

Studies on the Sorption Characteristics of ^{137}Cs onto Granite and Tuff

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^{137}Cs 의 화강암 및 응회암에 대한 흡착특성에 관한 연구

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Abstract

Batch sorption experiments were conducted to investigate the sorption characteristics of ^{137}Cs , known for the primary target of safety assessment in low-level radwaste disposal, onto domestic rocks such as Granite and Tuff. A response surface analysis method was applied to quantify the effect of 3 independent variables ($[\text{Cs}]$, $[\text{Vol}/\text{Wt}]$, $[\text{pH}]$) on the sorption. As a result, initial Cs concentration appeared to be the most important variable within the range of the study. A significant effect of $[\text{Vol}/\text{Wt}]$ on K_d was observed. The sorption of Cs was pH-insignificant. The sorption extent of nuclides onto tuff was more significant than that onto granite. The pH-insignificant sorption behavior of Cs was discussed in terms of the surface electrical properties and the solution chemistry. The sorption tendency of nuclides onto geomedia studied was interpreted by adopting the water structure modification theory.

요 약

저준위 방사성 폐기물의 대표핵종인 Cs의 국내 대표 암반구성 물질인 화강암과 응회암에의 흡착특성을 조사하기 위해 회분식 흡착실험을 수행하였다.

반응표면분석법을 이용하여 $[\text{Cs}]$, $[\text{Vol}/\text{Wt}]$, $[\text{pH}]$ 의 독립변수가 흡착에 미치는 영향을 정량적으로 평가하였다. 결과, 초기 세슘이온의 농도가 가장 중요한 변수로 나타났다. Cs의 흡착능의 pH 의존성은 미약한 것으로 나타났다. 핵종의 응회암에의 흡착량이 화강암보다 더 많았다. 이들 핵종흡착의 낮은 pH 의존성을 매질의 전기적 표면특성과 핵종의 수용액상 특성으로 설명하였다. 핵종간 과 매질간의 흡착능 비교는 물구조 변환론으로 설명하였다.

1. Introduction

Interactions between radionuclide/geological media are known to be an important mechanism of radionuclide retardation in groundwater systems. Much of previous work was focused on producing K_d values at various geochemical conditions in an attempt to provide the data base. Understanding chemical nature of the sorption process drawn from the well designed experimental format of interfacial chemical reactions may reduce tedious and numerous laboratory works and set safer formula on an assessment of the long-term fate of radionuclides[1]. Statistically designed experiments have been used to determine the effect of system parameters on sorption measurement[2, 3].

The sorption phenomena, especially occurring between the solid and the aqueous phase, should include characteristics of the surface in the aqueous media in addition to the inherent one, the adsorbate, and the aqueous solution chemistry[4]. Depending upon environments, any of the above three components can be the major factor determining the sorption extent. For the sorption of Cs representing one of the major nuclides in low level radwaste disposal, the surface properties are the most important parameter. The surface acidity and the surface charge as the surface characteristics are to be discussed among others. The surface charge (or potential) can be determined by several techniques. Zeta potential is the potential of the shear layer in the electrical double layer and can be directly measured.

In this study, we measured the extent of Cs sorption on granite and tuff and the effect of 3 independent variables on the sorption using response surface analysis method. An attempt was also made to correlate the water structure modification theory and the surface charge determined by measuring the zeta potential of the domestic solids to the sorption characteristics of nuclides studied.

2. Experimental

Solids

Granite and tuff were used for sorption experiment. Samples of these rocks were obtained from Hwang-deung and Young-il region, respectively. The rocks were crushed and sieved. The mesh size No. 80–100 fraction was used for sorption experiment. Rocks were characterized by X-ray diffraction method. Each diffractogram shows typical diffraction pattern of granite and tuff, respectively.(Figs. 1 and 2)

Solutions

A synthetic groundwater with composition listed in Table 1 was used[5]. Inactive CsCl was used to make concentrations of 10^{-5} , 10^{-6} , and 10^{-7} mole/L in the appropriate groundwater. Each solution was spiked with $^{137}\text{Cs}^+$ as a tracer.

Zeta Potential Measurement

Zeta potential of hydrous solids was determined by Laser Zee Model 500 Zeta Meter. It measures the zeta potential of colloidal particles by determining the rate at which the colloidal particles move in a known electrical field. 0.5g powdered solids were added into two separate 500 ml of 0.1 M NaClO_4 solutions, with continuous bubbling of N_2 gas to remove dissolved CO_2 (one for acid addition, the other for base). While the suspension was being stirred, the initial pH was measured and recorded. The pH was then adjusted with 0.1 M HClO_4 or 0.1 M NaOH to cover a range from 4 to 10 in approximately 0.5 pH unit increments.

Experimental Design

A three-level, three-variable statistically designed experimental procedure [6] was used to measure the sorption of ^{137}Cs on granite and tuff and the effect of experimental variables on that. Factorial design method is very efficient way for a study of the effects of two or more factors. The effect of a factor is defined to be the change in response produced by a change in the level of the factor. This factorial design and statistical analysis method provide an equation

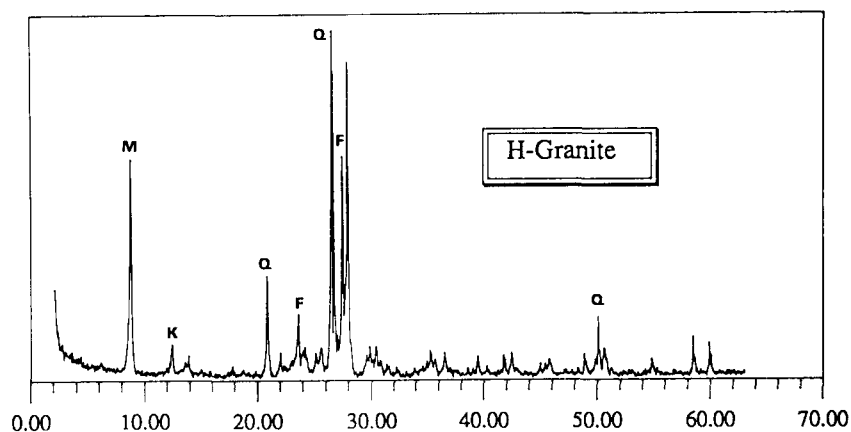


Fig. 1. X-ray Diffractogram of Granite and Used for Sorption Experiment

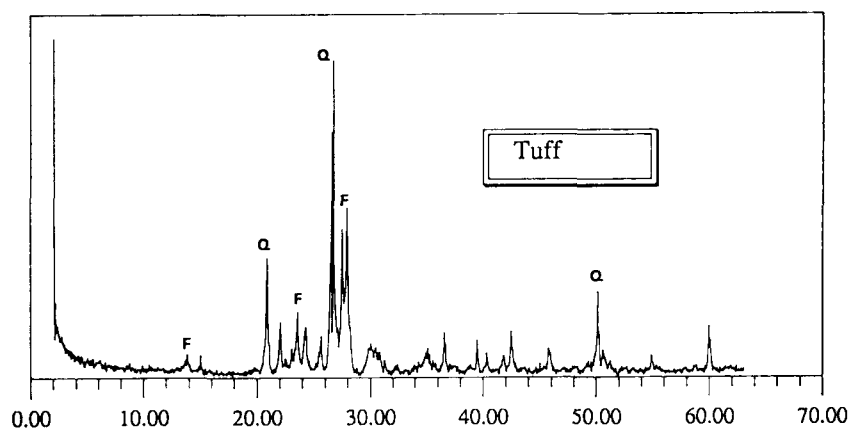


Fig. 2. X-ray Diffractogram of Tuff Used for Sorption Experiment

Table 1. Composition of Synthetic Groundwater

| Components | mg/L |
|-----------------|------|
| Na | 8.3 |
| K | 3.5 |
| Mg | 3.9 |
| Ca | 13.0 |
| Cl | 5.0 |
| SO ₄ | 8.6 |
| NO ₃ | 0.62 |
| F | 0.19 |

that can be used to predict sorption values within the range of the independent variables. The design dia-

gram of 3-level, 3-variable Box-Behnken model is shown in Fig.3.

The three independent variables studied include the initial hydrogen ion concentration [pH], the ratio of solution volume to solid weight [V/Wt], and the initial Cs ion concentration [C₀]. Those variables has been widely selected as very important factor in many sorption studies. The ranges of 3 variables were chosen to cover the real situations as possible. The coded design matrix is shown in Table 2. The values of the variables at each of the three levels are given in Table 3.

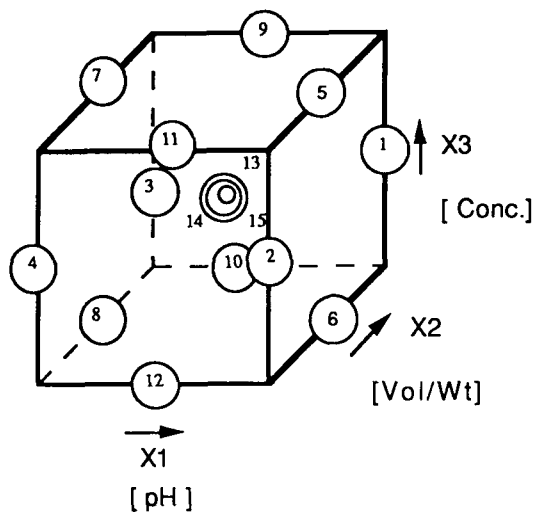


Fig. 3. The Design Diagram of 3-level, 3-variable Box-Behnken Model

Experimental Procedure

Each of the solid sample was equilibrated with 10 ml of the appropriate solution for 28 days. The vials were routinely shaken to ensure maximal exposure of the rock mineral surface to the solution. All procedures were conducted under the normal laboratory atmospheric conditions.

Aliquots of the contacting solutions were taken after the reaction period for radiometric analysis. Initial and equilibrium ^{137}Cs activities were measured with a gamma-counting spectrometer with NaI crystal detector.

The sorption coefficient, K_d (mL/g), was determined from

$$K_d = (V/Wt) [(C_0 - C_f) / C_f]$$

Table 2. Coded Design Matrix Used in Cs-173 Sorption Experiments

| No. | Exp. # | X ₁ | X ₂ | X ₃ | X ₁ ² | X ₂ ² | X ₃ ² | X ₁ X ₂ | X ₁ X ₃ | X ₂ X ₃ |
|-----|--------|----------------|----------------|----------------|-----------------------------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1 | 13 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 10 | 0 | 1 | -1 | 0 | 1 | 1 | 0 | 0 | -1 |
| 3 | 3 | -1 | 1 | 0 | 1 | 1 | 0 | -1 | 0 | 0 |
| 4 | 9 | 0 | 1 | 1 | 0 | 1 | 1 | 0 | 0 | 1 |
| 5 | 1 | 1 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 0 |
| 6 | 12 | 0 | -1 | -1 | 0 | 1 | 1 | 0 | 0 | 1 |
| 7 | 8 | -1 | 0 | -1 | 1 | 0 | 1 | 0 | 1 | 0 |
| 8 | 6 | 1 | 0 | -1 | 1 | 0 | 1 | 0 | -1 | 0 |
| 9 | 4 | -1 | -1 | 0 | 1 | 1 | 0 | 1 | 0 | 0 |
| 10 | 11 | 0 | -1 | 1 | 0 | 1 | 1 | 0 | 0 | -1 |
| 11 | 7 | -1 | 0 | 1 | 1 | 0 | 1 | 0 | -1 | 0 |
| 12 | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 13 | 2 | 1 | -1 | 0 | 1 | 1 | 0 | -1 | 0 | 0 |
| 14 | 5 | 1 | 0 | 1 | 1 | 0 | 1 | 0 | 1 | 0 |
| 15 | 14 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

Table 3. Value of the Variables at Each level of the Experimental Design

| Variables | Coded Levels | | |
|----------------------|--------------|-----|----|
| | -1 | 0 | 1 |
| X1, [pH] | 6 | 8 | 10 |
| X2, log[Vol/Wt] ml/g | 1 | 3.3 | 10 |
| X3, log[Cs] mole/L | -7 | -6 | -5 |

where, V: volume of solution (mL)

Wt: weight of solid (g)

C₀: initial ion concentration (cpm)

C_f: ion concentration after the contact period (cpm)

3. Results and Discussion

Experimental K_d and Empirical K_d Modeling

The experimental K_d values and those of calculated using the polynomial equation for sorption are given together in Table 4. For each solid, the experimental data were used to derive the b values required to solve the polynomial for any combination of the variables X₁, X₂, and X₃ that lie on or within the response surface of the experimental design.

The experimental design and statistical analysis allow an equation that can predict empirical sorption values. According to that, sorption results are described by the following general polynomial :

$$\log[K_d] = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3$$

The b values obtained through multiple regression analysis of the experimental data are given in Tables 5. The results of ANOVA (analysis of variance) and F-test and the large R² values suggest that the variation in the K_d for Cs can be adequately described by polynomial equations. The F-test results are well

above the F-value for 1% significance level F(0.01). In general, the larger the b values, the greater the effect of the parameter on the K_d values. Negative b values indicate the decreasing effect on K_d, while positive b values do the opposite effect.

Discussion

Figs. 4 and 5, plotted using above obtained polynomial equations, show the effect of pH, [Vol/Wt]

Table 5. Regression Coefficients for Polynomial Sorption Equation

| Coeff. | HG | TF |
|-----------------|---------|---------|
| b ₀ | 1.1058 | 1.9639 |
| b ₁ | -0.0302 | 0.0872 |
| b ₂ | 0.0400 | 0.2557 |
| b ₃ | -0.4743 | -0.6296 |
| b ₁₂ | -0.0319 | 0.1213 |
| b ₂₂ | 0.0276 | 0.0252 |
| b ₃₂ | 0.0825 | 0.1013 |
| b ₁₂ | 0.0224 | 0.0053 |
| b ₁₃ | -0.0041 | -0.0039 |
| b ₂₃ | -0.0226 | -0.0677 |
| R ² | 0.9964 | 0.9908 |

Table 4. Experimental and Calculated K_d Values for Cs-137 Sorption by Granite and Tuff

| X1 | X2 | X3 | HG | HG | TF | TF |
|----|----|----|------|------|-------|--------|
| | | | Exp. | Cal. | Exp. | Cal. |
| 0 | 0 | 0 | 11.8 | 12.8 | 94.2 | 92.0 |
| 0 | 1 | -1 | 48.1 | 56.6 | 773.0 | 1105.1 |
| -1 | 1 | 0 | 14.3 | 14.1 | 209.0 | 187.8 |
| 0 | 1 | 1 | 5.5 | 5.7 | 41.6 | 44.5 |
| 1 | 1 | 0 | 14.0 | 13.6 | 297.1 | 287.4 |
| 0 | -1 | -1 | 40.4 | 42.4 | 250.7 | 249.2 |
| -1 | 0 | -1 | 42.7 | 45.4 | 495.6 | 530.9 |
| 1 | 0 | -1 | 37.7 | 40.2 | 755.4 | 807.4 |
| -1 | -1 | 0 | 12.0 | 13.0 | 53.2 | 59.3 |
| 0 | -1 | 1 | 5.6 | 5.3 | 22.6 | 18.7 |
| -1 | 0 | 1 | 5.1 | 5.2 | 26.9 | 29.8 |
| 0 | 0 | 0 | 13.5 | 12.8 | 92.3 | 92.0 |
| 1 | -1 | 0 | 9.6 | 10.2 | 72.9 | 86.4 |
| 1 | 0 | 1 | 4.3 | 4.4 | 41.7 | 43.7 |
| 0 | 0 | 0 | 12.1 | 12.8 | 84.6 | 92.0 |

and Cs concentration on the sorption of Cs^+ onto granite and tuff, respectively. The effect of C_0 on the sorption appeared to be the most important one in this study. In this case the sorption isotherm is not linear. This happens in a sorption of one species on different sorption sites of one solid. If small amounts of sorption sites of high selectivity are present in the solid other than sorption sites of lower selectivity, the sorption isotherm $c_s = f(c)$ will not be linear in the range of low concentrations of the radionuclides[7]. In other words, this curvature of isotherm may be due to the presence of sorption sites of very different sorption energies.

A significant influence of $[\text{Vol}/\text{Wt}]$ on K_d was also observed. The sorption of Cs onto both solids is likely to be pH-insignificant in the pH range investigated. In understanding such interfacial phenomena, both the surface characteristics of the adsorbent and the solution chemistry of the adsorbate should be considered. The fact that the surfaces are negatively charged and Cs ions do not undergo the hydrolysis reaction rendered the pH-insignificant sorption.

However, the sorption capacity of these solids are quite different. Namely, the sorption density of granite is much lower than that of tuff. The solution chemistry approach may lead to the reasonable interpretation on this discrepancy. In general, large ions are less heavily hydrated and their relatively weak electrostatic fields can not 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 heat of hydration. The hydration energy is inversely proportional to the radius. Solids in solution are also charged and can be viewed as affecting water structure in similar ways as ions[8]. Namely, the surfaces with the higher heats of immersion are structure-making solids; the others, structure-breaking[9]. By using the ionic sorption sequences as a tool to determine the properties of

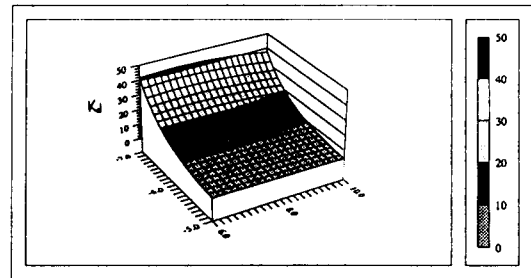


Fig. 4a. The Effects of pH and $\log[C_s]$ on K_d of Granite at $[\text{Vol}/\text{Wt}]=33.3 \text{ ml/g}$

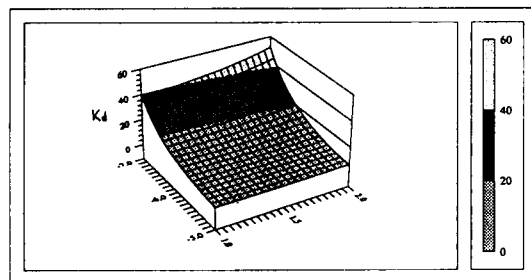


Fig. 4b. The Effects of $\log[\text{Bol}/\text{Wt}]$ and $\log[C_s]$ on K_d Granite at $\text{pH}=8.0$

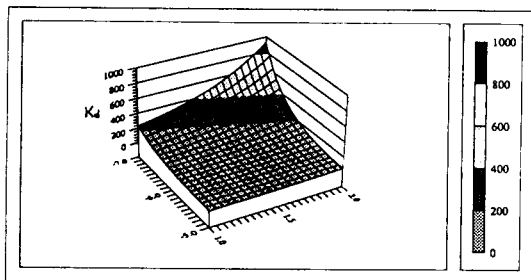


Fig. 5a. The Effects of pH $\log[C_s]$ on K_d of Tuff at $[\text{Vol}/\text{Wt}]=33.3 \text{ ml/g}$

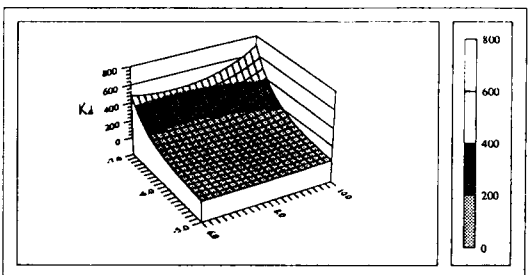


Fig. 5b. The Effects of pH $\log [\text{Vol}/\text{Wt}]$ and $\log[C_s]$ on K_d of Tuff at $\text{pH}=8.0$

the surface, a general trend is found: the surfaces characterized by a pH_{zpc} (pH at zero point charge) lower than 4 are structure breakers, the others are structure makers. Gierst, et al[10] and Berube and de Bruyn[11] applied the Gurney concept of the ion-ion interactions to the ion-surface interactions. They concluded that an interface will adsorb an ion strongly when both the ion and the surface have a similar effect on modifying the water structure. Otherwise, the ion will be rejected from the surface.

Fig. 6 and Fig. 7 show the zeta potentials of granite and tuff solids, respectively, as a function of pH in the presence of NaClO_4 . Two different concentrations of the ionic strength were chosen for zeta potential measurements because these concentrations are close to the range of the electrolyte concentration in the natural groundwater. The zeta potential is greatly affected by the small change of the H^+ or OH^- ions. The surfaces are negatively charged through the pH region studied and the surface charges become more negative as pH increases. This indicates that the surface hydroxyl functional groups are developed at the solid surface and behave amphotERICALLY. From the fact that the pH-dependency of the surface potential of these two rock samples is similar to each other, it can be inferred that their pH-dependent sorption behavior for the identical adsorbate should have same tendency with respect to pH.

Another interesting observation is that the zeta potentials of these two solids are not much affected by the ionic strength, indicating that these Na^+ and Cl^- ions are the indifferent electrolytes. It is generally known that the sorption nature of the indifferent ions is not the specific sorption but the electrostatic. Since chemical properties of Cs^+ in aqueous phase are similar to those of Na^+ , the sorption behavior of Cs^+ will be influenced by the presence of the supporting electrolytes.

Although pH_{zpc}s for two solids are not observed, it is obvious that pH_{zpc} of Tuff is lower than that of Granite if the surface potential at lower pHs are ex-

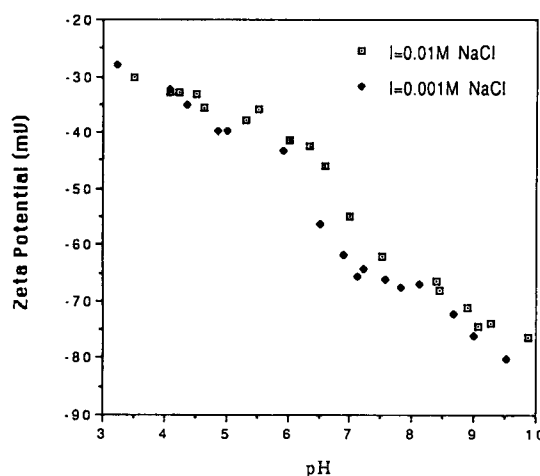


Fig. 6. Zeta Potential of Granite With Varying pH

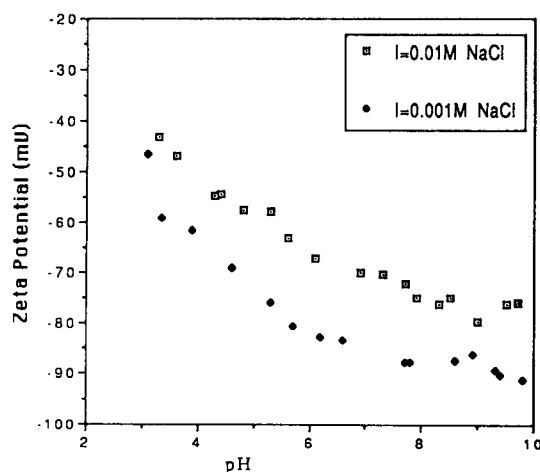


Fig. 7. Zeta Potential of Tuff With Varying pH

trapolated. It thus can be assumed that Tuff is stronger water structure breaker than Granite. Since Cs is known for the water structure breaker, its sorption onto Tuff is more significant than on Granite.

4. Conclusions

Batch sorption experiments were conducted to in-

investigate the sorption characteristics of ^{137}Cs onto domestic rocks such as Granite and Tuff. A response surface analysis method was applied to quantify the effect of 3 independent variables ([Cs], [Vol/Wt], [pH]) on the sorption. The conclusions obtained from the present study can be summarized as follows :

1. Initial Cs concentration appeared to be the most important variable within the range of the study.
2. A significant effect of [Vol/Wt] on Kd was observed.
3. The sorption of Cs was pH-insignificant.
4. The sorption extent of Cs-137 onto tuff was more significant than that onto granite.
5. From zeta potential measurements, pH is an important variable controlling the surface charge of granite and tuff. Dependency of the zeta potential on the electrolyte indicates that the sorption content of Cs on rock samples will be significantly affected by the concentration of the electrolytes. Namely, the retarding degree of the domestic rock matrix for Cs is much dependent on groundwater properties such as compositions of cations from the near disposal site to the biosphere.

Acknowledgments

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