21	This work and Wu et al., 2014
¹²⁵ I	1500	0.251	0.262	9.61	0.444	44	Tian et al., 2013
³⁶ Cl	1300	0.230 ± 0.004	0.209 ± 0.003	3.36 ± 0.20	0.546	54	Van Loon et al., 2007
³⁶ Cl	1600	0.098 ± 0.005	0.092 ± 0.005	2.40 ± 0.38	0.429	77	Van Loon et al., 2007
³⁶ Cl	1900	0.059 ± 0.019	0.055 ± 0.018	0.81 ± 0.41	0.322	82	Van Loon et al., 2007
³⁶ Cl	1900	0.080 ± 0.001	0.066 ± 0.001	0.82 ± 0.02	0.41 [#]	80	Glaus et al., 2010

* Data obtained from Wu et al. (2012)

[#] Data obtained from HTO diffusion in Na-montmorillonite at 1.0 mol/L NaClO₄ given in Glaus et al. (2010)

Table 6. The cementation factor for Re(VII), Se(IV) and ^{36}Cl

Species	Clay	Dry density kg/m^3	D_w $\times 10^{-9} \text{m}^2/\text{s}$	n	R^2	Reference
Re(VII)	GMZ bentonite	1600	1.46	2.9 ± 0.2	0.61	This work and Wu et al., 2014
Se(IV)	GMZ bentonite	1600	1.55	3.4 ± 0.1	0.81	This work and Wu et al., 2014
Se(IV)	Montmorillonite	1600	1.55	2.7 ± 0.2	-	This work
^{36}Cl	Volclay KWK	1300	2.03	2.2 ± 0.2	0.40	Van Loon et al., 2007
^{36}Cl	Volclay KWK	1600	2.03	2.0 ± 0.1	0.42	Van Loon et al., 2007
^{36}Cl	Volclay KWK	1900	2.03	2.1 ± 0.2	0.79	Van Loon et al., 2007
^{36}Cl	Na-montmorillonite	1900	2.03	2.8 ± 0.2	0.67	Glaus et al., 2010

Graphical abstract