Influence of Ionic Strength, pH, and Complex-forming Anions on the Adsorption of Cesium-137 and Strontium-90 by Kaolinite

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ABSTRACT : The effects of the major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+), complex-forming anions (SO_4^{2-}, HCO_3^-), and solution pH on the adsorption of ^{137}Cs and ^{90}Sr by kaolinite in groundwater chemistry were investigated. Three-dimensional Kd modelling designed by a statistical method was attempted to compare the relative effect among hydrated radii, charge and concentration of competing cations on the adsorption of Cs and Sr. The modelling results indicate that the hydrated radii of competing cations is the most important factor, and then their charges and concentrations are also important factors in order. The property of zeta potential of kaolinite particles was discussed in terms of the amphoteric reactions of a kaolinite surface affecting the adsorption of Cs and Sr. The ionic strength of competing cations on the adsorption of Cs and Sr exerts a greater effect than the solution pH. The sorption behaviour of Sr on kaolinite is also highly dependent on the concentration of bicarbonate. The speciation of Sr and the saturation state of a secondary phase were thermodynamically calculated by a computer program, WATEQ4F. This indicates that the change in solution pH with the concentration of bicarbonate and the precipitation of a strontianite ($SrCO_3$) are major factors controlling Sr adsorption behaviour in the presence of bicarbonate ion.

INTRODUCTION

The radionuclides ^{137}Cs (half life of 30.0 years) and ^{90}Sr (half life of 27.7 years) are hazardous alkali and alkaline earth elements present in radioactive waste. When radioactive waste is disposed in a geologic formation, it could be subjected to groundwater attack, and radionuclides could be released into a geologic barrier. While radionuclides are transported along migration pathways in underground, they may be adsorbed onto mineral surfaces around the pathways.

The adsorption reaction of hazardous nuclides on mineral surface in groundwater zone exerts an important effect on the aqueous concentration of nuclides and their migration velocities. The adsorption reaction in geologic environments can be highly dependent on the composition of the groundwater as well as the surface characteristics of minerals. It has been known that kaolinite is a common fracture-filling clay mineral in crystalline rock which can potentially react with radionuclide-bearing groundwater (Tullborg, Larson, 1982; 1983; Tullborg, 1986; Jeong et al., 1994). It was therefore used as an adsorbent of ^{137}Cs and ^{90}Sr in this study.

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The chemical parameters of groundwater affecting the adsorption reaction are the ionic strength of competing ions, pH, complexation, colloidal formation, etc. Major groundwater cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) will have a large influence on the adsorption of Cs and Sr in ion-exchange processes. The influence of cations on adsorption will depends on their charge and hydrated radius as well as concentration. In our previous study (Jeong et al., 1995; Jeong et al., 1996), the ionic strength-dependence on the adsorption of Cs and Sr onto clay minerals and the competiton order among cations were studied.

Major anions in groundwater composition such as bicarbonate and sulfate would determine the che- mical state of radionuclides in solutions. The concentration of bicarbonate ion (HCO_3^-) can also control the pH of groundwater. The dominant Cs species is Cs^+, regardless of the groundwater composition, while Sr may exist partly as sulfate or carbonate complexes in groundwater considering the relevant complex formation constants (Smith, Martell, 1976). The complexation of Sr in sulfate and bicarbonate solutions may be an important factor in controlling adsorption behaviour.

The solution pH have influence on the cation-exchange capacity of minerals as well as on the chemical state of radionuclides. Rafferty et al. (1981). showed the significant effect of pH on Sr(II) adsorption onto kaolinite. Torstenfelt et al. (1982) reported that the significant increment of Sr adsorption in high alkaline solution may be due to hydroly-

sis and precipitation of Sr.

The purpose of this study is to evaluate the parameters such as competiton effect of groundwater cations, effect of complex-forming anions and solution pH, which may affect the adsorption of ^{137}Cs and ^{90}Sr onto kaolinite. Firstly, we attempted to assess the relative importance of hydrated radii, charge and concentration of groundwater cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) as the parameters affecting the adsorption of Cs and Sr by a three-dimensional Kd(distribution coefficient) modelling. This approach may be useful to understand effective cations affecting the adsorption of Cs and Sr in natural groundwater. Secondly, we investigated the pH effect of background solution on the adsorption of Cs and Sr onto kaolinite, and discussed the association of surface charge of kaolinite with solution pH. Thirdly, the mechanism controlling the adsorption behaviour of Cs and Sr in sulfate and bicarbonate solutions was studied. Emphasis was especially given to the contribution of speciation, precipitation and pH change upon the adsorption behaviour of strontium.

ADSORPTION EXPERIMENT

Clay and aqueous solutions

Clay material used for the adsorption experiment is "Georgia kaolinite" obtained from Ward's Natural Science Establishment Inc. in the USA. The average particle size of kaolinite measured by Jeong et al. (1995) was 5.92 μm.

NaCl, CaCl$_2$, MgSO$_4$, KCl and NaHCO$_3$ solutions with ionic strength of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4} and 10^{-5} M were prepared as two sets; One included inactive CsCl of 10^{-6} M as background concentration, the other inactive SrCl$_2$. All chemicals used were of reagent grade quality. Each solution was spiked with ^{137}Cs (or ^{90}Sr) as a radiotracer. Activities of radionuclides were below 0.01 μCi/ml.

A preliminary experiment was carried out to adjust the pH of solutions in equilibrium with clay particles. The pH of inactive NaCl solutions in equilibrium with clay particles was subsequently adjusted to 4.5±0.5, 6.0±0.5, 7.0±0.5, 9.0±0.5, and 10.5±0.5 with NaOH and HCl. The amounts of NaOH and HCl determined from preliminary experiments were added into active solutions to obtain the above pH values, and then the active solution was placed in contacts with clay particles. Bicarbonate ion (HCO$_3^-$) is a major pH-controlling anion in natural groundwater (Stum, Morgan, 1996). The pH variation of NaHCO$_3$ solution with 10^{-1} to 10^{-5} M concentration was measured before and after the reaction with the clay particles.

Speciation of cesium and strontium in NaHCO$_3$ and MgSO$_4$ solutions was calculated by using the speciation program WATEQ4F (Ball, Nordstrom, 1992). The program was also used to predict the saturation state of a secondary phase in sodium bicarbonate solution with the addition of strontium.

To determine relative competition among groundwater cations on Cs and Sr adsorption, ternary mixtures of cations with various concentrations were made using the Box-Behnken model (Box, Behnken, 1960), which is statistically designed by an experimental method. This model has been efficiently used to show the effects of two or more factors on adsorption (Cho et al., 1990; Ticknor, Cho, 1990). The experimental design of the Box-Behnken model has three levels and three variables (Fig. 1). In this study three independent variables (X_1, X_2, X_3) correspond to cation types. Na, Mg and Ca were respectively used as X_1, X_2 and X_3 for the Sr adsorption experiment. For the Cs adsorption ex- periment, Na, K and Ca were used as X_1, X_2, and X_3, respectively. Three levels (-1, 0, 1) indicate the concentration of cations. Typical concentrations of Ca, Mg and Na in natural groundwater show a range between 10^{-2} and 10^{-4} M. The concentration of K generally shows a low value of about 10^{-4} M, Thus, the 10^{-2}, 10^{-3}, and 10^{-4} M of Mg, Ca and Na were used as their concentration
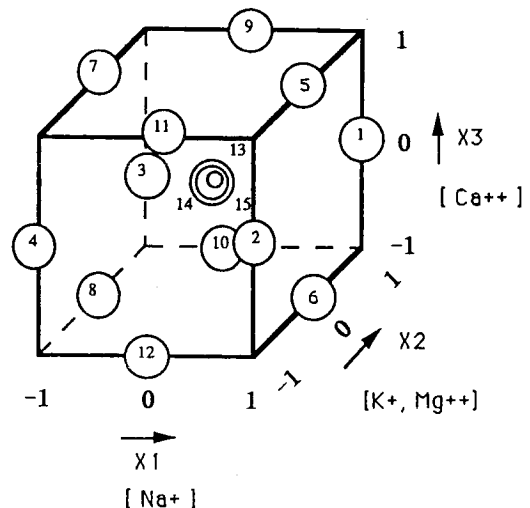

Fig. 1. The statistically designed diagram of three levels and three variables of Box-Behnken Model (Box, Behnken, 1960). Three independent variables are Na(X_1), K or Mg(X_2) and Ca(X_3). Three levels (-1, 0, 1) include the 10^{-2} to 10^{-4} M MgSO$_4$, CaCl$_2$ and NaCl, and 10^{-3} to 10^{-5} M KCl. The numbers in the box are data points needed to cover any effect of the ionic strength of competing cations on adsorption.

levels in this experiment, and 10^{-3}, 10^{-4} and 10^{-5} M of K were also used.

According to this model, a total of 15 data points are needed to cover any effect of the concentration of competing cations on adsorption; twelve points in the center of edges and three center points in triplicate of the design cubic box. Thus, ternary mixture solutions at 15 points were prepared for the batch adsorption experiment.

Experimental procedure

Adsorption experiments were performed at room temperature using 20 ml polypropylene vials as reaction vessels. The solid/solution ratio is an important parameter affecting to the adsorption of Cs and Sr (Cho *et al.* 1995). In this study, solid particles of 0.33 grams were immersed in 10 ml spike solution. The ratio of 0.33 g/10 ml corresponds to the intermediate range of solid/aqueous solution ratios of batch experiments carried out by Cho *et al.* (1995). The reaction vessels were routinely shaken to ensure maximum exposure of the mineral surface to the solution for four weeks (Park *et al.*, 1992). After four weeks the liquid was separated from the solid by gravity settling and centrifugation. The su- pernatant 0.5 ml of active solution was pipetted into the vial filled with 5 ml of scintillator (Packard ScINT-A XF). ^{90}Sr, which has the half life of 27.7 years, decays by beta emission to metastable ^{90}Y, and then is stabilized to ^{90}Zr by beta emission in 64 hours (KAERI, 1991). Hence, the seperated active solutions were preserved for four weeks (about ten times of half life) to decay enough from ^{90}Y to ^{90}Zr. The solutions cocktailed with scintillator were used to measure the β-activities of ^{137}Cs and ^{90}Sr in the solutions before and after the adsorption reaction. The β-activities were counted with a liquid scintillation analyzer (Packard model Tri-carb 2550TR). The results of batch sorption were represented by a distribution coefficient (Kd) or percent adsorption (P):

$$Kd\ (ml/g)=(V/Wt)[C_o-C_f)/Cf],$$
$$P(\%)=(100\times Kd)/(Kd+V/Wt) \qquad (1)$$

where, V =volume of solution (ml)
      Wt =weight of solid (g)
      C_o =concentration of nuclide in initial solution (cpm)
      C_f =concentration of nuclide in solution after sorption reaction (cpm)

Zeta potential measurement

Zeta potential of kaolinite was measured to obtain the information of surface charge of the kaolinite clay particles. Zeta potential was determined from the electrophoretic mobility. In the presence of 0.01 M NaCl, suspensions containing 0.2 g/500 ml of clay solid were prepared. The pH of the solution was adjusted from 2.5 to 10.5 in increments of about 0.5 pH units. Aliquots were taken from the suspension approximately 30 minutes after each pH adjustment to measure the mobility. The electrophoretic mobility was measured with zetamaster particle electrophoresis analyzer (Malvern, ZEM 5002).

RESULTS AND DISCUSSION

Effect of ionic strength of groundwater cations

Fig. 2 shows that the adsorption behaviors of Cs and Sr onto kaolinite are significantly dependent on
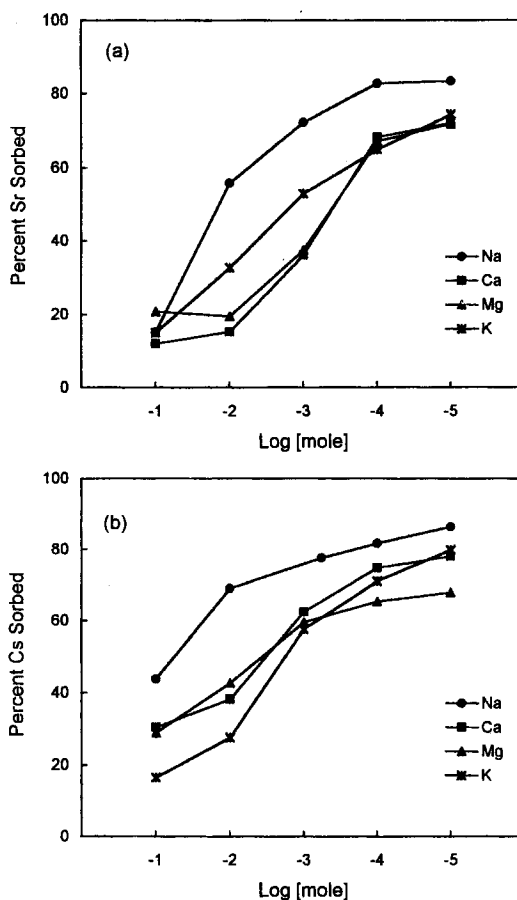

Fig. 2. Percent of Cs and Sr adsorbed onto kaolinite as a function of ionic strength of major groundwater cations. The pHs of all solutions are adjusted to 7.0±0.5.

the ionic strength of groundwater cations. That is, the percent of Cs and Sr adsorbed onto kaolinite greatly increases with decreasing ionic strength from 10^{-1} to 10^{-5} M. Ionic-strength dependence on the adsorption of Cs and Sr indicates that they are electrostatically bound as an outer-sphere complex at the kaolinite-water interface (Kinniburge, Jackson, 1981). Fig. 2 also indicates that divalent cations such as Ca^{2+} and Mg^{2+}, or large monovalent cation such as K^+, have greater competition on the adsorption of Cs and Sr than the small monovalent cation, Na^+. In most solutions, the percent of Cs adsorbed onto kaolinite is higher than that of Sr.

Large cations such as Cs^+ and K^+ are more polarizable and more readily allow distortions to their hydration sphere than small cation such as Sr^+ and Na^+ (Kinniburge, Jackson, 1981). Thus, small hydrated cations can approach closer to the kaolinite surface where they interact strongly with surface sites. Large and stable hydrated cations, however, would only be weakly bound onto kaolinite surface.

Three-dimensional Kd modelling in ternay mixtures of cations

The cation charge, hydration radius and polarizability are factors affecting the adsorption of cations (Swartzen-Allen, Matijevic, 1974). In this study the relative importance of the hydrated radius, the charge, and the concentration of groundwater cations on the adsorption of Cs and Sr onto kaolinite was assessed by the statistical method of Box-Behnken. The experimental design of Box-Behnken and statistical analysis provide an equation that can be used to predict adsorption values (K_d) within the range of the independent variables:

$$\log[K_d]=b_0+b_1X_1+b_2X_2+b_3X_3+b_{11}X_12+b_{22}X_2^2+$$
$$b_{33}X_{32}+b_{12}X_1X_2+b_{13}X_1X_3+b_{23}X_2X_3 \qquad (2)$$

Experimental data were used to derive b values required to solve the polynomial for any combination of the variables X_1, X_2 and X_3 that lie on or within the response surface of the experimental design. The b values can be obtained through multiple regression analysis of the experimental data.

Fig. 3, which is modeled by values obtained from polynomial equations, shows relative competition in ternary mixtures of cations with various concentration on the adsorption of Cs and Sr onto kaolinite. In spite of the higher concentration of Na, the Na coexisting with Ca and Mg have little influence on Cs and Sr adsorption (Fig. 3a, 3e and 3f). Although the concentration of K is about 10 times lower than that of Na and Ca, the competition of K on Cs

adsorption is much higher than that of Na (Fig. 3b), and is nearly same to that of Ca (Fig. 3c). The divalent cations such as Ca and Mg show nearly equivalent competition on Sr adsorption (Fig. 3d).

The modeling results suggest that the hydrated radius is the most important factor affecting the adsorption of Cs and Sr onto kaolinite, and then the charge and the concentrations of groundwater cations exert an effect on the adsorption of Cs and Sr. It could be an important criteria to understand the effect of groundwater composition on Cs and Sr adsorption. Although the concentration of K is lower than other cations in natural groundwater, potassium would be the most competitive cation among groundwater cations controlling the adsorption of Cs and Sr.

Effect of solution pH

The percentage of Cs and Sr adsorbed onto kaolinite in 10^{-1} to 10^{-4} M NaCl solution is plotted as a function of pH (4.5 to 10.5) (Fig. 4). The percentage of Cs adsorbed onto kaolinite slightly increases with solution pH (Fig. 4a). In particular, at a high concentration of NaCl solution (10^{-1} M) the solution pH has little effect on the adsorption behaviour of Cs. However, the percentage of Sr adsorbed onto kaolinite is highly dependent on solution pH (Fig. 4b).

Since the non-hydrolyzed Cs and Sr ions would be the dominating species in the solution, the observed pH effect may be related to the surface charge of kaolinite. Kaolinite is 1:1 dioctahedral clay that consists of octahedral sheets and tetrahedral sheets, and has no structural charge in its pure stoichiometric form (Giese, 1988). The sorption of aqueous species and the development of surface charge of kaolinite are controlled mainly by amphoteric reactions at oxygen sites on aluminol and siloxane surfaces that are non-bridging Al-OH (inner or surface) and Si-O on edges, respectively (Follet, 1965; Fordam, 1973; Parfitt, 1978; Sposito, 1984).

Zeta potential of kaolinite particles in NaCl solution was measured to determine the characteristics of its surface charge, which actually control the adsorption of Cs and Sr. The potential at the shearing plane, which is associated with particle/solution interface is defined as zeta potential. Fig. 5 shows that the zeta potential of kaolinite clay negatively increases from+2.3 mV to -66.5 mV as pH increases from 2.7 to 10.1. Silanol ($\equiv$SiOH) or aluminol ($\equiv$AlOH) groups of kaolinite are deprotonated with increasing pH as follows: $\equiv$SiOH or $\equiv$AlOH $\rightarrow$ $\equiv$SiO$^-$ or AlO$^-$. In more alkaline solution, more deprotonated silanol and aluminol would play a role as the adsorption sites for
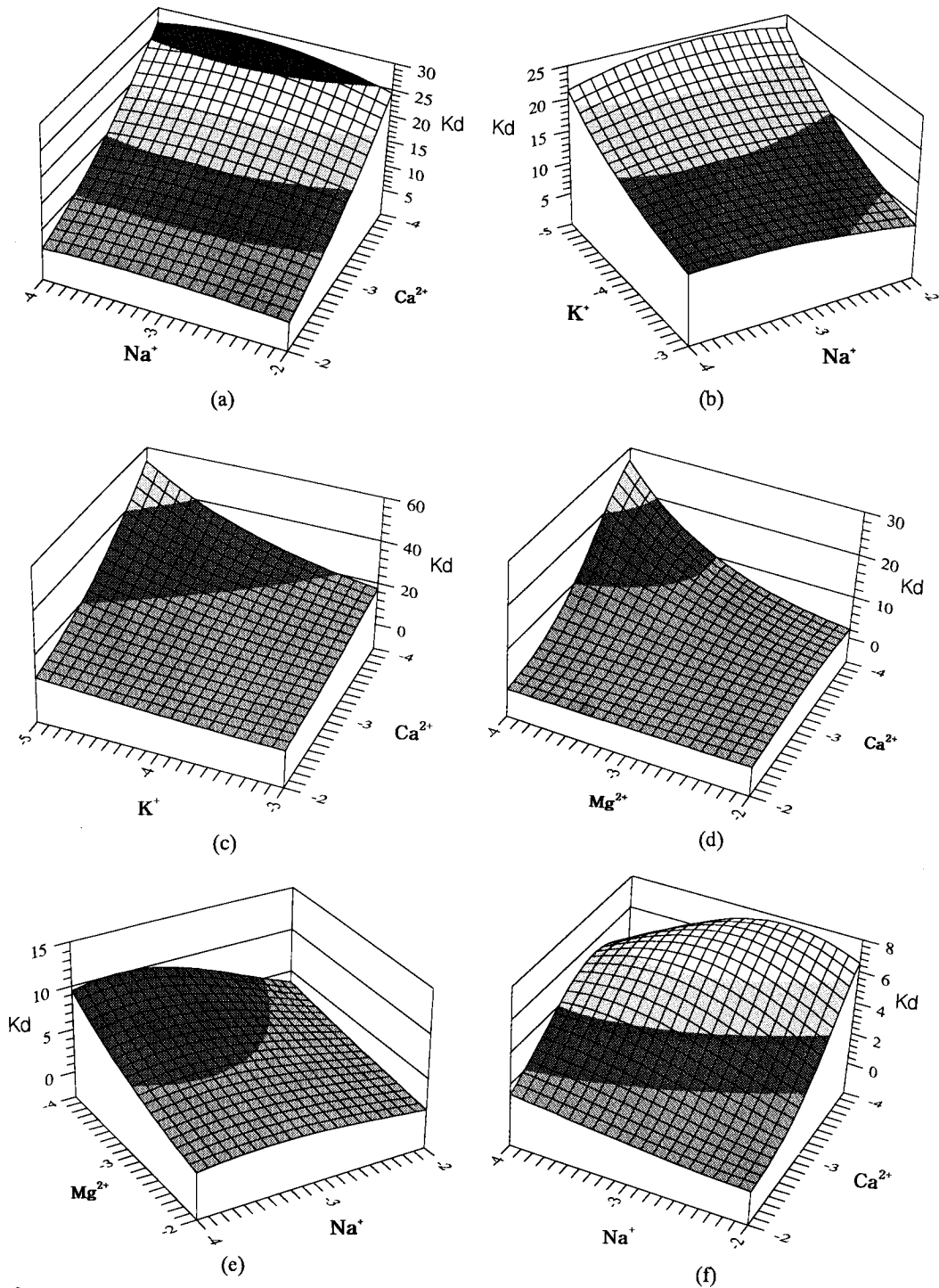
Fig. 3. Kd modeling of Cs and Sr adsorption onto kaolinite in the presence of major groundwater cations : (a), (b) and (c) show the adsorption behaviour of Cs onto kaolinite. (d), (e) and (f) show the adsorption of Sr onto kaolinite. The a, b, c, d, e and f solutions include K of 10^{-4} M, Ca of 10^{-3} M, Na of 10^{-3} M, Na of 10^{-3} M, Ca of 10^{-3} M and Mg of 10^{-3} M as background cations, respectively. The concentration of background cations are logarism mole. The pHs of solutions in the e-quilibrium with kaolinite clay range between 4.5 and 5.0.
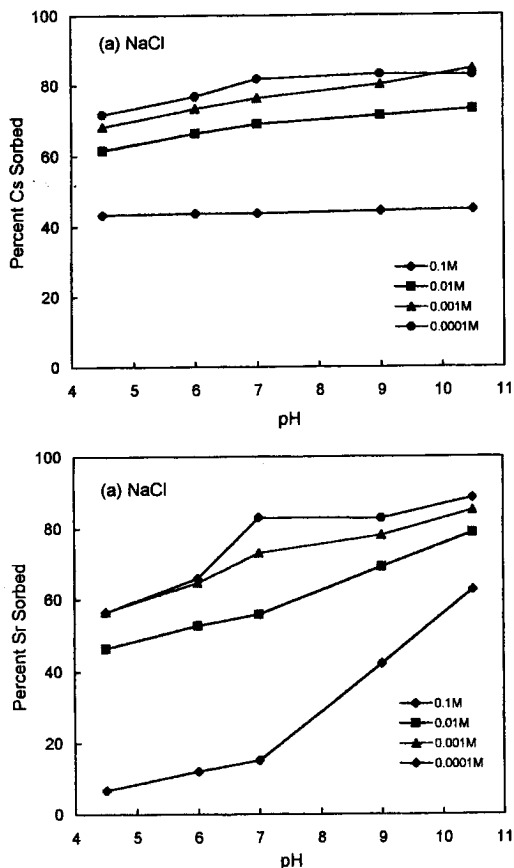
Fig. 4. Percent of Cs and Sr adsorbed onto kaolinite as a function of pH in the background electrolyte NaCl.

Cs and Sr. However, it seems that pH-dependence on Sr adsorption is caused by other mechanisms such as hydrolysis and precipitation as well as the surface charge of kaolinite.
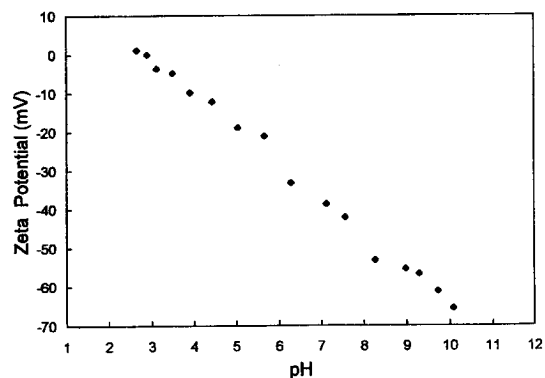

Fig. 5. Zeta potential of kaolinite particles in 10^{-2} M NaCl solution as a function of pH.

Considering the pH range (7 to 9) of natural groundwater, the pH plays an important role on Sr adsorption rather than the removal of Cs by kaolinite from groundwater.

Effect of major anions

Bicarbonate, sulfate and chloride are the major anions of natural groundwater composition. Fig. 6 shows the effect of anions such as bicarbonate and chloride on the adsorption of Cs and Sr onto kaolinite. The adsorption behaviour of Cs onto kaolinite shows a little difference between sodium bicarbonate and sodium chloride as background electrolytes (Fig. 6a). In the NaCl solution the adsorption behaviour of Sr is highly competed by the ionic strength of a background electrolyte (Fig. 7b). How-
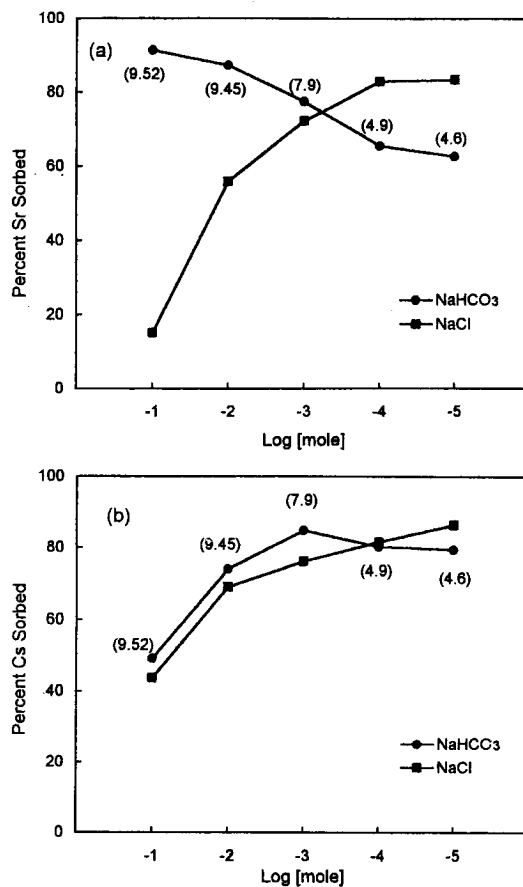

Fig. 6. Effect of bicarbonate and chloride ions on the adsorption of Cs and Sr onto kaolinite. Numbers in parenthesis indicate the pH values of NaHCO₃ solutions in which kaolinite particles are immersed. The pHs of NaCl solutions are adjusted into 7.0±0.5.
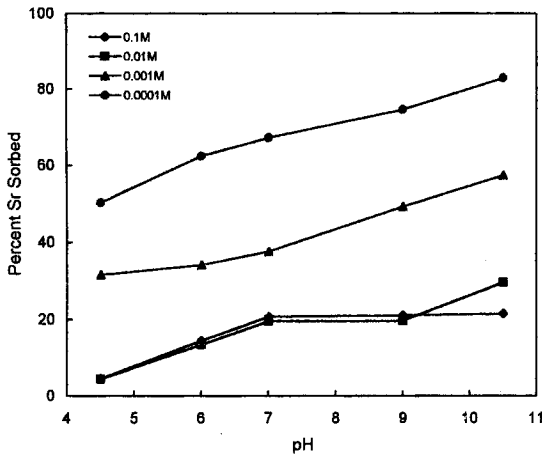
Fig. 7. Effect of sulfate ion on the adsorption of Sr onto kaolinite in various pH condition.

Table 1. Speciation of strontium in $NaHCO_3$ and $MgSO_4$ solutions.

Species	\-Log activity				
	10^{-1} M (pH 9.52)	10^{-2} M (pH 9.45)	10^{-3} M (pH 7.5)	10^{-4} M (pH 4.9)	10^{-5} M (pH 4.6)
CO_3^{2-}	2.238	3.110	5.846	9.434	10.727
HCO_3-	1.409	2.181	3.017	4.005	5.003
H_2CO_3	4.557	5.229	4.165	2.553	3.254
Na^+	1.155	2.053	3.016	4.005	5.002
$NaCO_3^-$	2.123	3.893	7.591	12.182	14.449
$NaHCO_{3(aq)}$	2.814	4.485	6.283	8.274	10.255
Sr^{2+}	6.864	6.321	6.060	6.015	6.004
$SrCO_{3(aq)}$	6.297	6.625	9.101	12.643	13.919
$SrHCO_3^+$	7.088	7.317	7.893	8.835	9.814
Mg^{2+}	1.779	2.422	3.160	4.047	5.014
$MgSO_4$	1.255	2.487	3.953	5.725	7.659
SO_4^{2-}	1.846	2.434	3.162	4.048	5.014
Sr^{2+}	6.755	6.404	6.156	6.049	6.017
$SrSO_{4(aq)}$	6.311	6.549	7.028	7.807	8.741

Initial concentration of strontium is 10^{-6} M., The pHs of all $MgSO_4$ solutions for model calculation are 7.0.

ever, the percent Sr adsorbed onto kaolinite dramatically increases as the $NaHCO_3$ concentration increases (Fig. 6b).

Since cesium is present only as ionic form Cs^+ in solutions, the effect of anions on the adsorption of Cs onto kaolinite is mainly attributed to solution pH. As explained in previous section, the solution pH has an effect on the number of the adsorption site of kaolinite for Cs and Sr. The percent Cs adsorbed onto kaolinite in the 10^{-1} to 10^{-3} M $NaHCO_3$ solutions of pH 9.5 to 7.9 is a little higher than that in NaCl solutions of pH 7.0$\pm$0.5. However, the percent Cs adsorbed onto kaolinite in $NaHCO_3$ solutions of 10^{-4} to 10^{-5} M (pH 4.9 to 4.6) is a little lower than that in NaCl solutions (pH 7.0). The pH of sodium bicarbonate solution greatly changes with their concentration. The mechanisms of pH change are,

$$NaHCO_3 \rightarrow Na^+ + HCO_3 \qquad (3)$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3$$
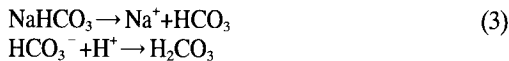
The reactions result in the consumption of hydrogen ion and production of hydroxyl ion in the solution. Thus, the pHs of sodium bicarbonate solutions show between 8.52 and 6.50 in the range of 10^{-1} to 10^{-5} M. When kaolinite reacts with water, the reaction produces hydrogen ions in water:

$$Al_2Si_2O_5(OH)_4 + 7H_2O \rightleftarrows 2Al(OH)_4^- + 2Si(OH)_4 + 2H^+ \ (4)$$
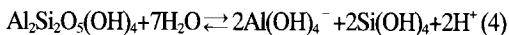
The pH of kaolinite suspensions in distilled water shows about 4.4. However, when kaolinite was immersed into sodium bicarbonate solution, the solution pH changes to the range of 9.5 to 4.6 in the range of 10^{-1} to 10^{-5} M (Table 1 and Fig. 6). The pHs are higher or lower than those of $NaHCO_3$

solutions before reacting with clay particles.

Based on Fig. 4a, however, the pH variation could not be a reasonable answer to explain the dramatic increase of percent Sr adsorbed onto kaolinite in $NaHCO_3$ solution shown in Fig. 6b. Since bicarbonate is major complex-forming anion in groundwater composition. we calculated the speciation of strontium in $NaHCO_3$ solution by using WATEQ4F program. The results are listed in Table 1. Strontium in $NaHCO_3$ solution is present as a free ionic form or complexes such as Sr^{2+}, $SrCO_3$ and $SrHCO_3$. The sodium competing with Sr^{2+} in sorption reaction is present as Na^+, $NaCO_3^-$ and $NaHCO_3^{\circ}$. Their relative distributions in solution are dependent on the pH and concentration of anions.

The species distribution of strontium indicates the possibility of precipitation of a secondary phase ($SrCO_3$) as a mechanism of the removal of Sr from the solution. The saturation index (SI) of a complexed phase such as $SrCO_3$ (strontianite) was also calculated by WATEQ4F program. The saturation index is useful for examining the possibility of a mineral dissolution-precipitation reaction at given thermodynamic equilibrium condition (Freeze, Cherry, 1979).

In the solution of 10^{-1} M $NaHCO_3$, species distribution of strontium show $SrCO_3$, Sr^{2+} and $SrHCO_3$ in the order of dominance. In the $NaHCO_3$ solution below of 10^{-2} M, the dominationg order of strontium species is $Sr^{2+} > SrCO_3 > SrHCO_3$. The saturation index of strontianite ($SrCO_3$) shows positive values in 10^{-1} M sodium bicarbonate solution (Table 2). This means

Table 2. Saturation index(SI) of a secondary phase (strontianite) according to the variation of pH and NaHCO$_3$ concentration.
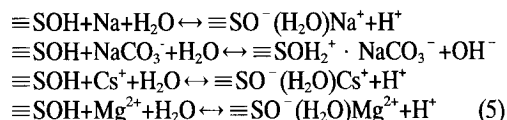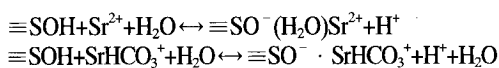
pH	Concentration of NaHCO$_3$	*SI of Strontianite	Log IAP	Log K$_{25°C}$
9.52	10^{-1} M	0.169	-9.162	-9.271
9.45	10^{-2} M	-0.160	-9.430	-9.271
7.9	10^{-3} M	-2.636	-11.906	-9.271
4.9	10^{-4} M	-6.178	-15.449	-9.271
4.6	10^{-5} M	-7.460	-16.731	-9.271

* SI = Log IAP/K$_{25°C}$, IAP; Ion Activity Product, K$_{25°C}$; E-quilibrium Constant at 25°C, Initial concentration of strontium is 10^{-6} M.

that Sr can be precipitated as a secondary phase such as SrCO$_3$ in an alkaline bicarbonate solution. Thus, the precipitation can be a major mechanism for the removal of strontium from the solution phase at 10^{-1} M NaHCO$_3$ solution. In NaHCO$_3$ solution below 10^{-2} M, however, the solution pH exerts more important effect on the removal of Sr than the precipitation. The complexed forms such as NaCO$_3^-$ and NaHCO$_3^\circ$ in 10^{-1} to 10^{-2} M NaHCO$_3$ solution can also contribute to the decrease of competing effect of a background cation (Na).

The effect of sulfate ions on the adsorption behaviour of Sr onto kaolinite is illustrated in Fig. 7. The adsorption behaviour of Sr can not detected clearly between 10^{-1} and 10^{-2} M MgSO$_4$ solution as a background electrolyte. The species distribution of magnesium and strontium in MgSO$_4$ solution was examined to find the reason for such adsorption behaviour. Sulfate is also a major anion in groundwater which can form a complex with strontium. The strontium speciation in a MgSO$_4$ solution shows that strontium is present as Sr^{2+} and SrSO$_4$ (Table 1). The activities of complex forms such as SrSO$_4$ and MgSO$_4$ at 10^{-1} M solution is higher than those of Mg^{2+} and Sr^{2+}. Although the activity of Mg^{2+} competing with Sr^{2+} in sorption reaction decreases from 10^{-1} to 10^{-2} M MgSO$_4$ solution, the activity of Sr^{2+} increases with decreasing sulfate concentration. In other words, the decrease of competition of Mg^{2+} is compensated with the increase of the adsorbed ion, Sr^{2+}. However, the competition effect is distinctly recognized in MgSO$_4$ solution below 10^{-3} M.

The adsorption reactions between Cs and Sr and the hydroxyl functional groups ($\equiv$SOH) of kaolinite in NaHCO$_3$ and MgSO$_4$ solutions are summarized as follows:

$$\equiv SOH + Sr^{2+} + H_2O \leftrightarrow \equiv SO^-(H_2O)Sr^{2+} + H^+$$
$$\equiv SOH + SrHCO_3^+ + H_2O \leftrightarrow \equiv SO^- \cdot SrHCO_3^+ + H^+ + H_2O$$

$$\equiv SOH + Na + H_2O \leftrightarrow \equiv SO^-(H_2O)Na^+ + H^+$$
$$\equiv SOH + NaCO_3^- + H_2O \leftrightarrow \equiv SOH_2^+ \cdot NaCO_3^- + OH^-$$
$$\equiv SOH + Cs^+ + H_2O \leftrightarrow \equiv SO^-(H_2O)Cs^+ + H^+$$
$$\equiv SOH + Mg^{2+} + H_2O \leftrightarrow \equiv SO^-(H_2O)Mg^{2+} + H^+ \qquad (5)$$

Noncomplexed cations such as Cs$^+$ and Sr^{2+} are electrostatically adsorbed due to exchange with ions of the same charge on the surface of the adsorbent. The reaction 5 shows that the weakly adsorbed ions such as Cs and Sr have at least one layer of water separating them from the hydroxyl functional groups of kaolinite. They form ion pairs or outer-sphere complexes and are incorporated in β-plane of triple-layer surface complexation model (Hayes, Leckie, 1987; Hayes, et al., 1987). The strontium can be adsorbed as a complexed form such as SrHCO$_3^+$ onto kaolinite.

CONCLUSIONS

1. The results of three-dimensional Kd modelling suggest that the most important factor affecting adsorption behaviors of ^{137}Cs and ^{90}Sr onto kaolinite in the presence of groundwater cations (Ca^{2+}, Mg^{2+}, K$^+$, Na$^+$) is their hydrated radius, and then their charges and concentrations are important factors in order.

2. Ionic strength of groundwater cations have a strong effect on the adsorption of Cs and Sr onto kaolinite. Whereas solution pH and complex-forming anions (SO$_4^{2-}$, HCO$_3^-$) have a little effect on the Cs adsorption, these exert a strong effect on the adsorption behaviour of Sr onto kaolinite. In most solution conditions, Cs is preferentially adsorbed onto kaolinite in comparison with Sr.

3. The zeta potential measurement supports that the effect of solution pH on the adsorption of Cs and Sr onto kaolinite is mainly due to the amphoteric reactions of kaolinite surface. However, the pH-dependence on the Sr adsorption may be due to other reasons such as surface charge.

4. The mechanisms controlling the sorption behaviour of Sr onto kaolinite in the presence of sodium bicarbonate are the change of solution pH. the precipitation of a strontianite (SrCO$_3$), and the complexation of a background cation (Na). The complexation effect of sulfate ion on the Sr adsorption is recognized in MgSO$_4$ solution of 10^{-1} to 10^{-2} M.

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카올리나이트에 의한 세슘-137 및 스트론튬-90 흡착에 대한 이온강도, pH, 복합체-형성 음이온의 영향

정찬호 · 조영환 · 한필수

요   약 : 카올리나이트에 의한 세슘-137 및 스트론튬-90 흡착에 대한 지하수의 주요 양이온 (Ca^{2+}, Mg^{2+}, K^+, Na^+) 및 음이온 (SO_4^{2-}, HCO_3^-)의 영향 그리고 pH 의 영향을 뱃치실험을 통하여 알아보았다. 세슘 및 스트론튬 흡착에 대한 지하수 양이온들의 농도, 전하, 이온반경사이의 상대적인 영향을 알아보기 위하여 통계적 방법으로 디자인된 3차원적인 Kd 모델링 방법이 시도되었다. 모델링결과 흡착에 미치는 정도는 양이온의 수화반경이 가장 큰 영향을 미치며, 그다음 이온들의 전하, 농도의 순서임이 밝혀졌다. pH변화에 따른 카올리나이트의 제타전위를 측정하고 amphoteric 반응측면에서 Cs, Sr 흡착 특성을 설명하였다. 카올리나이트의 Cs 및 Sr 흡착에 대한 경쟁양이온들의 이온강도가 pH 보다는 더 큰 영향을 미친다. 탄산수소이온의 농도는 스트론튬의 흡착거동에 상당한 영향을 미친다. 이는 탄산수소이온 (HCO_3^-)의 농도변화에 다른 pH 의 변화에 기인하는 것 뿐만아니라, WATWQ4F 프로그램을 이용한 열역학적 계산에 의하면 Strontianite ($SrCO_3$)의 침전에 의한 것으로 해석된다.