

Studies on the Sorption Characteristics of ^{90}Sr onto Granite and Tuff

Young-Hwan Cho, Chung-Kyun Park, and Pil-Soo Hahn

Korea Atomic Energy Research Institute
150 Dukjin-dong, Yusong-gu, Taejeon 305-353, Korea

(Received March 28, 1997)

Abstract

Batch sorption experiments were carried out to investigate the sorption characteristics of ^{90}Sr onto domestic granite(HG) and tuff(TF) samples. The effect of three independent variables ([Sr], [Vol/Wt], [pH]) on the sorption was investigated. [Sr] played as the most significant variable for the $^{90}\text{Sr}^{2+}$ sorption onto HG, whereas [pH] had the greatest effect among three variables onto TF. Tuff showed much greater sorption than granite, which was accounted for their differences in mineralogical properties. The selectivity of ^{90}Sr was much lower than that of ^{137}Cs .

1. Introductions

Interactions between radionuclides/geological media in groundwater condition are known to be an important retardation mechanism for the radionuclide release from a radioactive waste repository[1, 2]. The radionuclide ^{90}Sr ($t_{1/2}=28.6\text{year}$) is one of the key elements in the safety assessment of radioactive waste disposal. ^{90}Sr is a representative divalent radioactive alkaline earth metal ion and is generated from the nuclear reactor as a fission product. In our previous papers, we have shown how the ^{137}Cs sorption is affected by system parameters such as pH, solution volume to solid weight ratio [Vol/Wt] and cesium concentration [3] and ionic strengths[4]. This knowledge is very important to understanding the migration behavior from a repository to its surrounding environment[1]. Here we report the sorption characteristics of ^{90}Sr onto domestic granite and tuff media.

2. Experimental

The experimental detail is almost the same as described in our previous paper[3].

2.1. Solids

Granite(denoted as HG) and tuff(TF) rock samples 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 experiments. Rocks were characterized by X-ray diffraction method. Each diffractogram shows typical diffraction pattern of granite and tuff, respectively(Fig. 1).

2.2. Solutions

A synthetic groundwater with composition listed in Table 1 was used[5]. Inactive SrCl_2 was used to

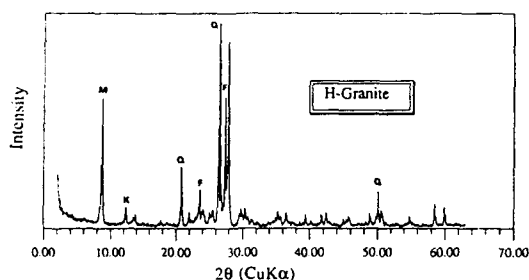


Fig. 1. X-ray Diffractogram of Granite(HG) Sample

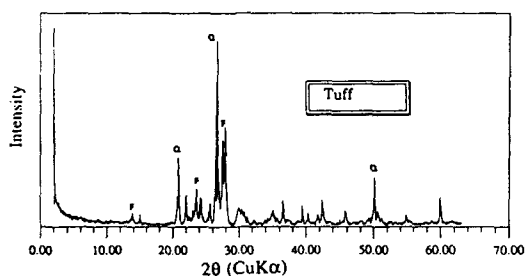


Fig. 2. X-ray Diffractogram of Tuff(TF) Sample

Table 1. Chemical Composition of Synthetic Groundwater

Components	mL/g
Na ⁺	8.3
K ⁺	3.5
Mg ²⁺	3.9
Ca ²⁺	13.0
Cl ⁻	5.0
SO ₄ ²⁻	8.6
NO ₃ ⁻	0.62
F ⁻	0.19

make concentrations of 10^{-5} , 10^{-6} and 10^{-7} mole/L in the appropriate synthetic groundwater solution. Each solution was spiked with $^{90}\text{Sr}^{2+}$ as a tracer.

2.3. Zeta Potential Measurement

Zeta potential of rock powders 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 500mL of 0.01 and 0.001 Mole NaCl solutions, with continuous bubbling of nitrogen 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 N HCl and 0.1 N NaOH to cover a range from 4 to 10 in approximately 0.5pH unit increments.

2.4. Experimental Procedure

Each of the solid samples was equilibrated with 10mL of the appropriate solution for 4 weeks. The vials were routinely shaken to ensure exposure of the rock mineral surface to the solution. All procedures were conducted under the normal laboratory conditions. Aliquots of the contacting solutions were taken after the reaction period and aged for 2 weeks for radiometric analysis. The aqueous phase was separated from the solid by gravity settling, which gives the same result by centrifugation method. Initial and equilibrium ^{90}Sr activities were measured with a LSC (Liquid Scintillation Counter, Packard Tri-Carb 1900 TR Model). A Packard SciNT-A-XF was used as a scintillator for cocktail solution.

The distribution coefficient, $K_d(\text{mL/g})$, was determined from the equation

$$K_d = (V/W_t)[(C_0 - C_i)/C_i]$$

where, V : volume of solution (mL)

W_t : weight of solid (g)

C_0 : initial [Sr] concentration (cpm)

C_i : [Sr] concentration after the contact period (cpm)

3. Results and Discussion

3.1. Experimental K_d

The measured $K_d(\text{Sr})$ values for various combina-

Table 2. The Measured $K_d(\text{Sr})$ Values for Various Combinations of Parameter Condition.

Exp. Variables			Granite(HG)		Tuff(TF)	
pH	log[V/wt]	log[Sr]	Kd(mL/g)		Kd(mL/g)	
	mL/g	Mole/L	$K_d(\text{Sr})$	$K_d(\text{Cs})$	$K_d(\text{Sr})$	$K_d(\text{Cs})$
6.0	1.0	-6	3.0	12.0	19.5	53.2
6.0	1.5	-7	5.9	42.7	24.6	496
6.0	1.5	-5	1.9	5.1	14.4	27
6.0	2.0	-	0.1	14.3	3.4	210
8.0	1.0	-7	4.4	40.4	21.8	251
8.0	1.0	-5	4.0	5.6	29.4	22.6
8.0	1.5	-6	0.1	12.5	15	90
8.0	2.0	-7	2.0	48.1	52.9	773
8.0	2.0	-5	22.8	5.5	21.2	41.6
10.0	1.0	-6	3.9	9.6	32.7	73
10.0	1.5	-7	7.5	37.7	39.8	755
10.0	1.5	-5	14.3	4.3	39.9	41.7
10.0	2.	-6	0.1	14	19.5	297

tions of parameter conditions are given in Table 2. The K_d values for ^{137}Cs measured at the same experimental conditions are also given for comparison[3].

3.2. Comparison of Sorption Capacity Between Granite and Tuff

The K_d Value in this study can be regarded as a measure of relative affinity for different rocks. It is determined by both the properties of the sorbing ion and rocks, with the solution playing as important intermediary role.

Igneous rocks are composed of major rock forming minerals such as quartz, feldspars, micas, amphiboles, pyroxenes and olivine, and they have different sorption properties. The sorption characteristics of a rock depends largely on the composition of these minerals. Therefore, the different sorption behavior of granite and tuff could be attributed to their differences in mineralogical properties. Here, one need to understand the sorption properties of each rock-forming minerals in order to fully interpret the sorption characteristics of rocks.

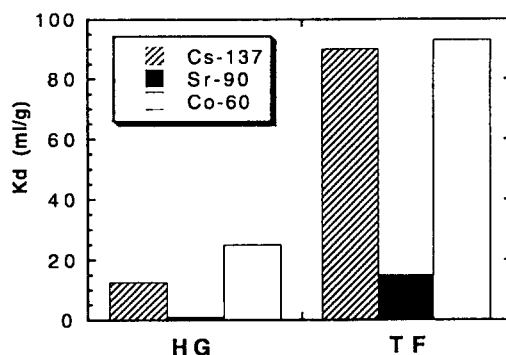


Fig. 3. The Sorption Extents of ^{90}Sr , ^{137}Cs and ^{60}Co onto HG and TF and Variations in K_d Under Various Experimental Conditions

In the case of Sr^{2+} sorption onto geological materials, the driving force of sorption is mainly electrostatic in nature that is due to coulombic forces of attraction between negatively charged mineral surfaces and Sr^{2+} ion. Therefore, electrical properties at solid/solution interfaces play a key role in ion sorption.

The difference in mineralogical composition qualitatively accounts for the different sorption capacity between HG and TF. Granite is a representative crystalline rock that is rich in quartz(SiO_2) mineral. The granite used in this study is commonly found fresh one that consists mainly of quartz, feldspar and mica minerals. In general, oxide minerals such as silica(SiO_2), alumina(Al_2O_3) do not have permanent structural charge which causes relatively poor sorption of cation. In contrast to granite, tuff is classified as volcanic rock that is silica poor, and dominated by feldspars, pyroxenes, and olivine. These are more favorable for cation sorption from the mineral structural point of view[4, 6]. Autoradiographic study which visually shows the selective sorption on certain minerals in granitic rock coupons supports our observed results[8]. Figure 3 clearly shows the larger sorption capacity of TF compared with that of HG for three chemically different radioactive metal cations[9].

3.3. pH Dependence

pH affects the cation sorption in two different ways. Firstly, the change in pH value alters the chemical forms of a metal (speciation), usually by hydrolysis reaction. Different species have different reactivity toward the sorption sites. The dominating Sr species is Sr^{2+} in common groundwater condition, and may exist partly as sulfate or carbonate complexes in groundwaters. The change in pH significantly affected the sorption of Sr on both type rocks, especially acting as a key parameter for tuff among three variables. This is comparable to the insignificant effect for Cs sorption[3] under the same experimental condition: the speciation of Cs is almost independent of pH. The pH effect is remarkable especially for the sorption of multivalent cations such as transition metals and actinides. Secondly, the change in pH alters the electrical properties of the surface, at which sorption reaction actually occurs. Fig. 4 5 illustrate the zeta potentials of granite and tuff samples, respectively, as a function of pH in the presence of NaCl electrolyte. The zeta potential is greatly affected by the small change in pH. 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 pH dependency 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[10]. Another interesting observation is that the zeta potentials of these two rocks are not much affected by the ionic strength, indicating that these Na^+ and Cl^- ions are the indifferent electrolytes[10]. It is generally known that the sorptive nature of the indifferent ions is not specific but electrostatic. Since the nature of Sr^{2+} sorption is mainly electrostatic, the sorption behavior of Sr^{2+} will be influenced by the presence of the supporting elec-

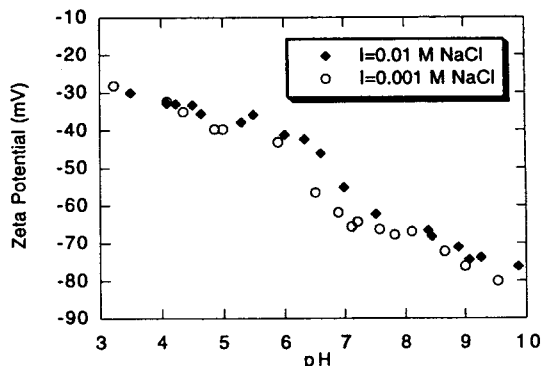


Fig. 4. Zeta Potential of Granite(HG) with Varying pH

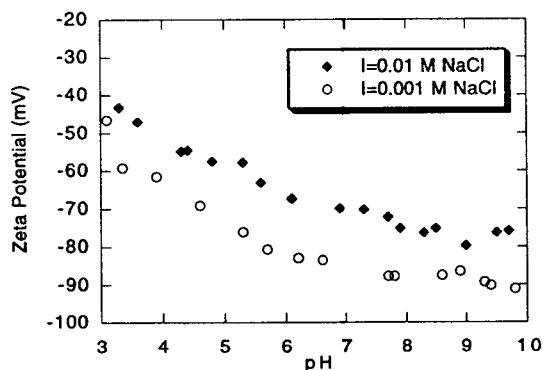


Fig. 5. Zeta Potential of Tuff(TF) with Varying pH

trolytes. Although pH_{zpc} (zero point charge) for two rock surfaces are not observed, it is obvious that pH_{zpc} of TF is lower than that of HG if the surface potentials at lower pHs are extrapolated. It can be expected that the tuff surface provides more favorable conditions for electrostatic sorption, resulting in higher Sr^{2+} and Cs^+ sorption onto TF than onto HG. However, there is no unifying principle governing the sorption of divalent cations such as Sr^{2+} onto rocks. In order to fully interpret the pH dependency, one has to study for single rock-forming minerals.

3.4. Concentration Dependence

The relationship between the amount of a substance adsorbed at constant temperature and its con-

centration in the equilibrium solution is called the adsorption isotherm. The principle governing adsorption at low solution concentration is Henry's Law, which gives a linear adsorption isotherm. The linearity is normally observed only at very low concentrations. At higher concentrations, adsorption is below what is expected from Henry's Law, a result arising partly by the filling up of a significant number of the total adsorption site. This is normally the observed phenomena for the sorption of metal ions onto geomedial[3, 4, 11]. This effect is remarkable for Cs^+ sorption[3]. Detailed analysis of the data in Table 2 showed significant effect of $[\text{Sr}]$ on ^{90}Sr sorption onto both rocks. The Freundlich adsorption takes this into account and is particularly suitable as an empirical isotherm for heterogeneous surfaces, enabling to fit the experimental data reasonably well over a fairly broad range of concentrations.

3.5. [Vol/Wt] Ratio Dependence

In many sorption studies, K_d was known to be dependent on solution volume to solid weight ratio. This effect is not so simple to explain. However, it is commonly the observed phenomena in the sorption of trace elements on heterogeneous media. Lieser has suggested that the Freundlich isotherm implies a dependence of K_d on $[\text{Vol}/\text{Wt}]$, especially for multicomponent systems[12]. This observation may be attributed to the sorption of one species in solution on different sorption sites of a solid medium.

3.6. Selectivity between ^{137}Cs and ^{90}Sr

The K_d of a radionuclide is a measure of its relative affinity for different solid phases. It is determined by the properties of the sorbing ion, given other conditions are the same. The K_d sequence can provide a qualitative clue to the microenvironment of the adsorbed ion. For most monovalent cations such as alkali metal(Cs^+), adsorption is usually nonspecific and

therefore depends directly on the surface properties of solid phases. In the whole ranges of experimental conditions, Cs^+ was more selectively sorbed onto HG and TF than Sr^{2+} . The high selectivity of Cs^+ over Sr^{2+} is attributed to their differences in physical and chemical behavior. When the solid phase and solution condition are given, physico-chemical properties of sorbing ions play a key role in sorption. In general, the larger cation, Cs^+ , is more polarizable and more readily allow distortion to their hydration spheres than small cations. Whereas the M^{2+} , alkaline earth metal ion, is smaller and considerably less polarizable[13], resulting in easier sorption for Cs^+ than Sr^{2+} . Figure 3 illustrates the different affinity of ^{90}Sr , ^{137}Cs and ^{60}Co for HG and TF. However, in order to fully understand the sorption behavior of rocks, it is highly recommended to study for single rock-forming minerals.

4. Summary

The sorption behavior of ^{90}Sr onto domestic granite and tuff was studied. The results can be summarized as follows :

- The K_d of ^{90}Sr onto tuff was much greater than that onto granite, which is attributed to their difference in mineralogy.
- The sorption of ^{90}Sr is pH-dependent which is mainly due to the change in surface properties of solids.
- The sorption selectivity of ^{90}Sr onto granite and tuff is lower than that of ^{137}Cs and ^{60}Co .
- The sorption characteristics of a rock can be properly interpreted by considering that of rock-forming minerals. In order to fully understand the sorption behavior of rocks, one need to study single rock-forming minerals such as quartz, feldspars and mica, etc.

References

1. N.A. Chapman, I.G. McKinley and M.D. Hill *The*

- Geological Disposal of Nuclear Waste*, John Wiley & Sons(1987)
2. OECD/NEA "Radionuclide Sorption from the Safety Evaluation Perspective", *Proceedings of an NEA Workshop, Interlaken, Switzerland* (1991)
 3. Y.H. Cho, P.S. Hahn and S.W. Park "Studies on the sorption Characteristics of ^{137}Cs onto Granite and Tuff", *J. Korean Nucl. Soc.*, 27, 25-32 (1995)
 4. Y.H. Cho, C.H. Jeong and P.S. Hahn "Sorption Characteristics of ^{137}Cs onto Clay Minerals : Effect of Mineral Structure and Ionic Strength", *J. Radioanal. Nucl. Chem., Article* 204, 33-43(1966)
 5. D.W. White, et al. "Chemical Composition of Sub-surface Waters", *U.S.Geological Survey Professional Papers*, No. 440-F (1963)
 6. B. Torstenfelt, K. Anderson and B. Allard, "Sorption of Strontium and Cesium on Rocks and Minerals", *Chemical Geology* 36, 123-137 (1982)
 7. P. Rafferty, S.Y. Shiao, C.M. Binz and R.E. Meyer "Adsorption of Sr(II) on Clay Minerals : Effects of Salt Concentration, Loading and pH" *J. Inorg. Nucl. Chem.* 43, 797-805 (1981)
 8. D.C. Kamineni, K.V. Ticknor, T.T. Vandergraaf "Occurrence, Composition and Radionuclide Sorption Characteristics of Illite from a Fractured Granite Pluton, Southeastern Manitoba, Canada", *Clay Minerals* 21, 909-924(1986)
 9. ^{90}Co data to be published. The experimental conditions are the same for three radionuclides.
 10. R.J. Hunter "Zeta Potential in Colloid Science", Chapter 6, Academic Press(1981)
 11. J.J. Mahoney, D.L. Langmuir "Adsorption of Sr on Kaolinite, Illite and Montmorillonite at High Ionic Strengths", *Radiochim. Acta* 54, 139(1991)
 12. K.H. Liser, T.H. Steinkoff "Sorption Equilibria of Radionuclides or Trace Elements in Multicomponent Systems" *Radiochim. Acta* 47, 55(1989)
 13. F.A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry", John Wiley & Sons, pp.255 (1980)