

Differentiation of Sorptive Bindings of Some Radionuclides with Sequential Chemical Extractions in Sandstones

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순차적화학추출법을 사용한 방사성핵종의 사암에 대한 수착유형 평가

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Abstract

Sorption experiments of ^{60}Co , ^{85}Sr , and ^{137}Cs onto sandstone particles in a batch were carried out to investigate the migration mobility. Sorption kinetics and reversibility as well as sorption mechanisms were examined. Sorption reaction occurred mostly within 10 hours on the outer surface of the sandstone particle but diffusion into the inner surface of the mineral has still occurred after that time. In order to distinguish sorption types of radionuclides, a sequential chemical extraction was introduced. The sorbed radionuclides were then extracted by applying different solutions of synthetic groundwater, CaCl_2 , KCl and KOH-HA . Especially KCl is adopted to extract the ion-exchanged cesium. Sorption types considered are reversible sorption under groundwater condition, ion exchange, association with ferro-manganese oxides or oxyhydroxides, and irreversible fixation. Strontium sorbs onto the sandstone surface mainly by fast and reversible ion exchange reaction. However, cobalt and cesium do not sorb by simple process. The main sorptive binding of cobalt was the association with ferro-manganese oxides and the secondary one was irreversible fixation. Diffusion into the lattice of minerals controlled the sorption rate of cobalt. The main sorption type of cesium was irreversible fixation, while ion exchange reaction was the secondary importance. Hence the order of migration mobility for the three radionuclides was $\text{Sr}^{2+} > \text{Co}^{2+} > \text{Cs}^+$ in the sandstones.

요 약

방사성 코발트, 스트론튬, 세슘의 사암에 대한 수착특성평가 실험을 수행하였다. 수착반응속도론적 평가와 더불어 수착유형 및 가역성 등을 파악하였다. 수착반응은 크게 두 단계로 나눌 수 있는데, 초기 10시간 이내에 사암외부표면에 대부분의 수착이 일어나고, 이후에는 사암입자내 미세공극을 통한 내부 수착

표면으로의 확산이 수착속도 결정단계로 작용하는 과정이다. 방사성핵종이 지하매질에 수착하는 주된 수착유형을 정량적으로 평가하기 위한 방법으로서 순차적화학추출법을 도입하여 방사성핵종이 수착되어 있는 사암에 대해 탈착 실험을 수행하였다. 특히 이온교환되어 있는 세습을 탈착시키기 위해 염화칼륨 용액으로 추출하는 공정을 도입하였다. 본 연구에서 고려한 수착유형은 지하수조건에서 가역적 수착, 이온 교환, 철망간산화/산수소화물과의 결합, 비가역적 고착등이다. 스트론튬은 사암표면에 상대적으로 반응이 빠르고 가역적인 이온교환반응을 하였다. 코발트와 세습은 복합적인 수착반응 양상을 보였다. 코발트의 경우, 주된 수착유형은 철망간산화/산수소화물과의 결합이고, 비가역적인 고착도 상당비율 일어났다. 세습의 경우, 비가역적 고착이 주된 수착유형이었으며, 이온교환도 상당비율 일어났다. 그러므로, 수착반응의 가역성 및 이동성은 스트론튬 > 코발트 > 세습 순이었다.

1. Introduction

When radioactive wastes are disposed of in geological media, radionuclides can be transported by the interaction with groundwater in the long run. To predict the migration of radionuclides through geologic media, sorption types and migration mobility are of importance. Migration mobility can be determined by the reversibility of the sorption. For example, ion exchange reaction occurs rapidly and reversibly for some radionuclides as the dominant sorption type, while mineralization (or fixation) occurs slowly and irreversibly for other group of radionuclides. The common practice in the interpretation of radionuclide sorption/migration behavior under hydro-geologic atmosphere is to assume that the main interaction between radionuclides and geologic minerals is ion exchange reaction.⁽¹⁾ Thus predicting migration behavior of some radionuclides could be misled when sorption occurs irreversibly or does not occur by the assumed simple ion exchange reaction. It is therefore of importance to examine not only the correlation between sorption rate and types but also migration mobility.

The first step to be taken in the appropriate interpretation of sorption kinetics is the investigation of the rate controlling step. Skagius et al.⁽²⁾ performed sorption experiments to characterize the diffusion and sorption properties of cesium and strontium in crushed granite particles. They assumed that the diffusion process through the internal pore of the rock

particles was the rate controlling step and determined the effective diffusivity.

Anderson et al.⁽³⁾ proposed two processes in explaining sorption of metal ions onto manganese oxides. Firstly, metallic cation might penetrate the electrical double layer and reach the oxide surface to substitute the exchangeable hydrogen. Secondly, metallic cation might substitute structural manganese or other cations occupying the structural lattice. Rundberg⁽⁴⁾ also studied kinetics of the sorption of ¹³⁷Cs, ⁸⁵Sr, and ¹³³Ba on tuff and explained that diffusion occurs in two stages. First the cations diffuse into rock through the water-filled pore space. Next, the cations may diffuse into the much narrower channels within the aluminosilicate crystals. After the species reach the mineral framework or between the mineral planes, the species may sorb on the empty sites. Sato et al.⁽⁵⁾ studied the penetration behavior of uranium on a tuff wafer. They explained that penetration of uranium was not a fully reversible process but a competitive process involved in both diffusion and adsorption. Walton et al.⁽⁶⁾ investigated sorption mechanisms and rates of radionuclides on a granitic rock. They also performed selective chemical extraction experiments to differentiate the sorption mechanisms of Co^{2+} , Sr^{2+} , Cs^+ and Ce^{3+} . Assuming that sorption reaction process was the rate controlling step, they observed that double sorption site models gave satisfactory explanation for the sorption data.

Park et al.⁽⁷⁾ investigated sorption and desorption

behavior of radionuclides on tuff. Sorption ratios for Co^{2+} and Cs^+ are significantly higher when measured in desorption experiment than those from the sorption experiment; ion-exchange alone cannot explain the sorption of those elements. They argued that the discrepancy between the two results is due to both the irreversibility of the sorption process and extra process involved in other than ion exchange reaction.

In order to investigate sorption types and reversibility of radionuclides on soils and rocks, sequential chemical extraction techniques have been developed.^(7, 8, 9) The sorbed radionuclides can be extracted from the soil and rock by using appropriate reagents. Tessier et al.⁽⁹⁾ developed a sequential chemical extraction method for the partitioning of particulate trace metals into five fractions; exchangeable in groundwater condition, bound to carbonate, bound to iron-manganese oxides, bound to organic matter, and residual. Going into more details, early studies performed on geologic media have demonstrated that the sorption of species is dependent on groundwater condition; alteration of ionic composition in water is likely to affect sorption-desorption processes.^(3, 10, 11) In other words, sorption process is exchangeable or reversible. Some workers have shown that trace metal can be associated with sedimented carbonates and organic substances, which are known to have high sorption capacity.⁽¹²⁾ Manganese existing as various oxides and hydrous oxides in soils and rocks is associated with iron oxides. Generally the degree of sorption affinity of cations follows the order: manganese oxides > organics > ferro oxides > clay minerals. The reason is that manganese oxides have unusually a high negative surface charge and a high cation exchange capacity (CEC). For example, the CEC of manganese oxide at pH=8.3 is 1.5 eq./100g while that of montmorillonite is about 0.1/100g.⁽¹³⁾ Chao⁽⁸⁾ studied sorption mechanisms of radionuclides in soils and sediments. He found that cobalt sorbed preferentially on manganese oxides

and readily dissolved in a hydroxylamine hydrochloride solution. Therefore, when all possible fractions of sorbed species (exchangeable, bound to carbonate, organic matter, and iron-manganese oxides) have been removed from the sorption media, the media may still hold species within the crystal structure. The remaining sorbed species are not expected to be released in solution under the natural conditions. The residual portion can be regarded as a mineralized or fixed.

In the present study, the sorptive binding of ^{60}Co , ^{88}Sr , and ^{137}Cs in sandstones is investigated. A modified sequential chemical extraction was introduced to identify the main sorption type and its reversibility. Extraction by KCl was performed for removal of ion-exchanged species, especially for cesium. The sorption characteristics of potassium is expected to be similar to cesium because potassium has similar ionic size and charge with cesium. Potassium may thus substitute the sorbed cesium ion more intensively than other ion-exchangers in the crystal of the mineral.^(3, 14)

2. Experimental

2.1. Sample Preparation

Two kinds of sandstones, sandstone-A and sandstone-B, were collected. Sandstone-A was sampled near subsurface and sandstone-B from tens of meters under ground. Porosities of the sandstone-A and -B were turned out to be 0.28 and 0.43, respectively, indicating that the sandstones are very porous. Chemical compositions of the sandstones are analyzed on the basis of standard analyzing method and shown in Table 1. Iron and manganese exist as oxides or oxyhydroxides as indicated in Table 1. Mineral compositions of the samples are analyzed with a XRD and a microscope and shown in Table 2. With the information from Table 2 regarding the content of smectite, the sandstone samples are regarded as

somewhat weathered. The content of humic acid is less than 1 mg of carbon per 100g of sandstone. A synthetic groundwater (SGW) was used to simulate the chemical compositions of the natural groundwater where the sandstones were sampled. The composition of SGW is shown in Table 3 and pH of the SGW was 6.6. Sandstone samples were crushed and sieved with particle size of ϕ 1–1.5mm and ϕ 2–3mm for sandstone-A and -B, respectively. Specific surface area determined by BET method is shown in Table 4.

Table 1. Chemical Compositions of Sandstone Samples

| Component | SiO ₂ | Al ₂ O ₃ | TiO ₂ | Fe ₂ O ₃ | CaO | MgO | FeO | Na ₂ O | K ₂ O | MnO |
|-------------|------------------|--------------------------------|------------------|--------------------------------|------|-----|-----|-------------------|------------------|------|
| Sandstone-A | 39.2 | 13.29 | 0.5 | 11.9 | 13.5 | 5.0 | 1.3 | 1.7 | 0.6 | 0.08 |
| Sandstone-B | 38.5 | 14.6 | 0.8 | 18.7 | 9.7 | 2.2 | 2.9 | 2.2 | 0.9 | 0.08 |

Table 2. Mineral Composition of Sandstone Samples

| Portion | Sandstone-A | Sandstone-B |
|-----------|----------------------|---|
| primary | plagioclase, calcite | plagioclase |
| secondary | smectite(22.8%) | clinopyroxene |
| tertiary | quartz, stilbite | quartz, calcite, orthopyroxene, smectite(15.7%) |
| trace | K-feldspar, chlorite | amphibopar |

Table 3. Composition of the Synthetic Groundwater

| Component | K ⁺ | Na ⁺ | Mg ⁺² | Ca ⁺² | Cl ⁻ | HCO ₃ ⁻ | SO ₄ ⁻² |
|-----------|----------------|-----------------|------------------|------------------|-----------------|-------------------------------|-------------------------------|
| mg/l | 0.84 | 8.6 | 1.9 | 20 | 15.2 | 6.2 | 6.2 |

2.2. Sorption Experiment

Sandstones had been contacted with SGW for more than two weeks to get pre-equilibrium between two phases before sorption experiment in a closed system. 10g of each sandstone and 200ml of SGW were prepared in a glass flask with a cap. Radioactive tracers were added in the flask at a certain time. The radioactivities for ⁶⁰Co, ⁸⁵Sr, and ¹³⁷Cs are about 0.01

Table 4. Sorption Ratios and Percentages onto the Sandstones in Sorption and Desorption steps

| | Surface Area (m ² /g) | Sorption Ratio and Percentage | | | |
|-------------|-------------------------------------|-------------------------------|------------------|------------------|-------------------|
| | | | ⁸⁵ Sr | ⁶⁰ Co | ¹³⁷ Cs |
| Sandstone-A | 32.5 | R | 393 | 4208 | 5222 |
| | | R% | 95.2 | 99.5 | 99.6 |
| | | R _d | 567 | 4605 | 11930 |
| | | R _d % | 3.4 | 0.6 | 0.2 |
| Sandstone-B | 41 | R | 1983 | 369 | 4627 |
| | | R% | 99.0 | 94.9 | 99.6 |
| | | R _d | 1763 | 6201 | 13139 |
| | | R _d % | 1.1 | 0.5 | 0.2 |

* R (ml/g): sorption ratio based on unit weight of sorbent at 400 hour

* R_d (ml/g): sorption ratio in desorption step with SGW

* R% = 100(qW-C/V): percentage of the sorbed to the total amount of the tracer

* R% = 100(CV/qW): percentage of the desorbed to the total amount of the sorbed

μCi/ml the SGW solution. The flask was shaken in a water bath for two weeks at 25°C. 5ml of the contacted solution was sampled at an appropriate time interval and centrifuged for 10 minutes at 3000 rpm. The radioactivity of 1ml of supernatant solution was measured with HPGe detector, and the remaining part was poured back into the flask.

2.3. Sequential Desorption Experiment

Desorption experiments for radionuclide-sorbed sandstone sample were then followed by to identify favorable sorption types and their reversibility.^(7,9)

The followings are the experimental sequences conducted:

1) The radionuclide-sorbed sandstone was kept in contact with tracer free SGW for 1week to measure the amount of reversibly sorbed radionuclide. 5ml of the solution was sampled at the predetermined time intervals and its radioactivity was measured. The sampled solutions were returned to the flask. After one week, all solid samples were recovered for sec-

ond step experiment.

2) The recovered radionuclide-sorbed sandstone was mixed with 200ml of 0.5mol/l CaCl_2 solution free of the radioactive tracers. The purpose of this process is to quantify the amount of ion-exchanged radionuclide.

3) The radionuclide-sorbed sandstone was separated from the CaCl_2 solution and further contacted with 200ml of 0.5mol/l KCl solution to determine the amount of remaining ion-exchanged radionuclide.

4) The similar procedure was repeated with a mixture solution containing 0.1mol/l potassium tetraoxalate and 0.1mol/l hydroxylamine hydrochloride (KOH-HA) to estimate the amount of radionuclides associated with ferro-manganese oxides or oxyhydroxides.

5) The remaining radioactivity in the sandstone sample was then counted to determine the amount of fixed radionuclide.

3. Results and Discussion

3.1. Sorption Rate and Sorption Capacity

Sorption ratio or sorption coefficient, R , is defined to describe the uptake of the radionuclide as

$$R = \frac{q}{C} = \frac{\text{amount of radionuclides sorbed per unit weight of the sandstone}}{\text{concentration of radionuclides in solution}}$$

$$= \left[\frac{\mu\text{Ci/g}}{\mu\text{Ci/ml}} \right] = \left[\frac{\text{ml}}{\text{g}} \right]$$

When the sorption system gets to an equilibrium state, sorption ratio, R , becomes equilibrium distribution coefficient, K_d .

The results of the sorption experiments for the cases of ^{60}Co , ^{89}Sr , and ^{137}Cs are shown in Figures 1 and 2. As anticipated from the ion exchange reaction kinetics, the rate of sorption was rapid during the initial stage and slowed down as the equilibrium was approached. However sorption still occurs very slowly even after the quasi-equilibrium state. This delayed

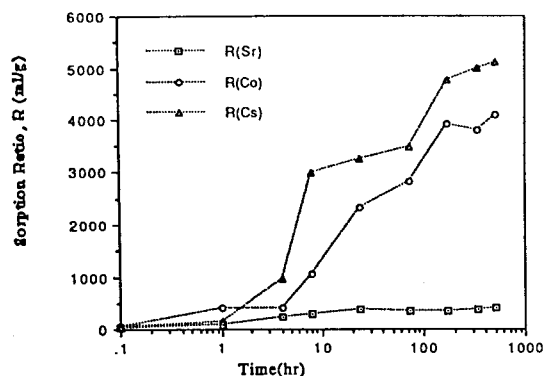


Fig. 1. Sorption Ratio with Time for Sandstone-A

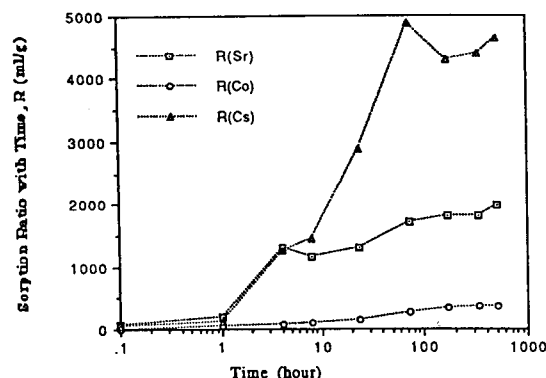


Fig. 2. Sorption Ratio with Time for Sandstone-B

sorption effect seems to be attributed to the continued sorption by the diffusion into the intracrystalline of the minerals or by extended weathering of the sandstone. Therefore, it is difficult to determine when the sorption system is completely reached to a real equilibrium state. For this reason, sorption ratio, R , is used to describe sorption capacity in this experiment instead of the equilibrium distribution coefficient, K_d .

Figures 1 and 2 as well as Table 5 provide infor-

mation regarding the sorption site and rate of the sorption process. It is shown that sandstone-B has a higher sorption affinity for strontium, while sandstone-A has a lower affinity. The difference in the sorption capacities is seemed mainly due to the surface area since strontium is known to sorb on the surface of the rock. Another possible explanation is that the difference in mineral composition between two sandstones makes the difference of the affinity for sorbate. Tickner et al.⁽¹⁵⁾ reported that pyroxene shows a high degree of sorption for strontium while calcite shows little affinity. Since sandstone-A contains much calcite and less pyroxene than sandstone-B as shown in Table 2, sandstone-A has a higher R value of strontium than sandstone-B.

Reaching times to 0.5 R and 0.9 R for strontium are shorter than for cobalt and cesium in both sandstones as shown in Table 5. Hence it is obvious that sorption rate of strontium is faster than those of cobalt and cesium. The reason for faster sorption rate of strontium than those of cobalt and cesium may be explained by a surface complexation model. In the triple layer model⁽¹⁶⁾ which is one of the surface complexation models, the space around the solid surface is arbitrarily broken into three layers, separated by the O, β , &, δ planes as shown in Figure 3. The O plane represents the interface between the solid surface and solution. Transition metal ions such as Pb^{2+} , Cu^{2+} , Co^{2+} can be strongly sorbed in the O plane. Sorption of these cations by hydrous oxides is little or weakly dependent upon ionic strength of the solution. Weakly sorbing cations such as Ca^{2+} , Mg^{2+} , Sr^{2+} , do not generally form covalent bonds, and sorption of these ions has been shown to be influenced by electrostatic forces, via its dependence on ionic strength. Those weakly sorbing ions are allowed in the β layer. Because the binding force in the β layer is weaker than the force in the O layer, binding of strontium is easier and weaker than binding of cobalt. This is one of the reason why strontium sorbs rapidly and reversibly than cobalt and cesium. The third layer is the diffuse zone, where

ions are not strongly influenced by electrostatic forces emanating from the solid surface.

For the sorption of cesium, it is not easy to thoroughly explain sorption phenomena only with the surface complexation model. Sorption of cesium is influenced not only by the surface reaction and electrostatic interaction but also by the steric hinderance of cesium movement within the sorbent matrix. According to Sawhney⁽¹⁷⁾, minerals are selectively sorbing ions with low hydration energy due to interlayer collapse. These ions such as Cs^+ , K^+ , Rb^+ , or NH_4^+ are fixed in interlayer position, i.e, a reduction of the lattice spacing to about 10\AA , causing a physical entrapment. It will be discussed more precisely in the following section.

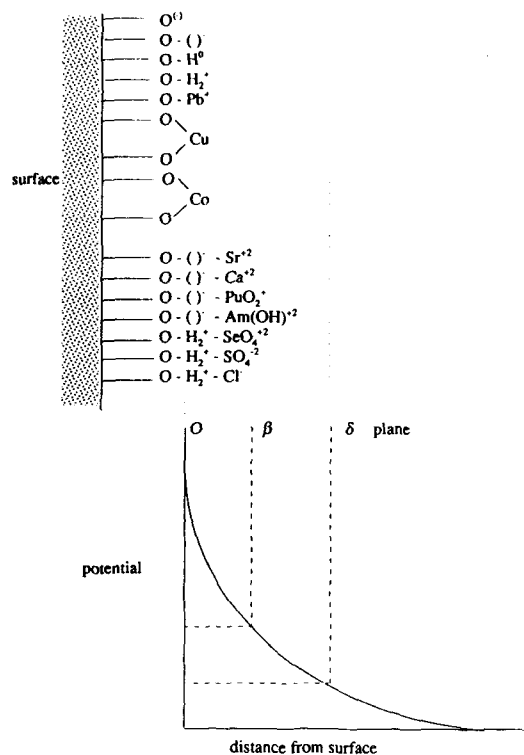


Fig. 3. Schematic Representation of Triple Layer Sorption Model

3.2. Desorption with Synthetic Groundwater

Comparing the desorbed amount with the sorbed

amount at the sorption step in the SGW in one of the purpose in this step. Table 4 shows the experimental result that radionuclide-sorbed sandstone contacted with tracer-free SGW. Desorption by SGW gave no significant extraction of sorbed radionuclides. Radionuclide desorbed by SGW was almost negligible even after several days as shown in Figures 4 and 5. A few percents of strontium was desorbed, while cobalt and cesium was desorbed less than 1%. The value of R_d , sorption ratio in desorption step by SGW, was close to R defined in the sorption step for strontium. That is, the sorption ratio maintained its value even though the solution concentration changed in the equation of $R = q/C$. In other words, strontium kept sorption relationship and sorbed reversibly in SGW condition. For cesium, R_d was larger than R . It implies that cesium is hardly desorbed or has irreversible tendency on sorption. However, in the case of cobalt, experimental results did not show simple phenomena. R_d in sandstone-A has same order of magnitude as R , which means sorption is occurred reversibly. While R_d in sandstone-B was about 20 times larger than R , which means sorption is occurred irreversibly. It may be due to the difficulty of the radionuclides in diffusing out from the lattice of the minerals. Judging from the fact that the particle size of sandstone-B is larger than that of sandstone-A as mentioned in the sample preparation section, sorption of cobalt onto sandstone-A occurs reversibly owing to shorter diffusion path than that of the sandstone-B, larger particle. These results give some suggestions on the binding between radionuclides and the sandstone; Sorption of strontium occurs reversibly on the rock surface, while sorption of cobalt is influenced by the diffusion process to the inner surface of the sandstone particle.

3.3. Desorption with Sequential Chemical Extraction

The results from sequential chemical extraction experiments may explain clearly the suggestions from

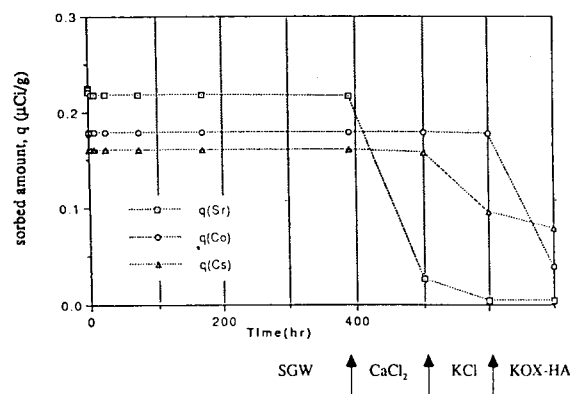


Fig. 4. Remaining Sorbed Amount for Different Desorption Step Applied for Sandstone-A

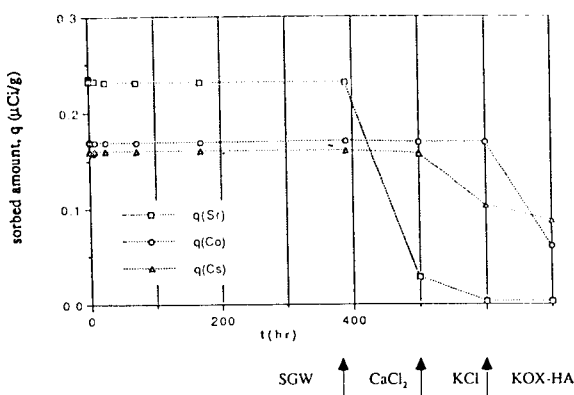


Fig. 5. Remaining Sorbed Amount for Different Desorption Step Applied for Sandstone-B

kinetic data of sorption. The remaining sorbed amounts of the sequential desorption steps for the two sandstones are shown in Figures 4 and 5. Percentages of desorbed amount of each desorption step to the total amount sorbed are arranged in Table 6. It shows no different trend for the two types of sandstone.

As shown in Table 6, Figures 4 and 5, the portion of strontium extracted by CaCl_2 solution is near to 90% of the total sorbed amount. Since Ca^{2+} and Sr^{2+} are the alkaline earth metals, Ca^{2+} may easily extract Sr^{2+} selectively. Another possible explanation is based on the hydrolysis. The magnitude of sorption stability is proportional to the magnitude of hydrolysis constant. The order of magnitude of hy-

Table 5. Reaching Times to 0.5 R and 0.9 R

| | unit: hour | | | |
|----|-------------|------|-------------|------|
| | Sandstone-A | | Sandstone-B | |
| | 0.5R | 0.9R | 0.5R | 0.9R |
| Sr | 3 | 24 | 3 | 70 |
| Co | 24 | 168 | 24 | 168 |
| Cs | 7 | 168 | 20 | 70 |

Table 6. Percentage of Desorbed Radionuclides for each Desorption Step to the Total Amount of Sorption

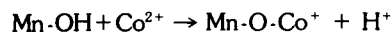
| | Percentage of the Extracted (%) | | | | |
|-------------|---------------------------------|-------------------|------|-------------------------|------|
| | Desorption | Ion Exchange | | (Fe, Mn), OOH* Fixation | |
| | SGW | CaCl ₂ | KCl | | |
| Sandstone-A | | | | | |
| Sr-85 | 3.4 | 84.8 | 9.8 | 0.0 | 1.3 |
| Co-60 | 0.6 | 0.2 | 0.3 | 77.0 | 21.5 |
| Cs-137 | 0.2 | 1.5 | 33.1 | 9.1 | 56.1 |
| Sandstone-B | | | | | |
| Sr-85 | 1.1 | 87.0 | 10.6 | 0.1 | 1.8 |
| Co-60 | 0.5 | 0.4 | 0.2 | 64.4 | 34.0 |
| Cs-137 | 0.2 | 1.6 | 27.6 | 7.8 | 62.9 |

* (Fe, Mn), OOH: association with ferro-manganese oxides or oxyhydroxides

drolsis constant is $\text{Co}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$. Thus Sr^{2+} can be exchanged easily by Ca^{2+} , but Co^{2+} can not be exchanged. Furthermore, about 98% of sorbed strontium was extracted after KCl solution treatment. Since calcium and potassium are reported to sorb onto the soils and rocks by ion exchange reaction,^(11, 12) the present results imply that sorption of strontium on the sandstone is mainly attributable to ion exchange.

In the case of cobalt, sorbed amounts on the sandstones were scarcely extracted by SGW, CaCl_2 , and KCl solutions. Whereas, about 60-80% of sorbed cobalt was extracted by KOX-HA solution. When the sandstones were treated with KOX-HA solution, carbonates, organics, and ferro-manganese oxides could be extracted. Strontium can sorb more easily on carbonates and organics than cobalt. If carbonates and organics are more than trace level in the sandstones, strontium should be extracted in this step. However there was not a detectable amount of

strontium desorbed in this step while there was a remarkable amount of cobalt. Therefore effects of carbonates and organics on sorption in the sandstones can be ignored and only ferro-manganese oxides are important. Means et al.⁽¹³⁾ insisted that cobalt was associated primary with manganese oxides and to a lesser extent with ferro oxides, insoluble organics, and possibly layer silicates. Cation sorption on manganese oxides and related oxides follows the general order: $\text{Mg}^{2+} < \text{Ca}^{2+} \ll \text{Mn}^{2+} \leq \text{Co}^{2+}$. That is, cobalt is one of the most strongly sorbing cations on manganese oxides. Murray et al.⁽¹⁸⁾ studied on the interaction of Co^{2+} on hydrous ferro-manganese surface and explained the interaction by the following equation.



Co^{2+} separates proton from the covalent bond at the surface and associate with this site. It is thus confirmed that radionuclides associated with manganese oxides or oxyhydroxides are extracted selectively in this step. About 20-30% of sorbed ones remained onto the sandstone. It is therefore possible to infer that cobalt sorbs on the sandstone mainly by the association with ferro-manganese oxides or oxyhydroxides. Secondary reaction is the irreversible fixation or mineralization. Ion exchange hardly occurs in this case.

For cesium, the desorbed amount after treating by SGW and CaCl_2 solution was not remarkable as shown in Table 6, Figures 4 and 5. The exchanged amount of cesium with CaCl_2 was 2% at most. About 30% of cesium was extracted with KCl solution. One of the factors influencing sorption selectivity involves steric hinderance of radionuclide movement within the mineral matrix, i.e., interlayers of mineral pores, such that only radionuclides of specific size and charge characteristics have access. Tamura et al.⁽¹⁴⁾ reported that sorption affinity for cesium was increased when the interlayer spacing of the clay mineral is about 10\AA . Thus conversion of the higher spacings of clay minerals into 10\AA should improve

their sorption characteristics. Potassium ion in clay mineral is inducing and maintaining the collapsed state of the c-axis of clay minerals as 10\AA . Therefore cesium can be released to some extent by potassium ion since K^+ can substitute Cs^+ in the lattice. About 8-9% of the sorbed cesium was extracted by KOX-HA solution. About 56-63% still remained on the sandstone after these extraction steps. Evans et al.⁽¹⁹⁾ explained on sorption of cesium according to binding sites to minerals. Three types of cesium binding sites to minerals are surface and planar sites, wedge, and interlayers. On planar (or exterior) surface of minerals cesium binding is relatively non-selective and ions of higher surface charge density would displace cesium. At the edges of interlayers of 10\AA spacing cesium is selectively fixed through collapse of the wedge to the 10\AA dimension, and displaced only by ions of similar size and charge. These ions would include K^+ , NH_4^+ , Rb^+ , and H^+ . Along the interlattice layers of collapsed or non-expanding clay minerals fixed cesium is not readily exchangeable with any ions. Above experimental results suggest that primary sorption type of cesium onto the sandstone is the irreversible fixation, and secondary one is the ion exchange reaction. The association of cesium with ferro-manganese oxides or oxyhydroxides seems to be some what involved in the above reaction. Thus cesium must be the strongest ion for sorption and difficult to desorb among the three radionuclides. Experimental results of other investigators also show that sorption of cesium is irreversible.^(6, 7, 19)

4. Conclusion

In sorption experiments carried out for strontium, cobalt and cesium onto the sandstone, sorption reaction occurred mainly on the outer surface of the sandstone particle during the first 10 hours. Diffusion into the inner surface of the mineral still occurred after that time. Sorption rate of strontium is faster

than those of cobalt and cesium. It is turned out that the sequential chemical extraction technique is an effective method to investigate the sorption types of radionuclides on the sandstones and KCl is an effective reagent to extract the ion-exchanged cesium.

Most of the sorbed strontium was extracted with SGW, $CaCl_2$ and KCl solutions. It implies that strontium sorbs mainly by the ion exchange reaction which is fast and reversible. The sorbed cobalt on the sandstones was hardly extracted with SGW, $CaCl_2$, and KCl, whereas 60-80% of the sorbed cobalt was extracted by KOX-HA, and 20-30% was remained on the sandstones. This shows that cobalt sorbs on the sandstone mainly by the association with ferro-manganese oxides or oxyhydroxides. Secondary reaction is the irreversible fixation or mineralization. Ion exchange hardly occurs. Some portion of the cesium binding on the sandstones is so strong that it is nearly irreversible, even when extracting reagents such as $CaCl_2$, KCl, and KOX-HA are used. Thus, the primary sorption type of cesium is the irreversible fixation, secondary one is the ion exchange reaction. Only the slight association with ferro-manganese oxides or oxyhydroxides seems to occur. Therefore, the order of migration mobility for the three radionuclides was $Sr^{2+} > Co^{2+} > Cs^+$ in the sandstones.

References

1. C.K. Park, H.S. Lee, K.W. Han, H.H. Park, A preliminary safety analysis for selecting candidate disposal sites, 12th Int. Symposium on the scientific basis for nuclear waste management, Berlin, Germany, Oct. 10, 1988
2. K. Skagius, G. Svedberg and I. Neretniks, A study of strontium and cesium sorption on granite, *Nuclear Technology* **59**, 302 (1982)
3. B. Anderson, E. Jenne, and T. Chao, The sorption of silver by poorly crystallized manganese oxides, *Geochim. Acta* **37**, 611 (1973)

4. R. Rundburg, Kinetics of the adsorption of radionuclides on tuff from Yucca mountain, *MRS Symp. Proc.* **26**, 827 (1984)
5. S. Sato, H. Furuya, S. Araya and K. Matsuo, Migration behavior of U(VI) in tuff, *MRS Symp. Proc.* **50**, 763 (1985)
6. F. Walton, T. Melnyk, J. Ross and A. Skeet, Radionuclide sorption mechanisms and rates on granitic rock, *American Chemical Society Symposium series* 246 (1984)
7. C.K. Park, S.I. Woo, T. Tanaka, and H. Kamiyama, "Sorption and Desorption Behavior of Co, Sr and Cs onto a Porous Tuff", *J. of Nuclear Science and Technology*, **29**, No. 12, p. 1184 (1992)
8. T. Chao, Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride, *Soil Sci. Am. Proc.* **36**, 764 (1972)
9. A. Tessier, P. Campbell, and M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry* **51**, 844 (1979)
10. Y.H. Cho, S.W. Park, P.S. Hahn, Studies on the sorption characteristics of ^{137}Cs onto granite and tuff, *J. Korean Nuclear Society*, Submitted
11. T. Torstenfelt, K. Andersson and B. Allard, Sorption of Sr and Cs on rocks and minerals, *Chemical Geology*, **36**, 123 (1982)
12. K. Andersson, *Transport of radionuclides in water/mineral systems*, Chalmers Univ. of Tech., (1983)
13. J. Means, D. Crerar, and M. Borcsik, Adsorption of Co and selected actinides by Mn and Fe oxides in soils and sediments, *Geochimica et Cosmochimica Acta*, **42**, 1763 (1978)
14. T. Tamura and D. Jacobs, Structural implications in cesium sorption, *Health Physics* **2**, 391 (1960)
15. K. Tickner, T. Vandergraaf and D. Kaminen, Radionuclide sorption on mineral and rock thin sections, AECL-365 (1985)
16. R. Serne, Conceptual adsorption models and open issues pertaining to performance assessment, *NEA Sorption Workshop*, Interlaken, Oct. 1991
17. B. Sawhney, Selective sorption and fixation of cations by clay minerals: A review, *Clay and Clay minerals*, **20**, 93 (1972)
18. J. Murray, The interaction of metal ions at the manganese dioxide-solution interface, *Geochimica et Cosmochimica Acta*, **39**, 505 (1975)
19. D. Evans, J. Alberts and R. Clark III, Reversible ion-exchange fixation of Cs-137 leading to mobilization from reservoir sediments, *Geochimica et Cosmochimica*, **47**, 1041 (1983)