

Reversibility and Linearity of Sorption for Some Cations onto a Bulguksa Granite

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Abstract—Sorption experiments for ^{60}Co , ^{85}Sr , and ^{137}Cs onto a Bulguksa granite were carried out to investigate the migration mobility. Reversibility and linearity of sorption as well as sorption mechanism were examined. Sorption isotherms were fitted in the range of 10^{-3} M and 10^{-11} M and the applicability of the two isotherm equations, Langmuir and Freundlich, was examined. ^{85}Sr give rise to almost linear isotherms, while ^{60}Co and ^{137}Cs show non-linear behavior. In order to distinguish sorption types of the cations, a sequential chemical extraction was introduced. The sorbed cations were extracted by applying different solutions of synthetic groundwater CaCl_2 , KCl , and $\text{KTOX}(\text{K}_2\text{C}_2\text{O}_4 + \text{NH}_2\text{OH} - \text{HCl})$. Sorption types considered are reversible sorption under a groundwater condition, ion exchange, association with ferro-manganese oxides, and irreversible fixation.

Key words: Sorption Reversibility, Sorption Linearity, Sorption Isotherm, Sequential Chemical Extraction, Surface Complexation Model

INTRODUCTION

To describe the migration of cations in geologic media, sorption types and migration mobility are of importance. Migration mobility can be determined by the sorption capacity and reversibility [Park et al., 1997]. For example, ion exchange reaction occurs rapidly and reversibly for some cations as the dominant sorption type, while mineralization or fixation occurs slowly and irreversibly for other group of cations. Although many types of reactions occur in a geohydrologic system, ion exchange is commonly considered as the predominant process [Anderson, 1983]. The reversibility and capacity of sorption on geologic media determine the mobility of the solute. The reversibility of sorption reflects the ability of the sorbed species to be released to the aqueous phase with changing conditions and is therefore pertinent to the environmental question. The reversibility of sorption has mainly been dealt with by studying exchange of sorbed species with competing ions.

Such sorption phenomena are commonly represented by the distribution coefficient K_d , which defines an equilibrium partitioning of the solute between the solution and solid phases. The use of a distribution coefficient describing cation migration requires some assumptions. First, the sorption process during migration keeps reversible equilibrium. Second, the ratio of the solute concentration between solid and solution phases also remains constant. One of the objectives in the study is to investigate the validity of the above assumptions for some cations in a granite. Anderson [1983] performed batch experiments for a number of crushed rocks at higher concentration ranges of 10^{-2} – 10^{-4} M. He concluded Sr satisfies the above assumptions while others, including actinides, do not.

Geologic media may consist of a variety of sorbing minerals such as silicate, micas, iron or manganese oxides each with

their own sorbed site preferences for individual solutes and each with a different sorption capacity. For example, silicate minerals, especially micas, possess an enhanced sorption affinity for cesium [Evans et al., 1983]. Means et al. [1978] found that cobalt sorbed preferentially on manganese oxides. The sorbed cations can be extracted from the soil and rock by using appropriate reagents. Tessier et al. [1979] developed a sequential 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. When all possible fractions of sorbed species 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 into solution under natural conditions. The residual portion can be regarded as a mineralized or fixed [Clark et al., 1996]. Walton et al. [1984] investigated the sorption mechanism of Co^{2+} , Sr^{2+} , Cs^+ and Ce^{3+} and concluded that cations have multi-sorption mechanism rather than a predominant one. Assuming that the sorption reaction process was the rate controlling step, they observed that double sorption site models gave a satisfactory explanation for the data.

Park et al. [1992, 1997] investigated sorption and desorption behavior of cations on geomedia. The sorption ratios for Co^{2+} and Cs^+ are significantly higher when measured in desorption experiment than those from the sorption experiment; ion-exchange cannot alone 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 processes involved other than the ion exchange reaction.

In the present study, the sorptive binding of ^{60}Co , ^{85}Sr , and ^{137}Cs in a Bulguksa granite is investigated with wide concentration ranges of 10^{-3} – 10^{-11} M. A modified sequential chemical extraction was introduced to identify the main sorption type and its reversibility.

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Table 1. Chemical composition of the Granite

Mineral	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	FeO	MnO	CaO
%	76.7	13.2	1.1	5.0	3.1	0.7	0.08	trace

Table 2. Mineral composition of the Granite by XRD and Microscope

Main	Minor
feldspar>quartz	sericite > chlorite > kaolinite > montmorillonite

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	2.0	15.2	6.2	6.2

EXPERIMENTAL

1. Sample Preparation

Bulguksa granite was sampled near the southeast coast in Korea. The chemical composition of the granite was analyzed on the basis of the standard method and shown in Table 1. Iron and manganese exist as oxides as indicated in Table 1. The mineral composition of the sample was analyzed with an XRD and a microscope and shown in Table 2. With the information from Table 2 regarding the content of secondary minerals, the granite sample is somewhat weathered. Its cation exchange capacity is 6.77, porosity is 0.004, and specific surface area is 1.67 m²/g by BET method. The content of organic carbon is less than 0.1 mg of carbon per 100 g of granite. A synthetic groundwater (SGW) was used to simulate the chemical composition of the natural groundwater where the granite was sampled. The composition of SGW is shown in Table 3 and pH of which was 6.6. The granite sample was crushed and sieved to have particle sizes of ϕ 1-1.5 mm.

2. Sorption Experiment

Granite particles had been in contact with the SGW for more than one month to attain a pre-equilibrium between the two phases before a sorption experiment was carried out in a closed system. Ten grams of the granite and 250 ml of SGW were prepared in a glass flask with a cap. For the sorption isotherm experiment, the SGW contained nonradioactive CsCl, CoCl₂ and SrCl₂ in the concentration ranges of 10⁻³-10⁻⁷ M with radioactive ⁶⁰Co, ⁸⁵Sr and ¹³⁷Cs about 0.1 μ Ci/ml as a tracer. These radioactive tracers took a concentration range of less than 10⁻⁸ M. During the experiment, the flask was shaken in a water bath at 20 °C. 5 ml of the contacted solution was sampled at an appropriate time interval and centrifuged for 20 minutes at 3,000 rpm. The radioactivity of 0.5 ml of the supernatant solution was measured with an HPGe detector, and the remaining part was poured back into the flask.

3. Sequential Chemical Extraction

Desorption experiments for the cation-sorbed granite sample were then followed to identify favorable sorption types and their reversibilities. The following are the experimental sequences conducted:

(1) The cation-sorbed granite was kept in contact with tracer-free SGW for two weeks to measure the amount of reversibly sorbed cation in SGW condition. 5 ml of the solution was sampled at predetermined time intervals and its radioactivity was measured. The sampled solutions were returned to the flask. After two weeks, all solid samples were recovered for the second step.

(2) The recovered cation-sorbed granite was mixed with 250 ml of 0.5 M CaCl₂ solution, free of radioactive tracers. The purpose of this process is to quantify the amount of ion-exchanged cations.

(3) The mixture was then separated from the CaCl₂ solution and further contacted with 250 ml of 0.5 M KCl solution to determine the amount of remaining ion-exchanged cations.

(4) A similar procedure was repeated with a solution mixture containing 0.1 M potassium tetraoxalate and 0.1 M hydroxylamine hydrochloride (KTOX) to estimate the amount of cations associated with ferro-manganese oxides or oxyhydroxides.

(5) The remaining radioactivity in the granite sample was then counted to determine the amount of fixed cations.

RESULTS AND DISCUSSION

1. Sorption Rate and Sorption Capacity

As a means to describe the uptake of cations, the distribution ratio, R, is defined as the ratio of the amount of cations sorbed per unit weight of solid (q) to the remaining cations in the solution (C),

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

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

The results of the sorption kinetics for ⁶⁰Co, ⁸⁵Sr and ¹³⁷Cs are shown in Fig. 1. The concentrations of the tracers decrease rapidly within 20 hours and slowly go down afterwards with a time scale of weeks. When the rate of concentration change, $\Delta C/\Delta t$, becomes negligible, say less than 0.01 ($\mu\text{Ci/ml}\cdot\text{hr}$) for this experiment, the sorption system is assumed to be at a quasi-

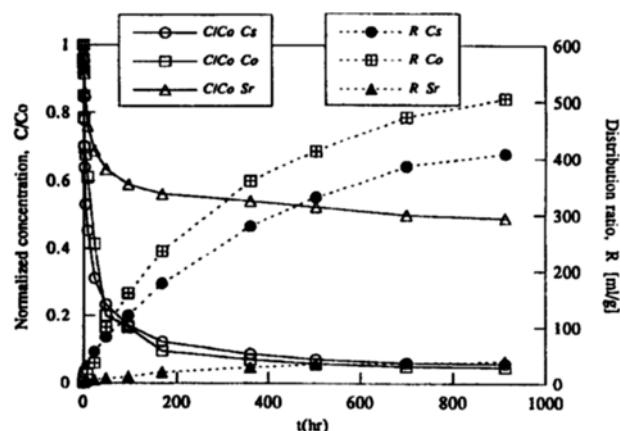


Fig. 1. Concentration and distribution ratio change with time.

equilibrium state and the sorption experiment is terminated. It takes more than a month to arrive at such a condition. Thus, the curves of the concentration change may be divided into two stages for convenience. At the initial stage, tracers may sorb mainly on the outer surface of the rock particles and at the later stage the tracers penetrate through the micropores of the rock to the inner surface of the rock. Diffusion process would be the rate controlling step of this later stage [Park et al., 1992; Skagius, 1982]. Considering the ionic radii of ^{60}Co , ^{85}Sr and ^{137}Cs which are 0.58, 1.2 and 1.67 Å, respectively, ^{60}Co may diffuse more easily than ^{85}Sr and ^{137}Cs . However, ^{137}Cs does not show a strong diffusion resistance as ^{85}Sr even though ^{137}Cs has the largest radius amongst them. This suggests a certain selectivity for Cs sorption in the minerals. By definition, R changes more sensitively at a lower concentration range than at higher ones. Thus R changes apparently even though the concentration only changes slightly at the later stage in Fig. 1. The concentration decrease or distribution ratio with time for ^{85}Sr are always less than those for ^{60}Co and ^{137}Cs . This implies that the strength of sorption for ^{85}Sr is weaker than the others. The values of R for the three cations at a quasi-equilibrium in tracer level are arranged in Table 4. The mean and variance of R are obtained from the five experimental sets with the same experimental conditions. The variance of R is very large owing to the sensitiveness of R at low concentrations as mentioned above.

In order to assess the effects of the concentration on sorption, isotherms for the three species are plotted with concentration ranges of 10^{-3} – 10^{-11} M. The results are interpreted with two isotherms: Langmuir and Freundlich type. The Freundlich

Table 4. Distribution ratios for ^{85}Sr , ^{60}Co and ^{137}Cs on the granite

	^{85}Sr		^{60}Co		^{137}Cs	
	$\mu^{(1)}$	$\sigma^{(2)}$	μ	σ	μ	σ
R (ml/g)	39	13	665	139	590	122
R_d (ml/g) ⁽³⁾	47		907		1230	

1) μ : Mean of R values

2) σ : Standard deviation of the R values

3) R_d : Distribution ratio in desorption step

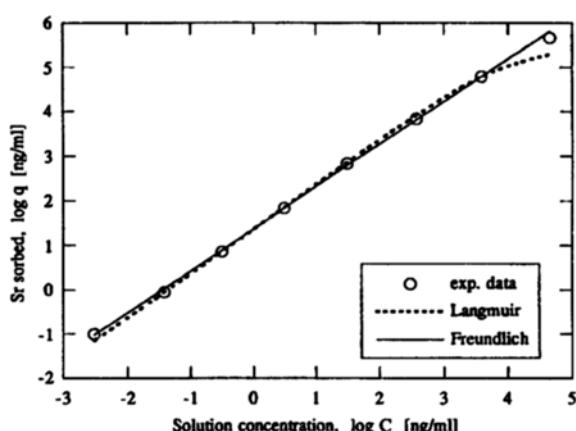


Fig. 2. Sorption isotherm curves for strontium.

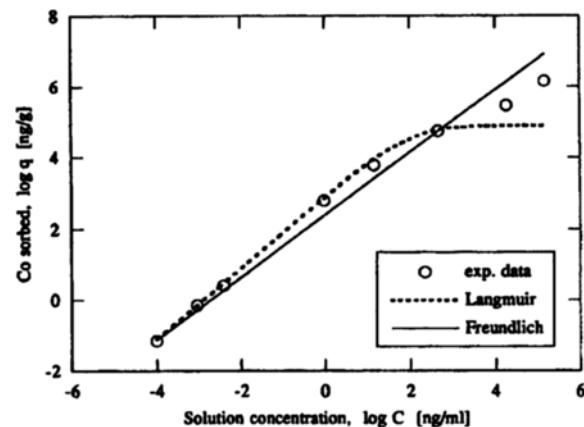


Fig. 3. Sorption isotherm curves for cobalt.

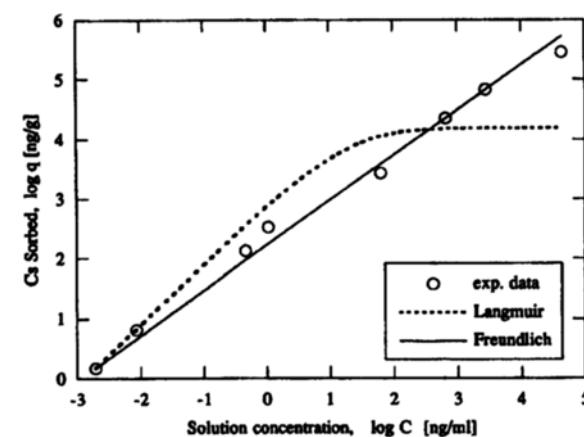


Fig. 4. Sorption isotherm curves for cesium.

Table 5. Constant values of Freundlich and Langmuir isotherms

	Freundlich		Langmuir	
	K	n	K_1	K_2
Sr	24	0.95	23	0.0001
Co	251	0.88	770	0.01
Cs	168	0.755	774	0.05

isotherm is expressed as $q=K C^n$ and the two constants, K and n are determined by curve fitting. The Langmuir isotherm is expressed as follows.

$$q = \frac{K_1 C}{1 + K_2 C}$$

The results of isotherm experiments are plotted in Figs. 2, 3 and 4 and arranged in Table 5. It is well fitted with the experimental data, except the Langmuir isotherm at high concentration range. To solve deviation in the Langmuir curve, Skagius and Neretnieks [1988] plotted the Langmuir isotherm centering around high concentration. Thus, it showed a certain deviation in the curve at low concentration, but it did not give a significant error in the point of the amount of sorption. On the other hand, our experimental range is much higher than

Skagius and Neretnieks'. And we did not give a weighting in fitting. Then, deviation appeared at high concentrations. The curve seemed to go to a saturated state of sorption. That is, the Langmuir isotherm shows a limit of sorption capacity and is not applicable at high concentration. In that range, the three cations show higher q than theoretically depicted Langmuir curve and lower q than Freundlich type. That is, the cations sorb more than monolayer sorption of Langmuir type and less than Freundlich type.

As the denominator approaches 1 when the concentration becomes negligible, then the Langmuir equation becomes a linear isotherm type as $q = K_1 C$. Therefore, K_1 can be assumed as the distribution coefficient, K_d at low concentration. In such a situation, the interactions among nuclides may be neglected, and it is possible to express the isotherm as linear by Henry's law. K_1 values for the three cations in Table 5 show a similar range of value compared to the distribution ratios in Table 4. In the expression of the Freundlich isotherm, exponent n is an indicator of linearity. As n approaches 1, the sorption system becomes linear. The isotherm curve of Sr almost shows a linear relationship in the concentration ranges between 10^{-3} and 10^{-11} M. Thus, the dependence of sorption on concentration of Sr is negligible. Usually ion exchange shows a linear isotherm [Anderson, 1983]. The isotherm curves of ^{60}Co and ^{137}Cs are not linear.

2. Desorption with Synthetic Groundwater

Fig. 5 shows the experimental results that cation-sorbed granite contacted with a tracer-free SGW. Cation desorbed by SGW was not significant even after several days. About 10% of the sorbed strontium was desorbed, while only 5% of cobalt and cesium were desorbed. For strontium, R_d , the distribution ratio in the desorption step, was close to R defined in the sorption step. That is, the distribution ratio maintained its value even though the solution concentration changed. In other words, strontium kept a sorption relationship and sorbed reversibly in the SGW condition. For cesium, R_d was much larger than R . This implies that cesium is hardly desorbed or it has an irreversible tendency on sorption in the SGW condition. Co showed an intermediate result.

The reason that Sr is more reversible and has a weaker sorp-

tion than those of cobalt and cesium may be explained by the surface complexation model. In the triple layer model [Davis, 1990], 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 , and δ planes. The O plane represents the interface between the solid surface and solution. Transition metal ions such as Pb^{2+} , Cu^{2+} , and Co^{2+} can be strongly sorbed in the O plane. Sorption of these cations by hydrous oxides is weakly dependent upon ionic strength of the solution. Weakly sorbing cations such as Ca^{2+} , Mg^{2+} , and Sr^{2+} do not generally form covalent bonds, and sorption of these ions has been shown to be influenced by electrostatic forces, via their dependence on ionic strength. These 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, the binding of strontium is easier and weaker than binding of cobalt. This is one of the reasons why strontium sorbs more 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 with only the surface complexation model. It will be discussed more deeply in the following section.

3. Desorption with Sequential Chemical Extraction

The results from the sequential extraction may clearly explain the suggestions from the sorption step. The remaining sorbed amounts of the sequential desorption steps are shown in Fig. 5. Percentage of desorbed amount of each step based on the total initial sorbed amount is arranged in Table 6.

As shown in Table 6 and Fig. 5, the portion of strontium extracted by CaCl_2 solution is near 90% of the total sorbed amount. Since Ca^{2+} and Sr^{2+} are alkaline earth metals, Ca^{2+} may easily extract Sr^{2+} selectively. Another possible explanation is based on hydrolysis. The magnitude of the sorption stability is proportional to the magnitude of hydrolysis constant [Stumm and Morgan, 1981]. The order of magnitude of the hydrolysis constant is $\text{Co}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$. Thus Sr^{2+} can be exchanged easily by Ca^{2+} , but Co^{2+} cannot be exchanged. Furthermore, about 98% of the 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 [Clark et al., 1996], the present results imply that sorption of strontium on the granite is mainly attributable to the ion exchange.

Table 6. Percentage of the desorbed for each sequential extraction step

Extraction reagent	Sorption	Partitioning of the desorbed (%)		
		^{85}Sr	^{60}Co	^{137}Cs
Groundwater	Reversible in Gw condition	10.0	5.3	4.9
CaCl_2	Ion exchange	80.0	7.1	11.1
KCl	Ion exchange	9.0	20.1	18.7
KTOX	Association with ferromanganese oxides	0.0	63.1	4.4
Remains	Irreversible fixation	1.0	4.4	60.4

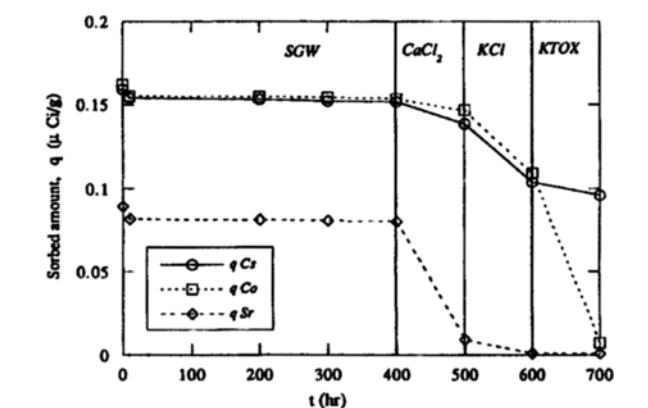
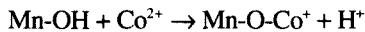


Fig. 5. Remaining sorbed amounts of 3 radionuclides for each extraction step.

In the case of cobalt, a little amount of the sorbed on the granite was extracted by SGW, CaCl_2 , and KCl solutions. On the other hand, about 60% of the sorbed cobalt was extracted by KTOX solution. When the cation-sorbed granite was treated with KTOX solution, carbonates, organics, and ferro-manganese oxides could also be extracted. Some workers have shown that trace metals can be associated with sedimented carbonates and organic substances, which are known to have high sorption capacity [Clark et al., 1996]. This is considering that strontium should also be extracted at this step if carbonates and organics are present at more than a trace level in the system. As mentioned in the sample preparation, the organic carbon is less than 0.1 mg of C/100 g of rock. By the way, there was not a detectable amount of strontium desorbed in this step while there was for cobalt. Therefore, effects of carbonates and organics on the sorption in this system can be ignored and only ferro-manganese oxides are important. 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 an unusually high specific surface area and a high cation exchange capacity (CEC). For example, its surface area reaches up to $350 \text{ m}^2/\text{g}$, and the CEC at $\text{pH}=8.3$ is 1.5 eq./100 g, while that of montmorillonite is about 0.1 eq./100 g [Means, 1978]. Murry [1975] reported that cobalt was associated primarily with manganese oxides and, to a lesser extent, with ferro oxides, insoluble organics, and possibly layer silicates. Cation sorption on manganese oxides and on related oxides follows the general order: $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Mn}^{2+} \leq \text{Co}^{2+}$. That is, cobalt is one of the most strongly sorbed cations on manganese oxides. The interaction of Co^{2+} on hydrous ferro-manganese surface can be explained by the following equation [Murry, 1975].



Co^{2+} separates protons from the covalent bond at the surface and associates with this site. It is thus confirmed that cations associated with ferro-manganese oxides or oxyhydroxides are extracted selectively during this step. Therefore, even though the content of manganese oxide is only 0.07%, its effect on Co sorption may be dominant. About 5% of the initially sorbed amount remained in the granite after all extracting steps. It is therefore possible to infer that cobalt sorbs on the granite mainly by association with ferro-manganese oxides or oxyhydroxides and, secondly, by ion exchange.

At each desorption step, a certain amount of the sorbed Cs was extracted, while about 61% of the sorbed amount still remained in the granite after all these extraction steps. Evans et al. [1983] explained the sorption of cesium by the concept of binding sites to minerals. They explained that three types of cesium binding sites to minerals were surface and exterior sites, wedge, and interlayers. On the exterior surface of minerals cesium binding is relatively non-selective and ions of higher surface charge density would displace cesium. It seems that the extracted by SGW belongs to the first type. 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. One of the factors influencing sorption selectivity involves steric hindrance of cation movement within the mineral matrix, i.e., interlayers of mineral pores, such that only cations of specific size and charge characteristics have access. These ions would include K^+ , NH_4^+ , Rb^+ , and H^+ . Sorption of cesium, therefore, is influenced not only by the surface reaction and electrostatic interaction, but also by the steric hindrance of cesium movement within the rock matrix. Davis and Kent [1990] also pointed out that 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. When the cation-sorbed granite is treated with KCl , K^+ ion may substitute for Cs^+ in this lattice. Along the interlattice layers of collapsed or non-expanding clay minerals, fixed cesium is not readily exchangeable with any ions. The remaining sorbed Cs may belong to this type. Therefore, the above experimental results suggest that primary sorption type of cesium onto the granite is the irreversible fixation, and secondary one is the ion exchange reaction. The association of Cs^+ with ferro-manganese oxides or oxyhydroxides seems to only be a little involved in the above reaction. Thus Cs^+ must be the strongest ion for sorption and consequently difficult to desorb among the three cations. Experimental results of other investigators also support this argument [Skagius, 1982].

CONCLUSIONS

Sorption experiments for strontium, cobalt, and cesium onto granite were carried out and the sorption reaction mainly occurred on the outer surface of the granite particle during the first 20 hours. Diffusion into the inner surface of the mineral still occurred after that time. Strontium approaches the quasi-equilibrium state faster than cobalt and cesium. The Freundlich isotherm is a valid representation for describing the concentration dependence of sorption of the cations onto rock in the range of 10^{-3} M and 10^{-11} M , and advantageous in showing nonlinearity. On the other hand, Langmuir isotherm is not applicable at high concentration range. Sr shows a linear isotherm, while Co and Cs show nonlinear ones.

It turns out that the sequential chemical extraction technique is an effective method for investigating the sorption types of cations on the granite and KCl is also an effective reagent to extract the ion-exchanged cesium. Most of the sorbed strontium was extracted with SGW, CaCl_2 , and KCl solutions. This implies that strontium sorbs mainly by the ion exchange reaction. 63% of the sorbed cobalt was extracted by KTOX. This indicates that association with ferro-manganese oxides or oxyhydroxides is the main sorption mode. Secondary reaction is the ion exchange. Major portion of cesium binding on the granite is so strong that it is nearly irreversible, even when extracting reagents such as CaCl_2 , KCl , and KTOX are used. Thus, the primary sorption type of cesium is the irreversible fixation, and the secondary type is the ion exchange reaction. Only a slight association with ferro-manganese oxides or oxyhydroxides seems to occur. Therefore, the order of sorption reversibility and mi-

gration mobility for the three cations was $\text{Sr}^{2+} > \text{Co}^{2+} > \text{Cs}^+$ in the granite.

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