Strontium adsorption and penetration in kaolinite at low Sr$^{2+}$ concentration

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Abstract

Behavior of radioactive Sr$^{2+}$ in contaminated soils is an important issue in relation to nuclear power plant accidents. The Sr$^{2+}$ adsorption on kaolinite and its migration in a kaolinite soil were investigated because toxic effects of radioactive Sr$^{2+}$ have been found very severe for living organisms at low Sr$^{2+}$ concentrations. Adsorption isotherms of Sr$^{2+}$ on kaolinite at different NaCl concentration and pH were obtained by the batch method. The calculated distribution coefficients ($K_D$) ranged between 600 and 40000 L kg$^{-1}$, which showed a strong preference for the adsorbed phase. The results were used to evaluate the ratio ($r$) of penetration length of Sr$^{2+}$ relative to that of water in a model kaolinite soil. When the Sr$^{2+}$ solution was percolated constantly into the kaolinite soil, the penetration of Sr$^{2+}$ was delayed strongly at low Sr$^{2+}$ concentration due to adsorption. The Sr$^{2+}$ penetration length was only 0.001 - 0.056 % of the water penetration length at pH 6.5 (0.1-10 mmol L$^{-1}$ NaCl). At pH 4.1 (1 mmol L$^{-1}$ NaCl) the effect was about 17 times less than at pH 6.5 (1 mmol L$^{-1}$ NaCl). Under all conditions, the Sr$^{2+}$ penetration increased when the Sr$^{2+}$ concentration increased due to the $K_D$ decrease. The Sr$^{2+}$ isotherms could be fitted well to the Langmuir adsorption equation, which indicates that only one site type is involved in the Sr$^{2+}$ adsorption.

Key Words: Adsorption, distribution coefficient, kaolinite, penetration length ratio, strontium

1. Introduction

Strontium (Sr)-90 is one product of the radioactive elements of nuclear fuel materials emitting beta particles. Its half-life is 29 years, and it is harmful to the human health (Fetter et al. 1988). During the nuclear power plant accidents in Fukushima, Japan and Chernobyl, Ukraine, large amounts of radioactive species, including Sr-90, were released into the environment (Bondarkov et al. 2011; Steinhauser et al. 2013). As the radioactive damage is serious, the environmental fate of Sr$^{2+}$ must be considered, especially at low Sr$^{2+}$ concentrations.

Kaolinite is one of the most ubiquitous phyllosilicates in soils and it has next to the basal

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plane surface a relatively large edge surface (White and Dixon 2002); therefore, \( \text{Sr}^{2+} \) adsorption and transport in kaolinite soils deserve specific attention. Some reports consider \( \text{Sr}^{2+} \) adsorption on kaolinite on the basis of ion exchange (Wahlberg et al. 1965; Parkman et al. 1998; Bascetin and Atun 2006; Keçeli 2015). \( \text{Sr}^{2+} \) transport in quartz sand (Rod et al. 2010), sediment (Wallace et al. 2012) and porous material (Prigiobbe et al. 2012) were reported. The fact that the distribution coefficient provides information on both adsorption and migration of a component, which is the simplest parameter to characterize the influence of environmental factors on the fate of a pollutant. Thus, the distribution coefficient has been used to characterize Sr-kaolinite systems (Meyer 1979; Rafferty et al. 1981; Erten et al. 1988; Bunde et al. 1997; Bascetin and Atun 2006; Rani and Sasidhar 2012). The distribution coefficient of the Sr-kaolinite system under the given conditions can be determined when the adsorption isotherm of \( \text{Sr}^{2+} \) on kaolinite is known. Migration of \( \text{Sr}^{2+} \) in kaolinite soil can be conveniently characterized by using the ratio of average penetration length of \( \text{Sr}^{2+} \) relative to that of water. This ratio is determined by the distribution coefficient and the solid and solution content in the kaolinite soil (Bolt 1978). The migration of \( \text{Sr}^{2+} \) is retarded because of the adsorption of \( \text{Sr}^{2+} \) to kaolinite soil. This retardation can be quantified by using the parameter of distribution coefficient. However, there has been little research of \( \text{Sr}^{2+} \) penetration length at low \( \text{Sr}^{2+} \) concentration compared with water penetration length.

The objectives of the present study are therefore to investigate both the characteristics of \( \text{Sr}^{2+} \) adsorption on kaolinite at different NaCl concentration and pH values with emphasis to low \( \text{Sr}^{2+} \) concentrations and the migration of \( \text{Sr}^{2+} \) in a kaolinite soil under these conditions. The \( \text{Sr}^{2+} \) distribution coefficients were derived and used to describe the \( \text{Sr}^{2+} \) migration. To gain further insight in the mechanism of the adsorption, the \( \text{Sr}^{2+} \) adsorption results were analyzed with the Langmuir model. The Langmuir model assumes ideal adsorption behavior in a monolayer and considers the adsorption capacity as independent parameter and neglects valence effects (Langmuir 1918; Rani and Sasidhar 2012).

2. Materials and Experiments

The kaolinite from Iriki, Kagoshima, was suspended in deionized water and the fraction with a diameter less than 2µm was obtained by centrifugation. The obtained fraction was freeze-dried and stored in a closed container. The sample was characterized by using the X-ray diffraction apparatus (RINT1200, Rigaku Group of companies, Japan); the kaolinite content was 98.1% and the alunite content was 1.9%.

Three g of kaolinite powder was put in a 400 mL centrifuge bottle, mixed well with 300 mL
of 1 mol L\(^{-1}\) NaCl solution and repeated for three times to reach a complete exchange. The clay was equilibrated with the prescribed NaCl solution at 0.1, 1 or 10 mmol L\(^{-1}\). This process was repeated until the electrical conductance of the suspension equaled that of the prescribed NaCl solution at 0.1, 1 or 10 mmol L\(^{-1}\). A suitable volume of 0.01 mol L\(^{-1}\) HCl or NaOH solution was added to adjust the pH of the Na-Kaolinite suspension to 6.5 or 4.1. The final 10 g L\(^{-1}\) Na-kaolinite suspension was kept for further use.

The Sr\(^{2+}\) adsorption experiments were conducted by the batch method using a series of polypropylene centrifuge tubes. Ten mL of the 10 g L\(^{-1}\) Na-kaolinite suspension was pipetted into the centrifuge tube. Subsequently, 20 mL of SrCl\(_2\) solution containing the prescribed NaCl concentration (0.1, 1 or 10 mmol L\(^{-1}\)) at prescribed pH (4.1 or 6.5) was added to reach an initial Sr\(^{2+}\) concentration in the range 2\(\times\)10\(^{-3}\) mmol L\(^{-1}\) to 6\(\times\)10\(^{-2}\) mmol L\(^{-1}\). The tubes were shaken for 24 hours at room temperature. The pH of the equilibrium suspension was measured and recorded. Triplicate runs were performed for all batch experiments.

The equilibrium suspensions were centrifuged and the supernatants were gathered to determine the Sr\(^{2+}\) concentrations by inductively coupled plasma mass spectrometry (ICP-MS: PerkinElmer SCIEX-ELAN DRC-e). The adsorbed amount of Sr\(^{2+}\) on the Na-kaolinite was calculated by subtracting the amount of Sr\(^{2+}\) in equilibrium solution from the total amount of Sr\(^{2+}\) added initially.

3. Modeling

3.1. Distribution coefficient

The distribution coefficient, \(K_D\) (L kg\(^{-1}\)), describes the distribution of the adsorbate over the solid phase and the solution phase that can be defined as

\[
K_D = \frac{Q_{Sr}}{[Sr]} \quad (1)
\]

where \(Q_{Sr}\) is the adsorbed amount of Sr\(^{2+}\) on kaolinite (mmol kg\(^{-1}\)) and [Sr] is the equilibrium Sr\(^{2+}\) concentration in the solution (mmol L\(^{-1}\)). The larger \(K_D\) is, the stronger is the accumulation in the adsorbed phase.

3.2. Retardation and penetration length ratio

Let a certain volume of solution containing a concentration [Sr] mmol L\(^{-1}\) of cation Sr\(^{2+}\) at the prescribed NaCl concentration and pH feed to per unit area of kaolinite. The distribution ratio, \(R_D\), is a commonly used physical parameter for estimating the retardation of a dissolved pollutant in
the case of a solution with pollutant that permeates in a column of soil. Because the retardation is caused by adsorption, \( R_D \) is related to the partition of the contaminant between the solution and the solid (adsorbed) phase. As \( K_D \) quantifies the partition, \( K_D \) and \( R_D \) are directly related:

\[
R_D = K_D \frac{\rho_b}{\theta} \quad (2)
\]

where, \( \rho_b \) (kg L\(^{-1}\)) the bulk density of the kaolinite soil (mass of kaolinite in the column per unit volume of kaolinite and void) and \( \theta \) the volumetric water content of the column of soil per unit soil volume in saturated condition (L L\(^{-1}\) or m\(^3\) m\(^{-3}\)). For the calculations, the soil bulk density of the hypothetical kaolinite soil has to be assumed to be homogeneous and constant. As the bulk density of natural soil usually ranges from 1.0 to 1.5 kg L\(^{-1}\), a kaolinite soil bulk density of 1.25 kg L\(^{-1}\) is used in this study. From this value, and the density of pure kaolinite of 2.65 kg L\(^{-1}\) (Kuroda et al. 2003), the volume fraction of kaolinite in the soil can be obtained:

\[
\frac{\rho_b}{\rho} = 0.472.
\]

Consequently, the volume fraction of solution in the soil equals 0.528 when the kaolinite soil is saturated and this implies that under these conditions \( \theta \) has reached its maximum value of 0.528.

When only the saturation condition is adopted, \( R_D \) is proportional to \( K_D \) because the \( \theta \) and \( \rho_b \) are constant.

In the saturated column, the average penetration length, \( x_p \), of Sr\(^{2+}\) fed into the soil by the Sr\(^{2+}\) solution is defined by the relation (Bolt 1978):

\[
x_p = \frac{V_F}{\theta} \frac{1}{1+R_D} \quad (3)
\]

where \( V_F \) is the feed volume of Sr\(^{2+}\) solution per m\(^2\) of soil (m\(^3\)/m\(^2\)) and \( \theta \) is the saturated water content (m\(^3\)/m\(^3\)). \( V_F/\theta \) is the average penetration length (m) of water in the soil. The ratio, \( r \), of the average penetration length of Sr\(^{2+}\) to that of water is thus obtained as:

\[
r = \frac{x_p}{V_F/\theta} = \frac{1}{1+R_D} \quad (4)
\]

The inverse of \( r \), \( 1+R_D \), is the retardation factor which is widely used for analyses of solute transport in soils.

As \( K_D \) is a positive quantity, \( R_D \) is positive and this implies that \( r < 1 \) and a small \( r \) implies a strong Sr\(^{2+}\) retardation. For large \( R_D \) (\( R_D > 100 \)), i.e., large \( K_D \), \( r \) is practically speaking inversely proportional to \( R_D \). We can also assume that \( \theta \) is a constant unsaturated volumetric water content. However, in order to obtain the largest penetration length ratio, the saturated condition is adopted here.

### 3.3 Langmuir model

The Langmuir model was used for the adsorption of Sr\(^{2+}\) on kaolinite as follows:
where $Q_{Sr}$ (mmol kg$^{-1}$) is the Sr$^{2+}$ adsorption, $Q_{Sr,m}$ (mmol kg$^{-1}$) is the maximum adsorption, $K_L$ the Langmuir adsorption constant (L mmol$^{-1}$) and $[\text{Sr}]$ (mmol L$^{-1}$) is the equilibrium Sr$^{2+}$ concentration. As the Langmuir model is the theoretically derived adsorption model, we use it for the theoretical consideration.

4. Results and discussion

4.1. The Sr$^{2+}$ distribution coefficient

The adsorption isotherms of Sr$^{2+}$ on Na-kaolinite at pH 6.5 and pH 4.1 and different NaCl concentrations are depicted in Fig. 1 as a double logarithmic plot. The measured adsorption increases linearly with slope $\approx 1$ at low Sr$^{2+}$ concentrations, but gradually levels off at higher Sr$^{2+}$ concentrations. Slope $\approx 1$ implies a constant adsorption affinity and $K_D$ value; the low concentration range for which the slope $\approx 1$ is the so-called ‘Henry region’; in this range the adsorption is directly proportional to the solution concentration, which can be well explained by the Langmuir model as written in the later part. The dotted lines (slope =1) are lines with different $K_D$ (L kg$^{-1}$) as indicated (see Eq.(1)). The constant values of $K_D$ at low Sr$^{2+}$ concentration are observed for each isotherm in Fig. 1. They ranged between 600 and 40000 L kg$^{-1}$. The magnitude of $K_D$ clearly depends on the solution conditions: $K_D$ strongly decreases with increasing salt concentration and decreasing pH. The $K_D$ value at low Sr$^{2+}$ concentration at 0.1 mmol L$^{-1}$ NaCl is about 53 times larger than that at 10 mmol L$^{-1}$ NaCl. The effect of pH is only investigated at 1 mmol L$^{-1}$ NaCl. $K_D$ at pH 6.5 is about 17 times larger than $K_D$ at pH 4.1. Similar effects for the kaolinite – Sr$^{2+}$ system have been observed by a few researchers (Meyer 1979; Rani and Sasidhar 2012). For all solution conditions $K_D$ decreases with increasing Sr$^{2+}$ concentrations at Sr$^{2+}$ concentrations beyond the Henry region, but the Sr$^{2+}$ concentration where $K_D$ starts to decrease depends on the solution conditions. Erten et al. (1988) and Bascetin and Atun (2006) also observed a decrease of $K_D$ with the increasing Sr$^{2+}$ concentration for kaolinite. Concluding this section, it is clear that pH and Na$^+$ concentration influence the adsorption of Sr$^{2+}$ on kaolinite and the Sr$^{2+}$ distribution coefficient strongly.

The fitting of the Sr$^{2+}$ adsorption data to the Langmuir equation are presented in Fig.1 as double logarithmic plot (solid lines). The measured values of Sr$^{2+}$ adsorbed on kaolinite are quite well fitted to the Langmuir model. The adsorption affinity or Langmuir constant, $K_L$, and the adsorption capacity, $Q_{Sr,m}$, are collected in Table 1. The values of $K_L$ are strongly influenced by

\[ Q_{Sr} = \frac{Q_{Sr,m} K_L [Sr]}{1 + K_L [Sr]} \quad (5) \]
NaCl concentration because the influence of competition between Sr\(^{2+}\) and Na\(^+\) on \(K_L\) differs with different Na\(^+\) concentration. Thus, \(K_L\) obtained in this study should be interpreted as a conditional constant; \(Q_{Sr,m}\) are almost identical under different NaCl concentration.

Fig. 1 Sr\(^{2+}\) adsorption isotherms on kaolinite at two pH values and three salt concentrations. The dotted lines are lines of equal distribution coefficient (\(K_D\)) and the solid lines are fitting curves of Langmuir model. The symbols are measured values. At pH 6.5: △0.1 mmol L\(^{-1}\) NaCl, □1 mmol L\(^{-1}\) NaCl, ○10 mmol L\(^{-1}\) NaCl. At pH 4.1: ◇1 mmol L\(^{-1}\) NaCl

<table>
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<tr>
<th>pH</th>
<th>Na conc.</th>
<th>(Q_{Sr,m})</th>
<th>(K_L)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>1</td>
<td>11.6</td>
<td>1100</td>
<td>0.995</td>
</tr>
<tr>
<td>4.1</td>
<td>1</td>
<td>0.2</td>
<td>2500</td>
<td>0.934</td>
</tr>
</tbody>
</table>

Table 1 Langmuir isotherm parameters

By comparing \(K_D\) and \(K_L\) at given solution conditions, it should be noted that \(K_L\) is a constant for all Sr\(^{2+}\) concentrations, but that \(K_D\) is only constant in the Henry region. The difference is due to the fact that Eq.(5) takes into account the adsorption capacity, \(Q_{Sr,m}\). At relatively high Sr\(^{2+}\) concentration the probability of adsorption is decreased by the decrease of the vacant sites for Sr\(^{2+}\) adsorption. Eq.(5) takes this decreased probability into account, while Eq.(1) does not take the adsorption capacity into account. At sufficiently low Sr\(^{2+}\) concentration (\(K_L[\text{Sr}]<<1\)) Eq.(5) reduces to the Henry equation, \(Q_{Sr}=Q_{Sr,m}K_L[\text{Sr}]\), and this relation equals Eq.(1) with \(Q_{Sr,m}K_L = K_D\).
indicating that in the Henry region $K_L$ and $K_D$ are closely related.

The Sr$^{2+}$ isotherms could be fitted well to the Langmuir adsorption equation, which indicates that only one site type is involved in the Sr$^{2+}$ adsorption. The values of $K_D$, keeping constant at low Sr$^{2+}$ concentration were observed. Therefore, even if the Sr$^{2+}$ concentration is extremely lower than those in this experiment, the values of $K_D$ in the Henry region can be valid from the theoretical viewpoint. The value can be applicable for the Sr-90 contaminated sites where the Sr$^{2+}$ concentration is supposed to be very low.

4.2. The Sr$^{2+}$ penetration length ratio

The average penetration length ratio $r$, representing the average penetration length of Sr$^{2+}$ relative to that of water is depicted in Fig. 2 as a function of the equilibrium Sr$^{2+}$ concentration of the solution fed in the kaolinite soil. The four depicted data sets correspond with the four-adsorption isotherms depicted in Fig. 1. Since the ratio $r$ is inversely proportional to $(1+R_D)$ and $R_D$ is proportional to $K_D$, the large $K_D$ values corresponding with the isotherms at low Sr$^{2+}$ concentration induce small $r$ values. As $K_D$ increased with decreasing NaCl concentration and increasing pH, the reverse trend should be observed for $r$ and this explains the decrease of $r$ with decreasing NaCl concentration and increasing pH observed in Fig. 2. The small values of $r$ indicate considerable retardation of Sr$^{2+}$ upon solution penetration in the kaolinite soil. The increase of the penetration length ratio of Sr$^{2+}$ in kaolinite with increasing Sr$^{2+}$ concentration is due to the decrease of $K_D$. By considering the above trends quantitatively, the following observations can be made. The dependence of the penetration length ratio of Sr$^{2+}$ in kaolinite on pH is considerable: a $t_{1.1}$ mmol L$^{-1}$ NaCl and low Sr$^{2+}$ concentration, the $r$ value at pH 4.1 ($7.04\times10^{-4}$) is 16.7 times larger than $r$ at pH 6.5($4.22\times10^{-5}$). It is favorable for Sr$^{2+}$ adsorption at high pH, which results in a strong retardation of Sr$^{2+}$ in sediments (Wallace et al. 2012) and iron oxides (Prigiobbe et al. 2012). The effect of the NaCl concentration at pH 6.5 and low Sr$^{2+}$ concentration on the penetration length of Sr$^{2+}$ is also large: at 0.1 mmol L$^{-1}$ NaCl $r$ equals $1\times10^{-5}$ which is 53.3 times smaller than $r$ at 10 mmol L$^{-1}$ NaCl ($5.63\times10^{-4}$). The trend of the present results corresponds well with literature results. Wallace et al. (2012) have reported that for sediments the presence of Na$^+$ resulted in the much lower sorption of Sr$^{2+}$ which caused a significant migration of Sr$^{2+}$ in the sediments. Hull et al. (2008) have reported that Sr$^{2+}$ transported rapidly in the vadose zone sediment at high Na$^+$ concentration and the Sr$^{2+}$ mobility decreased significantly in the absence of competing cations.
Fig. 2 The penetration length ratio of Sr$^{2+}$ versus the fed solution concentration Sr$^{2+}$. The dotted lines and indicated $r$ values are the penetration ratios corresponding with the largest $K_D$ values at low Sr$^{2+}$ concentration for each solution condition. At pH 6.5: △0.1 mmol L$^{-1}$ NaCl, □1 mmol L$^{-1}$ NaCl, ○10 mmol L$^{-1}$ NaCl. At pH 4.1: ◇1 mmol L$^{-1}$ NaCl

The evaluated penetration length ratios of the Sr$^{2+}$ at low [Sr] are very small. The Sr$^{2+}$ penetration length is about 0.001% of the water penetration length at the conditions of pH 6.5, 0.1 mmol L$^{-1}$ NaCl and [Sr] $<$ 5x10$^{-8}$ mmol L$^{-1}$. At pH 6.5, 1 mmol L$^{-1}$ NaCl and [Sr]=2x10$^{-7}$ mmol L$^{-1}$, the value is about 0.004%. At pH 6.5, 10 mmol L$^{-1}$ NaCl and [Sr]<2x10$^{-6}$ mmol L$^{-1}$, the value is 0.056 %. At pH 4.1, 1 mmol L$^{-1}$ NaCl and [Sr] $<$ 2x10$^{-8}$ mmol L$^{-1}$, the value is about 0.07 %. These values clearly indicate that Sr$^{2+}$ is most strongly retarded by kaolinite at low NaCl concentration and relatively high pH.

The values of extremely low penetration length ratio of Sr$^{2+}$ relative to that of water in kaolinite were calculated theoretically based on the distribution coefficient obtained from adsorption experiment. Although there are many complicated factors affecting the migration of Sr$^{2+}$ in soils such as preferential flow, the average penetration length in the soils with uniform soil structure can be predicted.

In conclusion, because only one site type is involved in the Sr$^{2+}$ adsorption in the kaolinite, the constant values of $K_D$ are valid to calculate the average penetration length of Sr$^{2+}$ even at extremely low Sr$^{2+}$ concentration theoretically. The low values of average penetration length ratio show the strong retardation in kaolinite soils for Sr$^{2+}$ at low Sr$^{2+}$ concentration. Although the penetration ratio is a simple and useful parameter to estimate the mobility of Sr$^{2+}$, direct
observations of Sr\(^{2+}\) migration in soil are also necessary to confirm the theoretically calculated retardation.

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