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Sorption of Uranium (VI) onto the Natural Fracture Surface of Granite Rock: A Kinetic Study

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Abstract

A surface sorption experiment of U(VI) onto the natural fracture surface of granite rock was carried out in order to investigate the kinetic sorption behavior of U(VI) as a function of pH and to determine the sorption capacity of the natural fracture surface of a domestic granite rock. It is found that the amount of U(VI) sorbed onto the natural fracture surface of granite strongly depends on the pH but the sorption rate does not depend upon the pH. The experimental results are fitted with a two step first-order kinetic sorption model and the results show a good agreement between the experimental results and the model. The sorption of U(VI) onto the natural fracture surface shows a fast initial sorption behavior and then slower sorption after 1 day. This slower second-step of the U(VI) sorption may be due to the diffusion-controlled sorption and mineral dissolution of the natural fracture surface.

1. Introduction

The study of the sorption of the radionuclides onto the geological media such as rocks or minerals has been an important part of the safety assessment of deep geological disposal of radioactive waste [1]. Sorption data for radionuclides in contact with minerals typical of those found in water-bearing fractures in rock are needed in the safety assessment of deep geological repositories. Furthermore, an understanding of the factors that influence the sorption characteristics of the radionuclides is essential when we apply an empirically derived sorption value outside the range of the experimental parameters.

Based on laboratory migration experiments of radionuclides in a single fracture, two types of retardation mechanisms were proposed [2]: (1) surface sorption at the fracture walls and (2) diffusion and bulk sorption into the rock matrix. Both types of sorption reactions were assumed to be fast and reversible processes which can be modeled using distribution coefficients obtained by equilibrating solutions containing the radionuclides of interest with the rock surface or rock matrix, respectively [2, 3]. There is a large potential for bulk sorption due to the large volumes of rock matrix available relative to fracture surfaces [4]. However, the diffusion rates into the rock matrix are generally much lower than the flow rates within an open fracture. Generally speaking, surface sorption may prevail at small timescales, whereas bulk sorption may be dominant at larger geological timescale [5].

A number of reviews on the sorption have been performed in the past, usually with the intention of recommending distribution coefficients of K_d values for various radionuclides [6-11]. Although these K_d values have been used in performance assessment model calculations, there are uncertainties from the choice of K_d values for individual radionuclides [12]. Among these uncertainties, the uncertainty that arises from the scaling of K_d values measured for rock particles to the values expected for the intact rocks or rock fractures is very important in safety assessment or performance assessment calculations. Most of the sorption experiments for rock materials have been performed using crushed rocks [11, 13-15], and only a limited number of sorption studies were performed for rock coupons, or rock cores [16-18].

Therefore, the purpose of this study is to study the sorption behavior of U(VI) onto the natural fracture surface of granite of a domestic granite rock as a function of pH and contact time. For this purpose the kinetics of U(VI) sorption onto the natural fracture surface is investigated.

2. Surface Sorption Experiment

The granite rock used in the study was sampled from a granite quarry site located at Dukjeong-myun, Kyongki-do, Korea. Rock core samples chosen for the surface sorption experiments were sections of drilling cores containing natural fracture surface on one side. The drill cores were cylindrical, about 10 cm in height and about 10 cm in diameter.

The mineralogical composition of the natural fracture surface was determined by X-ray diffraction (see Fig. 1). In this study, U(VI) in the nitrate form ($UO_2(NO_3)_2 \cdot 6H_2O$) was used as a sorbing nuclide. Under oxidizing geochemical conditions, the most stable valence of uranium is U(VI), which exists in acidic aqueous solutions as the uranyl ion, UO_2^{2+} [14]. The concentration of uranium was measured by ICP-MS (Varian, Ultramass 700). The surface area of the natural fracture surface was measured using a 3-dimensional laser scanner (Inter Tech Co., Ltd) (see Fig. 2). The surface area of the natural fracture surface was measured as 79.02 cm^2.

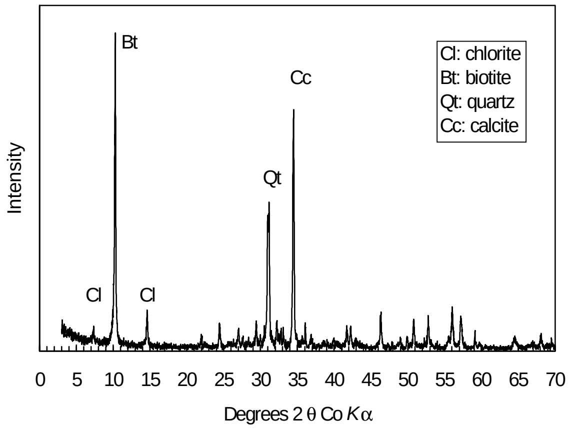

Fig. 1. X-ray diffraction result for the minerals in the natural fracture surface

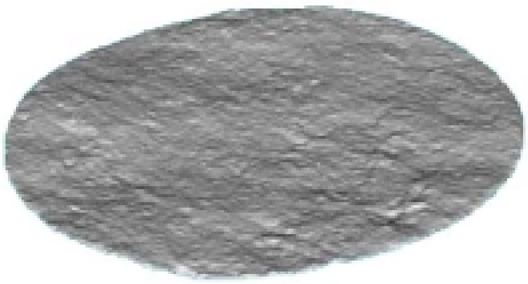

Fig. 2. 3-dimensional laser scanning results for the natural fracture surfaces

An experimental setup for the surface sorption experiment used in this study is shown in Fig. 3. Before granite cores were mounted to the sample holder they were kept in contact with $0.01\ \mathrm{mol/L}$ $NaClO_4$ solution, which is adjusted to a desired pH, for about one month. The granite cores were then mounted to the inflow and outflow plenums. Tracer solution was pumped directly to the space between the granite core and acryl cap.

Prior to each experiment, pH-adjusted $0.01\ \mathrm{mol/L}$ $NaClO_4$ solutions at pH 5.5, 7.0 and 8.5 were circulated through the experimental apparatus for at least 24 hours at a specified flow rate. Before injecting the uranium tracer solutions, the solutions were adjusted to desired pHs (i.e., pH 5.5, 7.0 and 8.5) using $NaOH$ or $HClO_4$ solutions. The tracer solution was then pumped to a narrow space between the granite core and the acryl cap at a flow rate of about 1.0 $\mathrm{cm^3/min}$. All sorption experiments were performed at about 23±2 ^{o}C under an ambient condition. The surface sorption coefficients (K_a) were determined in a kinetic process for 2 weeks. The amount of U(VI) sorbed on the tube wall and acryl cap was checked by leaching the uranium with a nitric acid solution after the sorption experiments and considered in the estimation of the amount of U(VI) sorbed on granite.

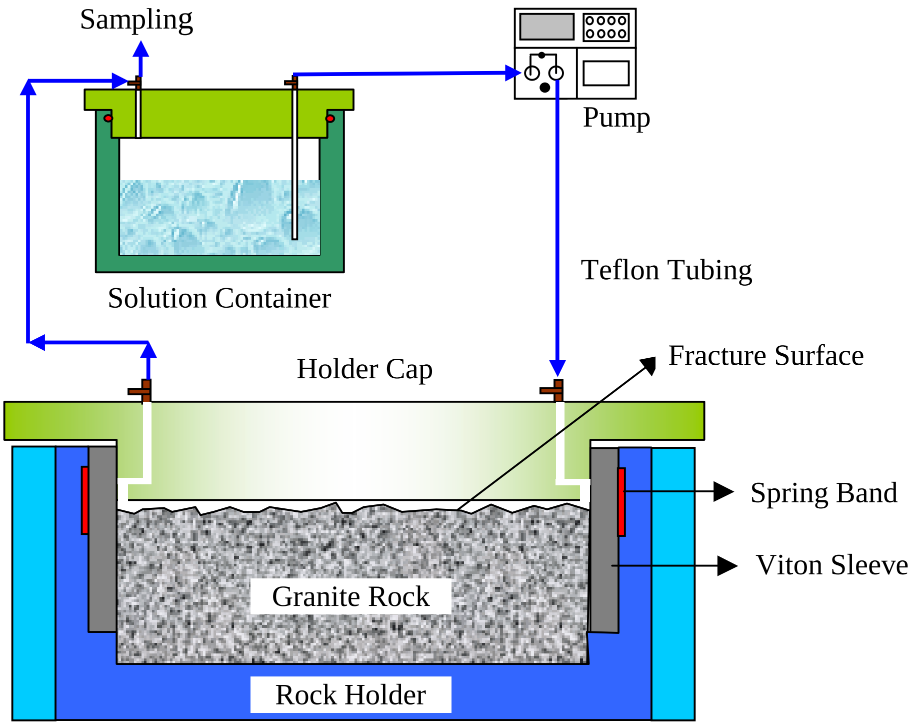

Fig. 3. Experimental setup for surface sorption of natural rock fracture

3. Results and Discussion

The surface sorption capacity determined experimentally by contacting rock cores with a radionuclide solution is usually expressed as a surface sorption coefficient. In general, the surface distribution coefficient of U(VI) between the solution and the granite surface, K_a (cm), is defined as:

$$K_a = \frac{\text{amount of nuclide sorbed}/\text{surface area}}{\text{amount of nuclide in solution}/\text{solution volume}} \left(\frac{\text{mol}/\text{cm}^2}{\text{mol}/\text{cm}^3}\right) \qquad (1)$$

Accordingly K_a is given as

$$K_a = \frac{[U_s]}{[U_q]} = \frac{([U_0]-[U_q])}{[U_q]} \cdot \frac{V}{A} \qquad (2)$$

where $[U_s]$ (mol/cm^2) is the concentration of sorbed uranium per unit surface area of a granite surface, and $[U_q]$ (mol/cm^3) is the concentration of uranium in the solution phase, $[U_0]$ (mol/cm^3) is the initial concentration of uranium, V (cm^3) is the solution volume in contact with granite surface, and A (cm^2) is the surface area of the granite surface contacting with solution.

The experimental results of the surface sorption of U(VI) onto the natural fracture surface for a static state is shown in Table 1. It is noticed from Table 1 that the equilibrium percent of U(VI) sorbed and K_a are strongly dependent on pH.

Table 1. Static state results of U(VI) sorption onto the natural fracture surface

Test	Sorption type	pH	Percent sorbed (%)	K_a (*cm*)
FS-1	Adsorption	5.5	32.7	2.242
FS-2	Adsorption	7.0	46.6	16.233
FS-3	Adsorption	8.5	24.4	1.150

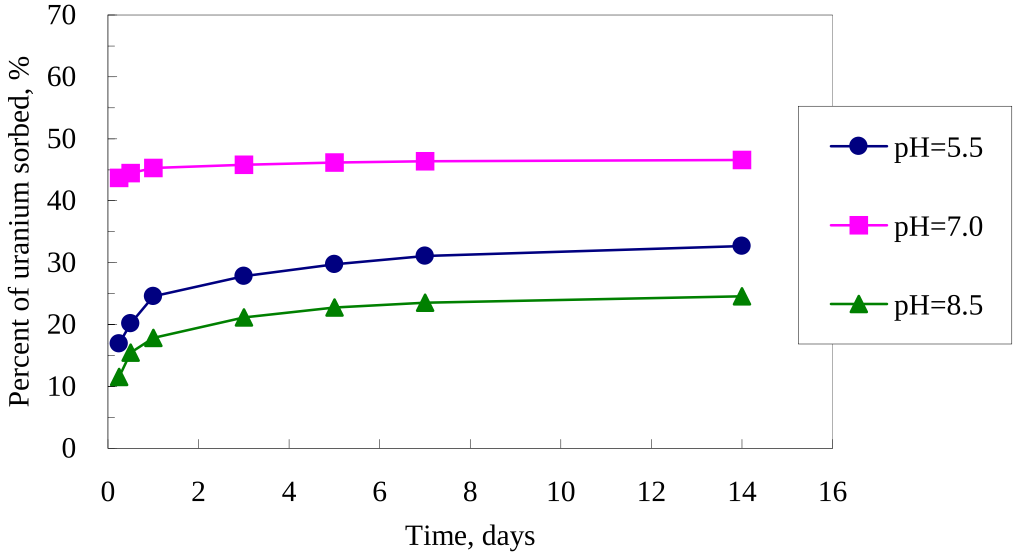

Fig. 4. Kinetic results for U(VI) sorption onto the natural fracture surface

The results of kinetic sorption experiments are shown in Fig. 4 for the natural fracture surface of granite core at different initial pH values of 5.5, 7.0, and 8.5. The results show that it takes about 7 days to reach a constant percent of U(VI) sorbed (i.e., a steady state), regardless of the starting pH.

The kinetic sorption data can be interpreted based on the assumption that the uranium sorbs on the surface of granite according to a first-order reaction. The time dependence can be given as:

$$P_t = P_s\left(1 - e^{-kt}\right) \tag{3}$$

and this equation is linearized as:

$$\ln\left(1 - \frac{P_t}{P_s}\right) = -k \cdot t \tag{4}$$

where P_t and P_s are the percents of uranium sorbed on the fracture surface at time t and at steady state, respectively, k (1/d) is a kinetic sorption rate constant, and t (d) is time in days. The plot of $\ln\left(1 - {P_t}/{P_s}\right)$ against *t* should be linear for a first-order kinetic reaction. The result of the plot for the three different pHs are shown in Fig. 5. The rate constants were estimated by the slopes of lines fitted by least squares methods and listed in Table 2.

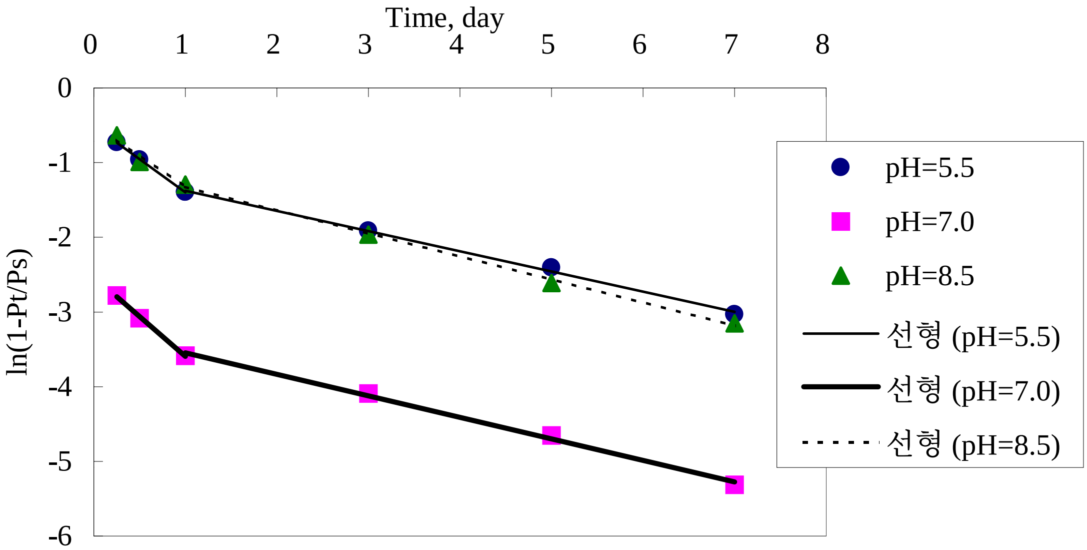

Fig. 5. The first-order kinetic modeling for the sorption of U(VI) onto the natural fracture surface

Table 2. The results of first-order kinetic fitting for the U(VI) sorption onto the natural fracture surface

Test	pH	k_1 (1/d)	k_2 (1/d)
FS-1	5.5	0.888	0.270
FS-2	7.0	1.063	0.288
FS-3	8.5	0.843	0.311

Fig. 5 shows that the initial sorption rate of the natural fracture surface is relatively large and then the sorption rate is reduced slowly after 1 day up to 2 weeks. Thus it can be concluded that a two-step kinetic behavior dominates in surface sorption of U(VI) onto the natural fracture surface of granite. The relatively slower second-step sorption of the natural fracture surface may be due to such effects as a diffusion-controlled sorption onto the fracture surface of micropores and mineral dissolution of the fracture surface [19]. It is also noticed from Table 2 that the reaction rates do not depend upon pH although the amount of U(VI) sorbed onto the fracture surface is greatly dependent on the pH.

4. Conclusions

In this study, we carried out kinetic sorption experiments of U(VI) onto the natural fracture surface of a domestic granite as a function of pH. From our experimental results, the following conclusions are made:

- It takes about 7 days to reach a steady state for the sorption of U(VI) onto the natural fracture surface regardless of the starting pH.
- It is found that the amount of U(VI) sorbed onto the natural fracture surface of granite strongly depends on the pH but the sorption rate does not depend upon the pH.
- Two-step first-order kinetic behavior dominates in the sorption of U(VI) onto the natural fracture surface of granite.
- A relatively slower second-step sorption of U(VI) after 1 day may be due to a diffusion-controlled sorption onto the fracture surface and mineral dissolution of the fracture surface.

Acknowledgement

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