Sorption Properties of Radionuclides onto a Granite : Sorption Reversibility and Concentration dependency

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1. Introduction

To describe the migration of radionuclides in geologic media, sorption types and migration mobility are of importance. Migration mobility can be determined by the sorption capacity and reversibility. The reversibility of sorption reflects the ability of the sorbed 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 competition ions. Sequential chemical extraction techniques have been developed for this purpose. the sorbed radionuclides can be extracted from the soil and rock by using appropriate reagents. Geologic media may consist of a variety of sorbing minerals with their own sorbed site preferences for individual solutes and each with a different sorption capacity. Sorption of radionuclides occurs through various types of reactions onto geologic media. The strength of binding is dependent on the sorption mechanism.

2. Experimental

2.1 Sorption Experiment

A domestic granite was sampled near the southeast coast in Korea. Regarding the content of secondary minerals, the granite sample is somewhat weathered. A synthetic groundwater(SGW) was used to simulate the chemical composition of the natural groundwater where the granite was sampled. Granite sample was crushed and sieved to have particle size of ø1-1.5

Granite particles had been in contact with SGW for more than one month to attain pre-equilibrium between two phases before sorption experiment was carried out in a closed system. Ten grams of the granite and 250ml of SGW sere prepared in a glass flask with a cap. For sorption isotherm experiment, the SGW contains nonradioactive CsCl, $CoCl_2$ and $SrCl_2$ in the concentration range of 10^{-3}-10^{-7}M with radioactive ^{60}Co, ^{85}Sr and ^{137}Cs about 0.1μCi/ml as tracers. These radioactive tracers take to the concentration range of less than 10^{-8} M. the flask was shaken in a water bath at 25 during the experiment. 5 ml of the contacted solution was sampled at an appropriate time interval and centrifuged for 20 minutes at 3000rpm.

2.2 Sequential Chemical Extraction

(1) The radionuclide-sorbed granite was kept in contact with tracer free SGW for two weeks to measure the amount of reversibly sorbed radionuclide in SGW condition. 5 *ml* of the solution was sampled at the predetermined time intervals and its radioactivity was measured.
(2) The recovered radionuclide-sorbed granite was mixed with 250 *ml* of 0.5 M $CaCl_2$ solution, free of the radioactive tracers.
(3) The mixture was then separated from the $CaCl_2$ solution and further contacted with 250 *ml* of 0.5M KCl solution.
(4) The similar procedure was repeated with a solution mixture containing 0.1 M potassium tetraoxalate and 0.1 M hydroxylamine hydrochloride(KTOX).
(5) The remaining radioactivity in the granite sample was then counted to determine the amount of fixed radionuclide.

3. Experimental Results and Discussion

3.1. Sorption Rate and Sorption Capacity

The results of the sorption kinetics for ^{60}Co, ^{85}Sr and ^{137}Cs are shown in Fig.1. The concentration of the tracers are decreased rapidly within 20 hours and goes down slowly afterward with time scale of weeks. Thus the curves of 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 tracers penetrate through the micopores of the rock to the inner surface of the rock. Diffusion process would be the rate controlling step at this later stage.
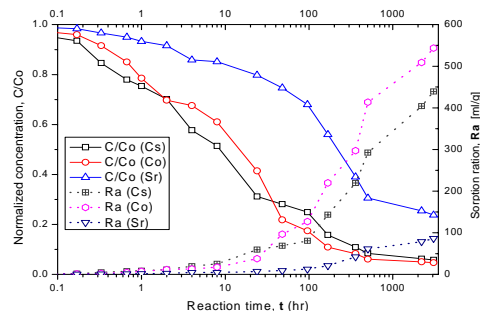

Fig.1. Sorption rate and Sorption ratio with time

In order to assess the effects of concentration on sorption, isotherms for three species are plotted in the concentration range of 10^{-3}-10^{-11}M. The results are

interpreted with 2 isotherms; Langmuir and Freundlich type and plotted in **Fig.2.** It is well fitted with the experimental data except at high concentration range, in which somewhat deviation is observed as the solute is going to a saturated state of sorption. That is, radionuclide sorbs more than monolayer sorption of Langmuir type and less than Freundlich type. As the denominator approaches to 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 K_d at low concentration. In the expression of the Freundlich isotherm, exponent n is an indicator of linearity. As n approaches to 1, the sorption system becomes linear. The isotherm curve of Sr shows almost linear relationship in the concentration range of 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. The isotherm curves of ^{60}Co and ^{137}Cs are not linear.
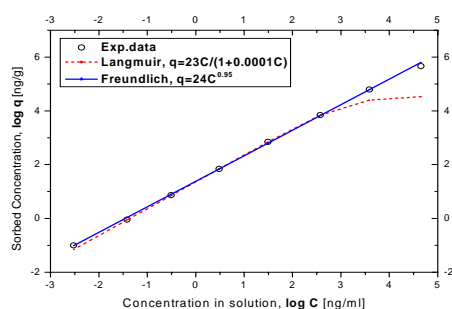

Fig.2. Isotherm curves of Sr

3.2. *Desorption with Sequential Chemical Extraction*

The portion of strontium extracted by $CaCl_2$ solution is near to 90% of the total sorbed amount. 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, the present results imply that sorption of strontium on the granite is mainly attributable to the ion exchange.

Co^{2+} separates proton from the covalent bond at the surface and associate with this site. It is thus confirmed that radionuclides associated with ferro-manganese oxides or oxyhydroxides are extracted selectively at 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 initially sorbed amount remained on the granite after all extracting steps. It is therefore possible to infer that cobalt sorbs on the granite mainly by the 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 still remained on the granite after all these extraction steps.. Therefore, the experimental results suggest that primary sorption type of cesium onto the granite is the

irreversible fixation, and secondary one is the ion exchange reaction. Thus Cs^+ must be the strongest ion for sorption and consequently difficult to desorb among the three radionuclides. Experimental results of other investigators also support this argument.

3. Conclusion

Sorption reaction was occurred mainly 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 faster than those of cobalt and cesium to a quasi-equilibrium state. Both of Langmuir and Freundlich isotherms are valid representation for describing concentration dependence of radionuclides sorption onto rock. Langmuir isotherm has an advantage to guess the sorption capacity, while Freundlich isotherm is advantageous in showing nonlinearity. Sr shows a linear isotherm, while Co and Cs^+ show nonlinear ones. It is turned out that the sequential chemical extraction technique is an effective method to investigate the sorption types of radionuclides on the granite. Therefore, the order of sorption reversibility and migration mobility for the three radionuclides was $Sr^{2+} > Co^{2+} > Cs^+$ in the granite.

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