A Parametric Study on the Sorption of U(VI) onto Granite

U(VI)의 화강암 수착에 대한 매개변수적 연구

Min-Hoon Baik, Won-Jin Cho and Pil-Soo Hahn

Korea Atomic Energy Research Institute, 150 Duck-Jin Dong, Yuseong-gu, Daejeon

mhbaik@kaeri.re.kr

백민훈, 조원진, 한필수

한국원자력연구소, 대전광역시 유성구 덕진동 150

Abstract

An experimental study on the sorption of U(VI) onto a Korean granite was performed as a function of the geochemical parameters such as contact time, pH, ionic strength, and carbonate concentration using a batch procedure. The distribution coefficient, K_d, was about 1-200 mL/g depending on the experimental conditions. The sorption of U(VI) onto granite particles was greatly dependent upon the contact time, pH, and carbonate concentration, but insignificantly dependent on the ionic strength. It was noticed that the sorption of U(VI) onto granite particles was highly correlated with the uranium speciation in the solution, which was dependent on the pH and carbonate concentrations. It was deduced from the kinetic sorption experiment that a two-step first-order kinetic behavior could dominate the kinetic sorption of U(VI) onto granite particles. In the alkaline range of a pH above 7, U(VI) sorption was greatly decreased and this might be due to the formation of anionic U(VI)-carbonate aqueous complexes as predicted by the speciation calculations.

요약

국산 화강암에 대한 U(VI) 수착에 대한 실험적 연구를 지화학적 매개변수들인 접촉시간, pH, 이온강도, 탄산염 농도 등의 함수로 회분식으로 수행하였다. 국산 화강암에 대한 U(VI)의 수착의 분배계수 K_d는 실험 조건에 따라 약 1-200 mL/g의 값의 범위를 가지는 것으로 나타났다. 화강암 입자에 대한 U(VI)의 수착은 접촉시간, pH 및 탄산염 농도 등에는 크게 의존하였으나 이온강도에는 크게 의존하지 않는 것으로 나타났다. 화강암 입자들에 대한 U(VI)의 수착은 용액에서 pH와 탄산염의 농도에

의존하는 우라늄 화학종과 밀접한 관계가 있음을 알 수 있었다. 또한 속도론적 수착 실험에 의하여 2단계 일차식 속도론적 거동이 화강암 입자들에 대한 우라늄의 속도론적 수착을 지배할 수 있는 것으로 유추되었다. pH 7 이상의 알칼리 영역에서 화강암에 대한 우라늄의 수착이 크게 감소되었는데 이는 화학종 계산에 의해 예측된 바에 따라 음이온의 U(VI)-탄산염 복합체 형성에 기인하였을 것이다.

중심단어 : 화강암, 수착, 우라늄(VI), 지화학적 변수, 분배계수

I. Introduction

During the last few years, safety assessments have been performed at KAERI (Korea Atomic Energy Research Institute) as a part of the high-level radioactive waste disposal technology development program. The disposal concept being conceived is to encapsulate spent fuel in corrosion resistant containers [1]. The spent fuel packages will then be disposed in an underground facility located at about 500 m below the surface in a crystalline rock. In Korea, no site for an underground repository has been specified for high-level radioactive wastes, even for low- and intermediate-level radioactive wastes. Therefore, a safety assessment has been performed for a generic site with crystalline rocks such as granite.

One of the major tasks in safety assessments is the prediction of the radionuclide migration behavior in the far-field, which takes account of the sorption characteristics of various radionuclides. Thus, the sorption study of radionuclides in the far-field is an important part of the overall investigations needed for the safety assessment of potential sites for radioactive wastes disposal [2]. In general, the sorption has been empirically characterized by the distribution coefficient, K_d, which describes the equilibrium partitioning of a solute between the solid and solution phases due to sorption. A number of reviews of sorption literature have been performed in the past, usually with the intention of recommending K_d values for various elements [3-7]. In fact, the current approach is to treat K_d as an empirical parameter and K_d is representative only of the specific conditions being studied. Therefore, an understanding of the factors that influence the sorption characteristics of the radionuclides is essential when we apply the empirically derived sorption value outside the range of the experimental parameters.

Therefore, the aims of this study are to determine the K_d values of U(VI) onto a domestic crushed granite by performing batch sorption experiments, to investigate the effects of the geochemical parameters such as contact time, pH, ionic strength, and carbonate concentration, and to analyze the sorption behavior of U(VI) correlated with the aqueous speciation of U(VI).

II. Experimental

1. Materials and Apparatus

The granite rock used in the study was sampled from a domestic granite quarry site located at Dukjeong-myun, Gyeonggi-do, Korea. The crushed granite particles were prepared by crushing the bulk granite rocks and sieving the crushed particles. The granulometric fraction, which was in the range of 0.15 mm to 0.3 mm in diameter, was taken for the sorption experiments. Mineralogical composition of the crushed granite rock was determined by point counter methods using electronic microscope and

X-ray diffraction. The crushed granite was mainly composed of quarts, plagioclase, K-feldspar, biotite, hornblende, and a small amount of the sphene and opaque phases [7].

In this study, U(VI) in the nitrate form $(UO_2(NO_3)_2 \cdot 6H_2O)$ was used, and the concentration of the uranium was measured by ICP-MS (Varian, Ultramass 700). The pH of each solution was adjusted by NaOH and $HClO_4$, and measured by Ion Analyzer EA-940 (ORION). Anaerobic sorption experiments were performed in a glove box, having the dimensions of $210 \times 80 \times 60$ cm, and N_2 gas of a high purity (99.999 %) was used as an inert gas (see Fig. 1). A column filled with LiF pellets was installed to remove CO_2 from the air in the glove box by circulating the air using a gas-circulating pump. In order to maintain the temperature in the glove box at 25 °C, the air was cooled by a cooling water system. The concentration of CO_2 in the glove box was analyzed by GC (DID, HP Agilent) and the almost CO_2 -free conditions were verified (< 1.0 ppm).
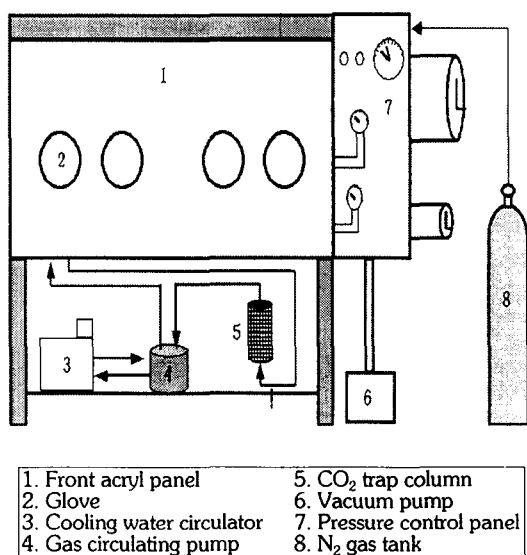

1. Front acryl panel	5. CO_2 trap column
2. Glove	6. Vacuum pump
3. Cooling water circulator	7. Pressure control panel
4. Gas circulating pump	8. N_2 gas tank

Fig. 1. Schematic diagram of the glove box filled with inert N_2 gas for the anaerobic sorption experiment

2. Method

The sorption of U(VI) onto the crushed domestic granite particles was studied as a function of pH, ionic strength, and carbonate concentration using a batch procedure. The experiments were performed at about 25 ± 2°C under an ambient and controlled condition. All the solutions used were made of AR grade reagents and high purity water with the resistivity of 18.3 MΩ-cm (Milli-Q, Millipore). In order to maintain a constant ionic strength in the system, an appropriate concentration of $NaClO_4$ was used as an electrolyte. One gram of the crushed granite was transferred to a 30 mL PP (polypropylene) flask and contacted with 20 mL of $NaClO_4$ solution with an appropriate concentration. The flask was adjusted to a desired pH using 0.1 and 1.0 M NaOH or $HClO_4$ solutions, respectively. When the pH was stabilized, 10^{-3} M $UO_2(NO_3)_2 \cdot 6H_2O$ (MERCK) stock solution (at pH 3) was added to the flask to achieve an initial uranium concentration of 10^{-6} M. We also conducted kinetic sorption experiments to investigate the effect of contact time of U(VI) with granite particles using the same electrolyte at three different initial pH values of 5.5, 7.0, and 8.5.

3. Control of Carbonate Concentration

To control the carbonate concentrations, the carbonate concentration was varied from 10^{-4} M to 10^{-2} M using $NaHCO_3$. For the sorption experiments in the ambient condition, water-saturated air was bubbled through the solutions in order to maintain an equilibrium with atmospheric CO_2 . On the other hand, the glove box system was used for the sorption experiments in the anaerobic conditions.

III. Results and Discussion

1. Distribution Coefficient

In general, the sorption is empirically

characterized by the distribution coefficient K_d (mL/g), which describes the equilibrium partitioning of a solute between the solid phase and the solution phase:

$$K_d = \frac{[U_s]}{[U_q]} = \frac{([U_T]-[U_q])}{[U_q]} \cdot \frac{V}{M}$$

where $[U_s]$ (mol/g) and $[U_q]$ (mol/mL) are the concentrations of the solute in the solid phase and in the solution phase, respectively, $[U_T]$ (mol/mL) is the initial concentration of U(VI), V is the solution volume (mL) in contact with the crushed granite particles, and M (g) is the mass of the crushed granite particles used.

2. Effects of Contact Time

We conducted kinetic sorption experiments to determine the change of the U(VI) sorbed over time at three different pH values of 5.5, 7.0 and 8.5. The experimental results are shown in Fig. 2. Fig. 2 indicates that it takes over 4 days to reach a steady state (or an equilibrium condition). The time needed for the equilibrium of the uranium sorption onto granite is relatively longer than that of the other geological minerals [8]. In some instances, however, even longer timescales have been required for equilibrium [8]. This longer time needed for equilibrium may be due to the
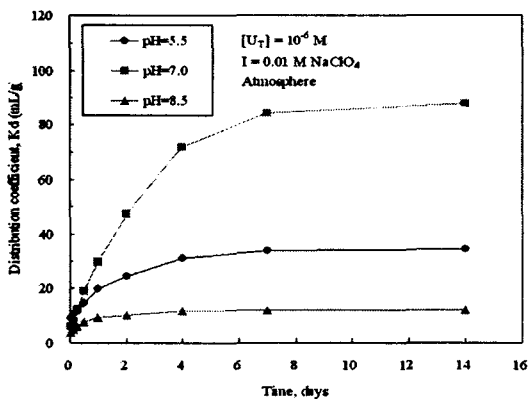
composite mineralogical composition of the granite particles.

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

$$P_t = P_s(1-e^{-kt})$$

and this equation is linearized as:

$$\ln\left(1-\frac{P_t}{P_s}\right) = -kt$$

where P_t and P_s are the percentages of uranium sorbed on the granite at time t and at steady state, respectively, k (1/day) is a kinetic sorption rate constant, and t is time in days. The plot of $\ln(1-P_t/P_s)$ against t should be linear for a first-order kinetic reaction.

It is shown in Fig. 3 that the sorption of U(VI) onto granite particles follows a two-step kinetic sorption process. Hsi and Langmuir [9] also concluded that uranium adsorption occurs in two steps. Recently, Baik et al. [10] have studied the kinetic behaviors of U(VI) sorption on granite surfaces using the linearlization technique proposed by Jannasch et al. [11]. They concluded that a two-step first-order kinetic behavior dominated the sorption of U(VI) onto granite particles [10]. We

Fig. 2. The effect of contact time on the sorption of U(VI) onto granite particles
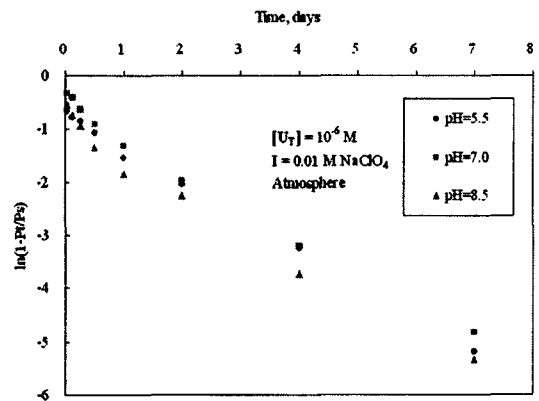

Fig. 3. The linearization plot of the kinetic U(VI) sorption on granite depending on the pH.

noticed that the sorption reaction rates did not greatly depend upon pH although the surface sorption coefficients of U(VI) sorbed onto the granite surfaces was dependent on the pH.

3. U(VI) Speciation

The chemical speciation of uranium was calculated by the geochemical code MINTEQA2 [12] with the thermodynamic data from Table 1 in order to provide information on the probable uranium speciation in the solutions depending on the atmospheric conditions. The distribution of the aqueous species of 10^{-6} M U(VI) in 0.01 M $NaClO_4$ solution equilibrated with air ($P_{CO_2}=10^{-3.5}$ atm) at 25 °C is given in Fig. 4.

Free uranyl ion UO_2^{2+} is the dominant species in the acidic pH range up to 5. $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ are the dominant species in the pH up to 6 and then the ternary anionic complex $(UO_2)_2CO_3(OH)_3^-$ in the pH range of 6 to 8. In the alkaline pH range over 8, $UO_2(CO_3)_3^{4-}$ is the dominant species. On the other hand, the calculated distribution of the aqueous species of U(VI) in the anaerobic condition is given in Fig. 5. As shown in Fig. 5, the speciation of U(VI) in the anaerobic condition is quite different from that in the atmosphere condition. UO_2OH^+ is the
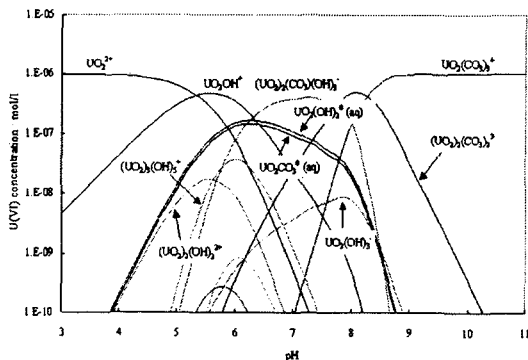

Fig. 4. Dissolved speciation of U(VI) as a function of pH in the open atmosphere ($P_{CO_2}=10^{-3.5}$ atm). [U_T]=10^{-6} M; I=0.01 M $NaClO_4$

Table 1. Formation constants for the calculation of U(VI) aqueous speciation

Reaction	$\log\beta$ (I=0) [a]
$UO_2^{2+}+H_2O - H^+ \leftrightarrow UO_2OH^+$	-5.20
$UO_2^{2+}+2H_2O - 2H^+ \leftrightarrow UO_2(OH)_2^0(aq)$	-11.5 [14]
$UO_2^{2+} + 3H_2O - 3H^+ \leftrightarrow UO_2(OH)_3^-$	-20.00 [15]
$UO_2^{2+} + 4H_2O - 4H^+ \leftrightarrow UO_2(OH)_4^{2-}$	-33.0
$2UO_2^{2+} + H_2O - H^+ \leftrightarrow (UO_2)_2OH^+$	-2.70
$2UO_2^{2+}+2H_2O - 2H^+ \leftrightarrow (UO_2)_2(OH)_2^{2+}$	-5.62
$3UO_2^{2+}+4H_2O - 4H^+ \leftrightarrow (UO_2)_3(OH)_4^{2+}$	-11.90
$3UO_2^{2+}+5H_2O- 5H^+ \leftrightarrow (UO_2)_3(OH)_5^+$	-15.55
$3UO_2^{2+}+7H_2O- 7H^+ \leftrightarrow (UO_2)_3(OH)_7^-$	-31.00
$4UO_2^{2+}+7H_2O-7H^+ \leftrightarrow (UO_2)_4(OH)_7^+$	-21.90
$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2CO_3^0(aq)$	9.67 [16]
$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_2^{2-}$	16.94
$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}$	21.60
$2UO_2^{2+}+CO_3^{2-}+3H_2O - 3H^+ \leftrightarrow (UO_2)_2(CO_3)(OH)_3^-$	-0.86
$3UO_2^{2+}+CO_3^{2-}+3H_2O - 3H^+ \leftrightarrow (UO_2)_3(CO_3)(OH)_3^+$	0.66
$11UO_2^{2+}+6CO_3^{2-}+18H_2O-24H^+ \leftrightarrow (UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$	-54.36
$UO_2^{2+} + NO_3^- \leftrightarrow UO_2NO_3^+$	0.3
$UO_2^{2+} + ClO_3^- \leftrightarrow UO_2ClO_3^+$	0.5
$UO_2^{2+} + ClO_4^- \leftrightarrow UO_2ClO_4^+$	0.26
$H^+ + CO_3^{2-} \leftrightarrow HCO_3^-$	10.33
$2H^+ + CO_3^{2-} \leftrightarrow H_2CO_3$	16.68
$2H^+ + CO_3^{2-} - H_2O \leftrightarrow CO_2(g)$	18.14

(a) Values from Grenthe et. al. (13), usless otherwise indicated

dominant species in the pH around 6 and then the complex $UO_2(OH)_2^0$(aq) in the pH range of 6 to 8.5. In the alkaline pH range over 8.5, the anionic species $UO_2(OH)_3^-$ is the dominant species.

4. Effects of Ionic Strength and pH

Sorption experiments were carried out to investigate the effect of ionic strength on the sorption of U(VI) onto the crushed granite particles at different pH values. These experiments were performed by varying the concentration of $NaClO_4$. As shown in Fig. 6, the distribution coefficient K_d (mL/g) at all the pH values are slightly decreased as the concentration of $NaClO_4$ increases.

Fig. 6 also shows the retention of uranium onto the crushed granite as a function of pH as well as the effects of ionic strength. As shown in Fig. 6, the K_d values are greatly dependent upon the pH. The distribution coefficient K_d increases from pH 3 continuously to a maximum value at pH ~6.5.

The increase of U(VI) sorption has to be related with the uranium speciation, which shows successively different cationic species, namely UO_2^{2+}, $UO_2(OH)^+$ and $(UO_2)_3(OH)_5^+$ (see Fig. 4).
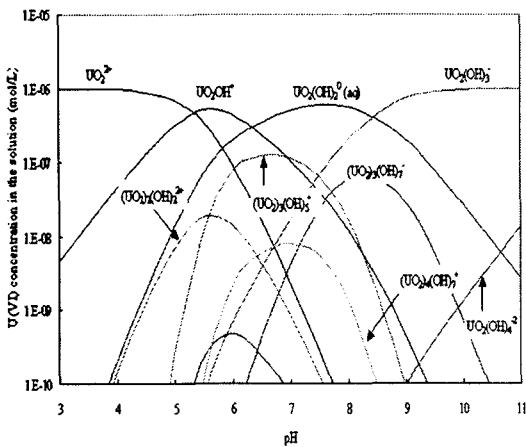
It is known that U(VI) sorption occurs in the pH range where U(VI) hydroxyl complexes are predominant [17]. However, when the pH increased above 6.5, K_d was greatly decreased. The decreased sorption of U(VI) sorbed in an alkaline pH and atmospheric conditions is correlated with the increased importance of the anionic U(VI)-carbonate aqueous complexes [18].

5. Effects of Carbonate

In the presence of CO_2(g) or dissolved carbonates, U(VI) sorption onto mineral surfaces is at a maximum at a near-neutral pH between ~6.0 and ~7.0 and decreases sharply towards a more acidic or alkaline conditions [18, 19]. The importance of aqueous carbonate complexation in reducing U(VI) sorption onto granite is emphasized by the data in Fig. 7. The figure compares the results of experiments on U(VI) sorption onto granite conducted under atmospheric ($P_{CO_2} = 10^{-3.5}$ atm) and anaerobic (P_{CO_2} ~10^{-6} atm) conditions as well as 10^{-4}-10^{-2} M total carbonate concentrations. Fig. 7 shows that the maximum value of the distribution coefficient, K_d, is increased about 5

Fig. 5. Dissolved speciation of U(VI) as a function of pH in the anaerobic condition.
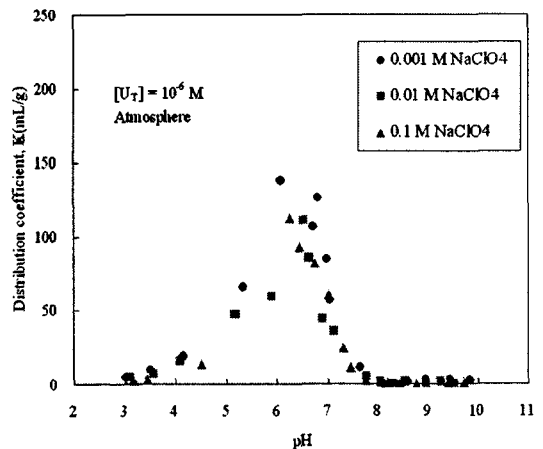$[U_T] = 10^{-6}$ M; I=0.01 M $NaClO_4$

Fig. 6. The effects of ionic strength on the sorption of U(VI) onto crushed granite particles as a function of pH.
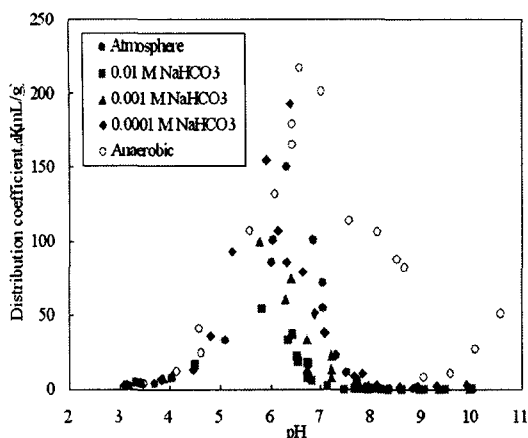
Fig. 7. The effects of carbonate concentration on the sorption of U(VI) onto crushed granite particles as a function of pH. $[U_T] = 10^{-6}$ M; I=0.01 M NaClO$_4$
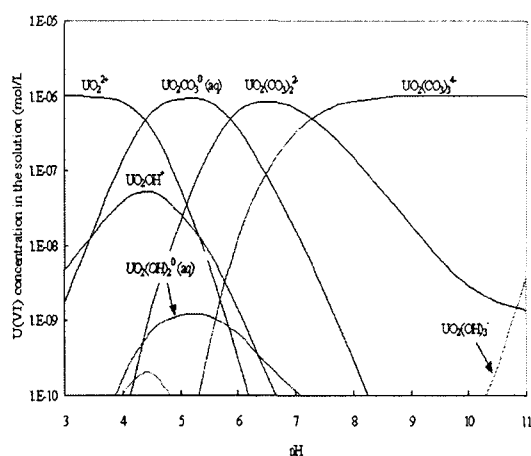

Fig. 8. Dissolved speciation of U(VI) as a function of pH in a closed atmosphere equilibrated with the total carbonate concentration (C_T) of 0.01 M NaHCO$_3$[U_T]= 10^{-6} M; I=0.01 M NaClO$_4$

times and the position of the peak of the sorption curve is shifted to a lower pH-side as the carbonate concentration decreases from atmospheric condition to anaerobic condition. Thus the effect of an increased carbonate concentration can be directly related to its effect on the aqueous speciation of U(VI).

Fig. 8 shows the aqueous speciation of U(VI) as a function of pH for a 10^{-6} M U(VI) solution at a 0.01 M NaHCO$_3$ total carbonate concentration in the atmosphere condition. Comparison of Fig. 4 with Fig. 8 shows that at a higher carbonate concentration, the predominant field of the monomeric U(VI) hydroxy species becomes reduced in a manner similar to the reduction in U(VI) sorption, i.e., the maximum is lowered and the high-pH side is shifted to a lower pH. This is due to the increased importance of the U(VI) carbonate complexes at a higher carbonate concentration.

IV. Conclusions

From this experimental sorption study, the following conclusions were made:

● The distribution coefficients of U(VI) for granite particles were about 1-200 mL/g depending on the experimental conditions.

● The sorption of U(VI) onto granite particles was greatly dependent on the contact time, pH, and carbonate concentration but little on the ionic strength.

● It can be deduced that a two-step first-order kinetic behavior dominates the kinetic sorption of U(VI) onto granite particles.

● It was noticed that the sorption of U(VI) onto granite particles could be highly correlated with the uranium speciation in the solution, which was dependent on the pH and carbonate concentrations.

● In the alkaline region, in the presence of carbonates, U(VI) sorption onto granite was greatly decreased and this may be due to the formation of the anionic U(VI)-carbonate aqueous complexes.

Ministry of Science and Technology, Korea.

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