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Strontium adsorption and penetration in clays

(ストロンチウムの粘土中における吸着と浸透)

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Introduction

The energy is very important for the human daily life and the development of the human society. The fossil fuel has been used as the main power source for many years, and which also has been considered as the primary factor causing the global warming in recent decade. Because global warming threatens the living of human beings, new clean energy must be used to replace the fossil fuel. The nuclear energy has been regarded as one of effective power source to relieve the global warming and reduce the dependency to fossil fuel. We must confront and handle the radioactive pollution induced by the using and development of nuclear energy. The radioactive elements are released into the environment due to the disposal of nuclear waste water or the accident of nuclear power plant, like which happened in Chernobyl, Ukraine in 1986 and in Fukushima, Japan in 2011. Nuclear disaster such as Chernobyl and Fukushima leads to the release of radioactive elements into the environment. They have the harmful effect on all living organisms because of their radioactive properties. Strontium-90 (Sr-90) is one of radioactive product of nuclear fission, which is present in significant amount in spent nuclear fuel from nuclear reactors and in nuclear fallout from nuclear tests. This makes the environmental behaviors of Sr-90 attracting significant attentions. The adsorption and desorption reactions of toxic elements onto clay minerals are critical geochemical processes that affect their bioavailability and movement in soils. It is very important to understand the adsorption behaviors and mechanisms of Sr^{2+} adsorbed onto clay minerals for handling the Sr^{2+} pollution or the treatment of nuclear waste water. Sr-90 is one of radioactive elements entering into environment. Even though the Sr-90 is not the most primary radioactive elements from the

nuclear power plant, it is worth to pay enough attention to investigate the environmental behaviors of Sr-90 because of its long half-life and emitting harmful beta particles.

The clay minerals in soils are in charge of the behaviors of ions in the soils solution because they have the high cation exchange capacity, swelling properties and large surface area, which are also routinely used as the effective barriers in nuclear waste to prevent contamination of groundwater and sub-soils (Murray, 2000; Gu *et al.*, 2010). The clay mineral is one kind of active component in soils to retard the pollutants, which can be divided into many categories according to the different charge types and structural properties. The phyllosilicate minerals are common in the soils, which strongly influence both the chemical and physical properties of soils because of their small particle sizes, high surface area and unique cation exchange properties. Kaolinite, illite, and vermiculite are three common and typical phyllosilicates in soils. Kaolinite is the 1:1 type mineral, consists of a unit made up of one octahedral and one tetrahedral sheet. The H bonding between oxygens of the tetrahedral sheet and the hydroxyls of the next octahedral sheets makes the kaolinite nonexpanding. Because the oxygens on the siloxane surface and the hydroxyls on the hydroxyl surface are almost charged satisfied, the unsatisfied bonds on the edges of kaolinite provide the main charge, usually called “variable charge” (White & Dixon, 2002). Both illite and vermiculite are 2:1 type minerals consisting of two tetrahedral sheets with one bound to each side of an octahedral sheet. They consist of 2:1 layers stacked one above the other. Because the isomorphic substitution (parts of Si or Al atoms replaced by cations of lower valence with the correct size) occurs in the basal sheet, a direct consequence of this substitution is a deficit of positive charge of the clay lattice. The deficits of positive charge of the clay minerals present the permanent negative charges. The permanent negative charges are predominant for both illite and vermiculite. The illite is nonexpanding (except for the frayed edge site) clay, its layers are held together by their strong attraction for the K cations that occur between the layers, and the negative layer charge is also balanced by the nonexchangeable K cations (Thompson & Ukrainczyk, 2002). On the contrary, the vermiculite is expanding clay because of the hydrated exchangeable cations (balancing the negative layer charge) occupying the interlayer spaces (Malia, 2002). Allophane is a common aluminosilicate mineral in soils, which occur as weathering product of volcanic ash and is the

very important minerals in the andisol. It consists of small spheres, and the spheres clump together to form irregular aggregate. The variable-charge properties of allophane result from protonation and dissociation of the surface aluminol and silanol functional groups, which are strongly affected by the ratio of Si/Al because the silanol groups are more strongly acidic than that the aluminol groups (Harsh et al., 2002). Even though fundamentally their chemical compositions are same, their main charge types and properties of physic structure are different. It is worth to consider the adsorption and retardation ability of four clay minerals for Sr^{2+} .

Many researchers have focused on the adsorption mechanisms of Sr^{2+} onto clay minerals (Sahai *et al.*, 2000; Bilgin *et al.*, 2001; Elvan and Atun, 2006; Ridley *et al.*, 2015). Elvan and Atun (2006) studied the adsorption behavior of Sr^{2+} on binary mineral mixtures of montmorillonite and kaolinite. They reported that the adsorption mechanism of Sr^{2+} was ion exchange according to the mean adsorption energy values of 8.0-9.5 kJ mol^{-1} . Bilgin *et al.* (2001) also reported that the adsorption mechanism of Sr^{2+} on illite was ion exchange because of the mean free energy between 8 and 16 kJ mol^{-1} . Missana *et al.* (2008) reported that Sr^{2+} adsorption on Na-smectite was strongly dependent on the ionic strength and practically independent from the pH because of the ionic exchange mechanism; the Sr^{2+} adsorption on illite was dominated by ionic exchange but the surface complexation contribution was observed at higher pH. The ionic exchange was in charge of the Sr^{2+} adsorbed on bentonite reported by Khan (2003). From the above previous studies, the location of Sr^{2+} adsorption is not in the surface layer and ion exchange is the predominant mechanism. Sahai *et al.* (2000) investigated the Sr^{2+} adsorbed by kaolinite at $\text{pH} > 7.5$, and reported that Sr^{2+} adsorption onto kaolinite primarily as a hydrated surface complex by the technology of Extend X-ray Adsorption Fine Structure. Parkman *et al.* (1998) reported that the Sr^{2+} was taken up as a partially hydrated species into octahedral sites on the kaolinite surface at the lowest initial Sr^{2+} concentrations according the coordination and bond distance data obtained by EXAFS. Ridley *et al.* (2015) reported that Sr^{2+} adsorbed as the inner-sphere Sr-tridentate surface species on anatase nanoparticles with a density functional theory. According to these reports, Sr^{2+} could be adsorbed on the surface of the clay minerals as the surface complex. The different adsorption mechanism of Sr^{2+} on clay minerals were reported in the previous references due to the

differences of the charge category and structure property among clay minerals. Anyway, it is still ambiguous. The objectives of this research are: (1) The Na^+ is the predominant component of soil solution in the soils along the coastline because of the influence of extremely high Na^+ concentration of seawater. The effects of Na^+ on Sr^{2+} adsorption and penetration in the four clay minerals will be considered. (2) The influences of pH on Sr^{2+} adsorption and retardation will be investigated and discussed for the four clay minerals. (3) The four typical clay minerals have their own special charge category and structure properties. The difference of Sr^{2+} adsorption ability and retardation efficiency among the four clay minerals will be compared. (4) The adsorption mechanism of Sr^{2+} ions in the clay-solution interface will be predicted briefly through measuring the zeta potential of the clay minerals after adsorbing Sr^{2+} .

Materials and Methods

The kaolinite sample from Iriki, Kagoshima, Japan, was purchased from Iwamoto Mineral Company. The illite (IMt-2) sample from Silver Hill, Montana, USA, was provided by Clay Minerals Society Source Clays Repository, Aurora, Colorado. The vermiculite sample from Sukagawa, Fukushima, Japan, was purchased from Nichika Company. And allophane was synthesized in the laboratory. A batch method was used to obtain the adsorbed amount of Sr^{2+} under different NaCl solution (1, 10 and 100 mmol L^{-1}) and pH (4, 6.5). Triplicate runs were performed for all batch experiments.

The experiment of the pH effect on the strontium adsorption on four clays were also performed by the batch method using a series of polypropylene centrifuge tubes. 0.1 M HCl or NaOH solution was added to adjust the pH of the suspension (4, 6, 8, 10). Duplicate runs were performed for all batch experiments.

The concentration of Sr^{2+} in equilibrium solution was measured with the Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The adsorbed amount of Sr^{2+} on the Na-clays were calculated by subtracting the amount of Sr^{2+} in equilibrium solution from the total amount of Sr^{2+} added initially. Zeta potential of the clay minerals adsorbing Sr^{2+} were obtained by measuring the electrophoretic mobility and calculated with the Smoluchowski Equation (Delgado et al., 2007).

Theory

Distribution coefficient

The distribution coefficient, K_D , describes the distribution of the adsorbate over the solid phase and the solution phase that can be defined as

$$K_D = \frac{Q_{Sr}}{[Sr]}$$

where Q_{Sr} is the adsorbed amount of Sr^{2+} on clay ($mmol\ kg^{-1}$) and $[Sr]$ is the equilibrium Sr^{2+} concentration in the solution ($mmol\ L^{-1}$).

Retardation and penetration length ratio

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 partitioning of the contaminant between the solution and the solid (adsorbed) phase. As K_D quantifies the partitioning, K_D and R_D are directly related:

$$R_D = K_D \frac{\rho_b}{\theta}$$

where, ρ_b ($kg\ L^{-1}$) the bulk density of the clay soil (mass of clay in the column per unit volume of clay and void) and θ the volumetric water content of the column of soil per unit soil volume in saturated condition ($L\ L^{-1}$ or $m^3\ m^{-3}$). As K_D has the dimension $L\ kg^{-1}$, R_D is dimensionless.

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 provided by Bolt (1978). The ratio, r , of the average penetration length of Sr^{2+} to that of water is defined as:

$$r = \frac{x_p}{V_F / \theta} = \frac{1}{1 + R_D}$$

where V_F is the feed volume of Sr^{2+} solution per m^2 of soil (m^3/m^2) and θ is the saturated water content (m^3/m^3). V_F/θ is the average penetration length (m) of water in the soil.

In practice, there are few soils that contain nearly 100% clay. Therefore, the influence of

the fraction clay in a soil on the Sr^{2+} penetration length ratio was calculated, assuming that other solid components in the soil did not adsorb Sr^{2+} . Thus, R_D at the mass fraction of clay, f , is

$$R_D = K_D \frac{f \rho_b}{\theta}$$

where ρ_b is the bulk density of the soil. Then, the Sr^{2+} penetration length ratio, $r(f)$, can be calculated as:

$$r(f) = \frac{1}{1 + \frac{K_D f \rho_b}{\theta}}$$

Langmuir model

The Langmuir model for adsorption from solution assumes that the adsorbate (Sr) binds to adsorption sites (X) according to the following chemical equilibrium:



where *prefix X* refers to the adsorbed state. By using activities, the thermodynamic equilibrium can be described with the mass action law. When the activities are expressed as a product of concentration and activity coefficient and it is assumed that the activity coefficients in solution and adsorbed layer are all equal to 1, the Langmuir equation results. When a similar notation is applied as for the distribution coefficient the result can be written as

$$Q_{\text{Sr}} = \frac{Q_{\text{Sr},m} K_L [\text{Sr}]}{1 + K_L [\text{Sr}]}$$

where Q_{Sr} ($=\{\text{XSr}\}$; mmol kg^{-1}) is the Sr^{2+} adsorption, Q_m ($=\{X\} + \{\text{XSr}\}$; mmol kg^{-1} ;) the adsorption maximum, K_L the Langmuir adsorption constant (L mmol^{-1}) and $[\text{Sr}]$ (mmol L^{-1}) the equilibrium Sr^{2+} concentration.

Results and discussions

The Sr^{2+} adsorption on the kaolinite under different NaCl concentration and pH was evaluated and used to calculate the distribution coefficient and the distribution ratio. The results show that the values of distribution coefficient keep constant at low Sr^{2+} concentration, and strongly decrease with increasing NaCl concentration and/or decreasing the pH; they also

decrease at high Sr^{2+} concentration. The ratio of average Sr^{2+} penetration length to average water penetration length was presented for kaolinite containing soils. Extremely low penetration ratios at low Sr^{2+} concentration were found for pure kaolinite soils; they indicated that the Sr^{2+} penetration delayed strongly at low Sr^{2+} concentration where the distribution coefficient was the largest. The penetration length ratios increased with a decrease of pH from 6.5 to 4.1, by increasing the Na^+ concentration (more site competition) and by a decreasing kaolinite content of the soil. Analysis of the Sr^{2+} adsorption showed a clear preference of the equivalent adsorbed fraction of Sr^{2+} over the equivalent solution fraction of Sr^{2+} . This suggests that the retardation of Sr^{2+} will be complete at low Sr^{2+} concentrations for soils containing abundant kaolinite. The Langmuir equation fitted the Sr^{2+} adsorption by kaolinite well; this indicates that no specific surface sites are required to describe the adsorption. However, the affinity parameter K_L is a *conditional constant*, which is strongly influenced by the NaCl concentration and pH. The obtained adsorption capacity depends weakly on the NaCl concentration and strongly on pH. The observed ζ potentials qualitatively support these trends.

The Sr^{2+} adsorption was measured under different pH by batch method and the effect of pH on Sr^{2+} adsorption on four clay minerals were indicated. Based on the distribution coefficient (K_D) obtained in adsorption experiment, the influence of pH on retardation efficiency of the clay minerals for Sr^{2+} were evaluated. The extents of pH effect on the Sr^{2+} adsorption and penetration in these four clay minerals were strongly dependent on charge category (variable or permanent charge). The variable charges from the edge of kaolinite or allophane are predominant, resulting in the significant pH dependence; but the permanent charges from basal plane are in charge of the adsorption sites vermiculite, the distinct pH effects do not occur. Because the allophane has significant amount of variable charges, the pH influence on the adsorption and penetration is the largest. Even at high NaCl concentration closed to sea water, the penetration length ratio to water is smaller than 0.0004 at the $\text{pH} \geq 6$; Sr^{2+} penetrates less than 0.4 mm when water penetrates 1 m

The Sr^{2+} adsorption on the kaolinite, illite, vermiculite, and allophane under different NaCl concentration at pH 6.5 were evaluated and used to calculate the distribution coefficient. The results show that the values of distribution coefficient keep constant at low Sr^{2+}

concentration, and strongly decrease with increasing NaCl concentration. They also decrease at high Sr^{2+} concentration. The ratio of average Sr^{2+} penetration length to average water penetration length were presented for kaolinite, illite, vermiculite, and allophane containing soils. Extremely low penetration ratios at low Sr^{2+} concentration were found for pure clay mineral soils; they indicated that the Sr^{2+} penetration delayed strongly at low Sr^{2+} concentration where the distribution coefficient was the largest. The retardation efficiency of the four clay minerals decreases in the following orders: Allophane > Vermiculite > Illite > Kaolinite. No matter what the ionic strength or clay type is, the Sr^{2+} penetration length ratio (r) increase with the decrease of the mass fraction (f) of clay minerals; the values of average penetration length ratio $r(f)$ decrease as the power function ($r(f)=A(f)^{-1}$) when the mass fraction of clay becomes larger. This indicates that Sr^{2+} retardation efficiency of soils containing clay minerals becomes better, when the clay content is larger. The Langmuir equation fitted the Sr^{2+} adsorption by kaolinite, illite, vermiculite and allophane well; these indicate that no specific surface sites are required to describe the adsorption. However, the affinity parameter K_L is a *conditional constant*, which is strongly influenced by the NaCl concentration. The CEC and charge category of the clay can strongly influence the Sr^{2+} adsorption and retardation at low Sr^{2+} concentrations. The observed relationships between zeta potentials and the fraction of Sr^{2+} adsorbed on the clays qualitatively predict that Sr^{2+} adsorbed not as inner-sphere complexes; the outer sphere complexes of Sr^{2+} maybe form on kaolinite and allophane when the adsorption fraction of Sr^{2+} on them is larger.

Conclusions

The values of the distribution coefficient (K_D) keep constant at low Sr concentration. The significant decrease of distribution coefficients (K_D) with increase of NaCl concentration are observed because of the screening of the electrostatic attraction and competition with Na. The measured values of Sr adsorbed on four clay minerals are quite well fitted to the Langmuir model; these indicate that the adsorption sites for each clay has the same adsorption energy. K_L represents the adsorption energy ($\Delta G=RT \ln(K_L)$), K_L (allophane) > K_L (kaolinite) > K_L (illite) > K_L (vermiculite) indicates that the variable charges (is predominant charge for kaolinite and allophane) have the higher affinity for Sr than that of permanent charges (is predominant for illite and

vermiculite). One site type is involved in the Sr adsorption in clays according to Langmuir equation, the constant values of K_D are valid to calculate the average penetration length of Sr even at extremely low Sr concentration theoretically. The low values of average penetration length ratio show the strong retardation in clay soils for Sr at low Sr concentration. The penetration ratio is a simple parameter, but it is useful to estimate the mobility of Sr in the soils with uniform soil structure. The retardation efficiency of four clay minerals for Sr^{2+} are compared under same condition by using the average penetration length ratios (r). The larger value of K_L represents the larger adsorption energy or higher affinity for Sr^{2+} . The combination of larger maximum adsorption amount and higher affinity for Sr^{2+} of the clay mineral at low Sr^{2+} concentration brings up the larger value of K_D , which leads to the extremely low values of r . Thus, the retardation efficiency of the four clay minerals decreases in the following order: Allophane > Vermiculite > Illite > Kaolinite.

Analysis of the Sr^{2+} adsorption using the Langmuir model for competitive Sr^{2+} and Na^+ adsorption at constant NaCl concentration showed that the Sr^{2+} adsorption on each clay could be described by two parameters, the maximum adsorption, Q_m , and the “conditional” Sr^{2+} affinity constant, $K_{\text{Sr}(cond)}$. In the Henry region K_D is also constant and equal to $Q_m K_{\text{Sr}(cond)}$, which shows that under these conditions the magnitude of K_D is determined by both Q_m and $K_{\text{Sr}(cond)}$. The observed values of Q_m scale with the cation exchange capacities of the clays, the conditional affinities decrease with increasing NaCl concentration and are higher for clays with a relatively large edge surface.

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