

^{137}Cs and ^{90}Sr Sorption of Kaolinite

캐올리나이트의 ^{137}Cs 및 ^{90}Sr 흡착특성

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ABSTRACT : ^{137}Cs and ^{90}Sr are representative radionuclides of interest in the disposal of low- and intermediate-level radioactive wastes. The present study is designed to determine the effect of ionic strength and pH on Cs and Sr sorption onto kaolinite. The NaCl, CaCl₂, MgSO₄, and KCl solution with concentration of 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} mole/l were prepared for the batch type sorption experiment. The pH of mineral-solution equilibrium was adjusted into 4.5, 7.0 and 10.5. The Cs and Sr sorption of kaolinite depends on ionic strength and pH. The competing order of cations on Cs sorption is as follows: $\text{K}^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{Na}^+$. The Sr sorption is competed by the order: $\text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. The results are closely related with the hydration energy of ions, and can be explained by water structure modification properties of ions and mineral particles. The sorption amount of Cs onto kaolinite is higher than that of Sr at pH 4.5 and 7.0. However, their sorption amounts are reversed at pH 10.5. Namely, the sorption preference between Cs and Sr depends on the pH of solution. In all solution Cs and Sr sorption amount onto kaolinite increases with increasing pH. This corresponds to pH dependence of the zeta potential of kaolinite particles in solution.

요약 : 중·저준위 방사성 폐기물의 대표적인 핵종인 ^{137}Cs , ^{90}Sr 에 대한 캐올리나이트의 흡착특성을 수용액의 이온강도와 pH의 영향하에서 알아보았다. 흡착실험은 회분식으로 하였고, 사용한 수용액은 NaCl, CaCl₂, MgSO₄, KCl 각각을 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} mole/l로 하였다. 수용액-광물 평형상태의 pH를 4.5, 7.0, 10.5로 조절하였다. 실험결과 캐올리나이트의 Cs, Sr 흡착은 이온강도와 pH에 상당한 영향을 받으며, Sr 흡착에 양이온들의 경쟁은 $\text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ 순을 보이고, Cs의 경우에는 $\text{K}^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{Na}^+$ 의 순을 보인다. 이는 수용액상에서 이온들의 수화에너지와 관련되며, 광물입자와 이온들의 물구조변환특성에 의해 설명된다. Cs과 Sr 사이에 흡착우선성은 산성 내지 약알카리에서는 Cs이 Sr보다 흡착이 잘 되나, 강알카리성 환경에서는 Sr이 Cs보다 흡착이 잘 되는 pH 의존성을 보였다. 수용액의 pH가 증가함에 따라 핵종의 흡착량이 증가하는데, 이는 캐올리나이트의 흡착자리인 실라놀과 알루미늄에 의한 제타전위가 pH에 의존함과 잘 일치한다.

INTRODUCTION

In the concept for disposal of radioactive

wastes, storage in a geological repository is visualized. Waste forms could be subjected to groundwater attack, and radionuclides could be released

into geologic barrier and adsorbed onto mineral surfaces (Mouline et al, 1992). The sorption study is needed to estimate of the nuclide transport in the event of water penetration into and through the repository. Accurate and reliable knowledge of the distribution coefficients of the nuclides between the solutions and minerals is therefore needed, and effects of pH, solution composition, temperature, speciation must be studied (Rafferty et al, 1981).

^{137}Cs and ^{90}Sr are representative radionuclides of interest in the disposal of low- and intermediate-level radioactive wastes. ^{137}Cs decays to metastable $^{137\text{m}}\text{Ba}$ by beta emission with half life of 30.0 year, and then is stabilized to ^{137}Ba in 2.54 minute by isomer transition which emits gamma ray. ^{90}Sr has half life of 27.7 year. It decays by beta emission to metastable $^{90\text{Y}}$, and then is stabilized to ^{90}Zr by beta emission in 64 hours. This decay are called as radioactive equilibrium.

This study was focused on the kaolinite which is frequently found as a fracture-filling clay mineral of the crystalline rocks. The surface hydroxyl groups of kaolinite are aluminol groups, silanol groups, and Lewis acid site (Sposito, 1984), all associated with ruptured bonds along the edges of layer sheets (Davis and Kent, 1989). Three surface functional groups play a role as sorption sites of kaolinite.

The influence of different parameters such as pH and ionic strength has investigated in order to elucidate Cs and Sr sorption behaviour by kaolinite. Emphasis has been on the water structure modification properties of ions and mineral particles affecting Cs and Sr sorption behaviour.

EXPERIMENTAL

Material

Sorption experiments were conducted with commercial pure kaolinite (Georgia China clays) supplied by Ward's company. The specific sur-

Table 1. Characteristics of kaolinite.

Average particle size(μm)	5.92
Cation exchange capacity(meq/100g)	11.5
Specific surface area(m^2/g)	7.99

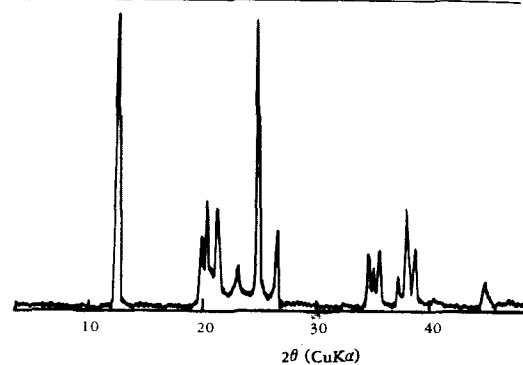


Fig. 1. The x-ray diffraction pattern of kaolinite.

face area of kaolinite is obtained by BET (Brunauer, Emmette and Teller) method. The cation exchange capacity(CEC) was measured by the sodium acetate method. The particle size of powder sample was measured by MALVERN master sizer. The specific surface area, the particle sizes and the cation exchange capacity of kaolinite are given in Table 1. The X-ray diffraction pattern of kaolinite is shown in Fig 1.

Solution

The NaCl, CaCl₂, MgSO₄ and KCl solutions with concentration of 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} mole/l were prepared for the batch experiment. All solutions were prepared into two sets for inactive CsCl and SrCl₂ of 10^{-6} mole/l. All chemicals used were reagent grade. The speciations of Cs and Sr in all solution were calculated by WATEQ4F program (Ball and Nordstrom, 1991).

Radiotracer

Every solution was spiked with ^{137}Cs and ^{90}Sr as radiotracers. The activities of nuclides are about 0.01 $\mu\text{Ci/ml}$.

Batch Sorption

All sorption experiments were conducted in batch at room temperature. 0.33 gram of powder sample was placed in the individual polypropylene vials used as reaction vessels. Each samples were contacted for two weeks with spiked 10 ml solution. This sorption equilibration period was considered to be sufficient. The vials were routinely shaken to ensure maximal exposure of the mineral surface to the solution. After two weeks, the aqueous phase was separated from the solid by gravity settling and centrifugation. Packard ScINT-A XF as scintillator for cocktail solution was used. The scintillation cocktail was added to an aliquot of the supernatant in the ratio of 10:1. Initial and equilibrium ¹³⁷Cs and ⁹⁰Sr activities were counted with liquid scintillation analyzer (Packard model Tri-carb 2550TR). The sorption coefficient (Kd) was calculated as follows:

$$Kd(\text{mg}/\ell) = (V/Wt)[(C_0 - C_f)/C_f]$$

V : volume of solution (ml)

Wt : weight of solid (g)

C₀ : initial nuclide concentration (cpm)

C_f : nuclide concentration after the contact period (cpm)

The blank test was carried out to ensure that nuclides was not being sorbed by the polypropylene vials. The final pH of mineral-solution equilibrium was adjusted to 4.5, 7.0 and 10.5 by the acid-base titration.

Zeta Potential Measurement

The zeta potential of hydrous kaolinite particles was measured by determining the rate at which the solid particles move in a known electrical field. Laser Zee Model 510 Zeta Meter was used for zeta potential measurement. 0.5 g powder sample was added into two separate 500 ml of 0.01 and 0.001 M NaCl solutions, with continuous bubbling of N₂ gas to remove dissolved CO₂ (one for acid addition, the other for base). While the

suspension was being stirred, the initial pH was measured. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH to cover the range from 3 to 10 in about 0.5 pH unit increments.

RESULTS AND DISCUSSION

The Sr and Cs sorption behaviours (expressed in log Kd) onto kaolinite as a function of ionic strength of cations and pH are shown in Fig 2. The amount of Cs and Sr sorption onto kaolinite increases with decreasing the ionic strength. The change of pH exerts significant effect on Cs and Sr sorption by kaolinite.

The competition sequence of cations onto cesium sorption is as follows: K⁺ > Ca²⁺ ≈ Mg²⁺ > Na⁺ (Fig 3). The cations are competed with strontium by the order: Ca²⁺ ≈ Mg²⁺ > K⁺ > Na⁺ (Fig 4). The sequences can be explained qualitatively by assuming that the binding force is derived from the coulombic interaction between the ion and surface and that the adsorbed ions retain their primary hydration sheath.

The ion with the smallest hydrated radius will be able to approach the surface of minerals most closely and will therefore be held most strongly. The larger cations, such as Cs⁺ and K⁺, are more polarizable and more readily allow distortions to their hydration spheres than smaller, strongly hydrated cations (Kinniburgh and Jackson, 1981). Their relatively weak electrostatic fields cannot reach much beyond the primary hydration layer. These ions are termed water structure breakers. The structuring properties of ions are directly related to their heat of hydration. The structure promoting ions are therefore comparatively small and have high heats of hydration. The hydration energy is inversely proportional to the radius (Nightingale, 1959).

Solids in solution are also charged and can be viewed as affecting water structure in similar ways as ions. Namely, the surface with the higher heats of hydration are structure-making

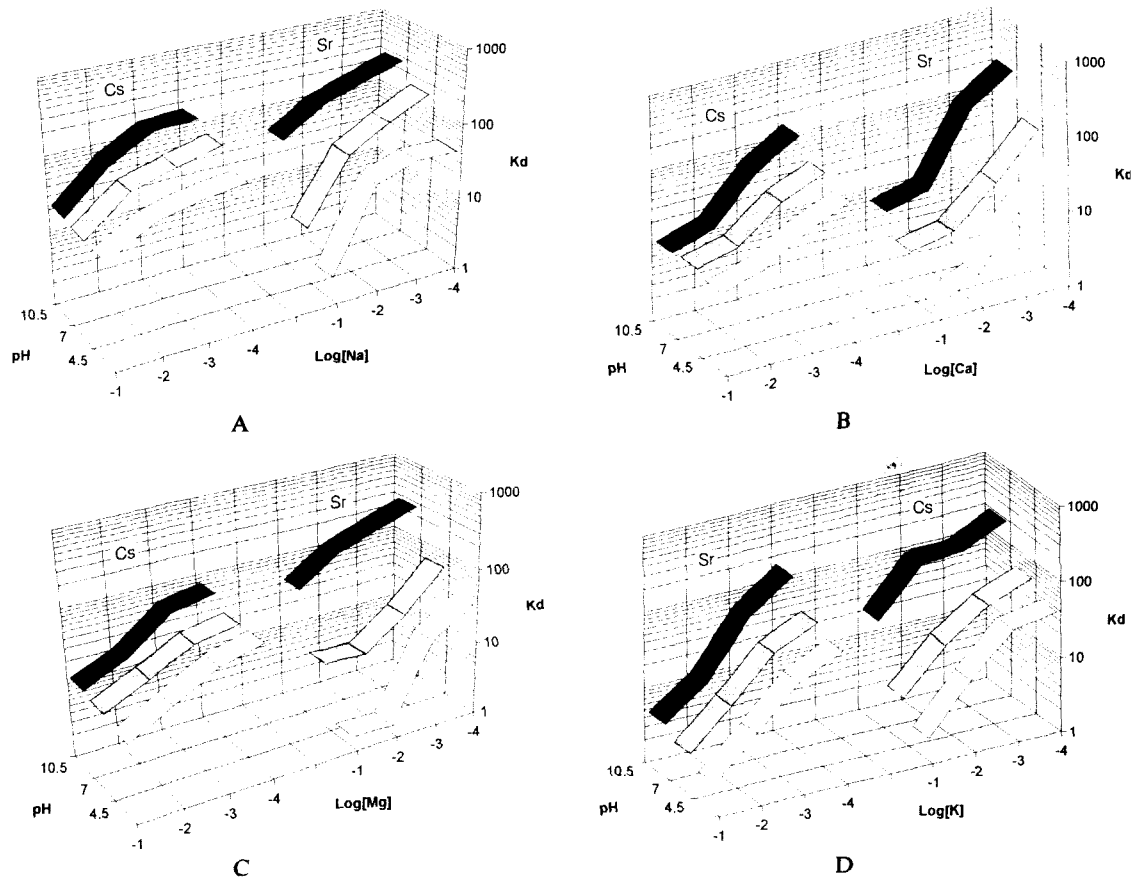


Fig. 2. Cs and Sr sorption coefficient of kaolinite as the function of pH and ionic strength of NaCl, CaCl₂, MgSO₄, and KCl solutions.

solids; the others structure-breaking (Stumm, et al, 1970). Gierst et al (1966) suggested that ion-solid interface will adsorb an ion strongly when the ion and the surface have similar effect on modifying the water structure.

The Sr sorption is preferentially competed by divalent ions such as Ca²⁺ and Mg²⁺, and then competed by small hydrated radius ion K⁺ and large hydrated radius ion Na⁺ in decreasing order. The Cs sorption is strongly influenced by monovalent ion, K⁺, which is the water structure breaker, and then is hindered by divalent ions, Ca²⁺ and Mg²⁺. It is weakly influenced by monovalent ion such as Na⁺.

The sorption amount of Cs onto kaolinite is

higher than that of Sr at pH 4.5 and 7.0. However, their sorption behaviour is reversed at pH 10.5 (Fig 2). Namely, the sorption preference between Cs and Sr depends on pH of solution. The pH can exert an influence on two factors: ion speciation and surface charge of kaolinite. The species of Cs and Sr in water is present almost entirely as simple ionic form, Cs⁺ and Sr²⁺, in the range of pH 4.5 to 10.5. The zeta potential of kaolinite decrease toward alkaline condition, that means the increment of negative charge of kaolinite (Fig 5). Therefore, the pH dependant sorption characteristics of Cs and Sr should include the following factors: (1) the effect of surface charge of kaolinite, (2) the effect of the hydrated radius of ions

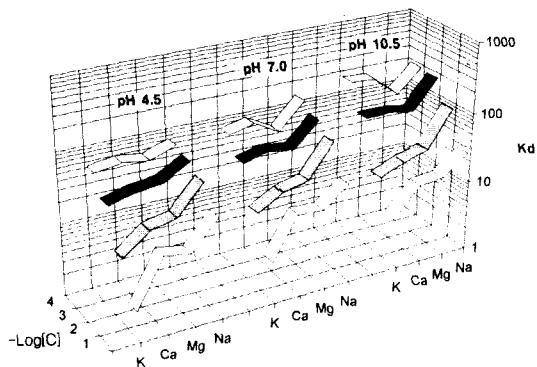


Fig. 3. Three dimensional diagram showing the cations competition on Cs sorption.

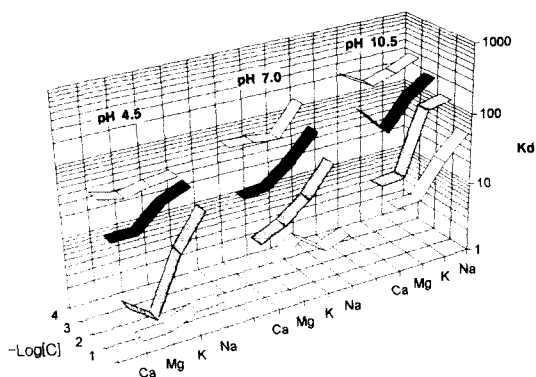


Fig. 4. Three dimensional diagram showing the cations competition on Sr sorption.

and kaolinite particles, (3) the effect of ion charge.

Fig 5 shows the zeta potential of kaolinite as a function of pH in the NaCl solution. The surface of kaolinite is negatively charged in the region of the pH 3 to 10. The zeta potential of kaolinite depends on the pH of solution, and decreased toward alkaline condition. The silanols in alkaline solution is negatively charged by the process as follows: $\text{SiOH} + \text{OH}^- \rightarrow \text{SiO}^- + \text{H}_2\text{O}$. Although the pH at zero point of charge (pH_{zpc}) of kaolinite is not observed in Fig 5, it can be extrapolated that pH_{zpc} of kaolinite is below 2. Solid particles of low pH_{zpc} is known to behave as water structure breaker in the aqueous solution. Kaolinite is considered as water structure breaker. Therefore,

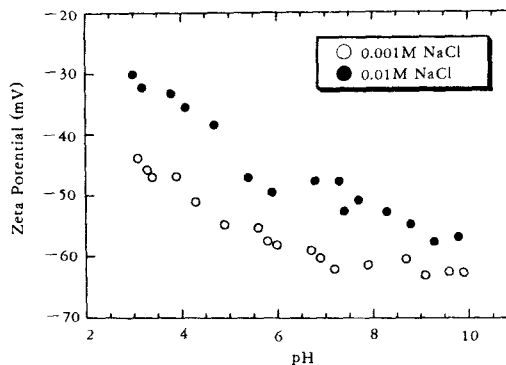


Fig. 5. The zeta potential of kaolinite as the function of pH in NaCl solution.

kaolinite surface can adsorb Cs ion strongly by the similar effect on modifying the water structure.

CONCLUSIONS

This study demonstrated that Cs and Sr sorption behaviour of kaolinite depends on ionic strength and pH of solution. The competition sequences of cations on the cesium sorption is as follows: $\text{K}^+ > \text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{Na}^+$. The strontium and cations are competed by the order: $\text{Ca}^{2+} \approx \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. The results are closely related with the hydration energy of ions, and can be explained by water structure modification properties of ions and mineral particles. The sorption amount of Cs onto kaolinite is higher than that of Sr at pH 4.5 and 7.0. However, their sorption amounts are reversed at pH 10.5. The Cs and Sr sorption coefficient onto kaolinite shows the increasing trend with pH increment of solution. This corresponds to pH dependence of the zeta potential of kaolinite particles in solution.

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