

An Experimental Study on the Sorption of U(VI) onto Granite

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Abstract

The sorption of U(VI) on a domestic granite is studied as a function of experimental conditions such as contact time, solution-solid ratio, ionic strength, and pH using a batch procedure. The distribution coefficients, K_d 's, of U(VI) are about 1-100 mL/g depending on the experimental conditions. The sorption of U(VI) onto granite particles is greatly dependent upon the contact time, solution-solid ratio, and pH, but very little is dependent on the ionic strength. It is noticed that an U(VI)-carbonato ternary surface complex can be formed in the neutral range of pH. In the alkaline range of pH above 7, U(VI) sorption onto granite particles is greatly decreased due to the formation of anionic U(VI)-carbonato aqueous complexes.

Key Words : sorption, granite, distribution coefficient (K_d), uranium speciation, U(VI)-carbonato complexes

1. Introduction

During last few years, safety assessments have been performed in KAERI (Korea Atomic Energy Research Institute) as a part of the HLW (high-level radioactive waste) disposal technology development. 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. One of the major tasks in safety assessments is the prediction of 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 has been an important part of the overall investigations needed for the safety assessment of potential sites for radioactive wastes disposal [2]. In Korea, no site for the underground repository has been specified for HLW, even for intermediate and low level radioactive wastes (ILLW). Therefore sorption studies for the safety assessment for a radioactive waste disposal have just been performed for a generic site with crystalline rocks such as a granite.

In general, the sorption has been empirically characterized by the distribution coefficient K_d , which describes the equilibrium partitioning of a solute between solid and solution phases due to

sorption. Although the K_d concept has a basis in thermodynamics, the sorption of radionuclides and other contaminants in natural (rock-water) systems is very complex such that the requirements for specifying this parameter (i.e., sorption at equilibrium, occurring rapidly and reversibly, and being independent of the concentration of the sorbing species) are not always established nor confirmed during experimental determinations. 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. A number of reviews about sorption literature have been performed in the past, usually with the intention of recommending K_d values for various elements [3-6].

In most experimental sorption studies, crushed geological materials have been used as sorbents and the measured distribution coefficients characterize the sorption properties of the whole material. The geological materials involved in the sorption studies are typically composite materials, consisting of mixtures of various minerals with a wide range of chemical properties. The sorption properties are also strongly dependent on the experimental conditions which simulate the geochemical conditions.

Uranium is the most important nuclide both in the environment and radioactive waste management. Under oxidizing geochemical conditions, the most stable valence of U is U(VI) [9], which exists in acidic aqueous solutions as the uranyl ion, UO_2^{2+} . Uranyl hydrolyses extensively at high pH, forming monomers, dimers, and trimers. The uranyl ion is fairly mobile in oxidizing groundwater through formation of anionic carbonate complexes, which are weakly sorbed by many mineral forms [7, 8]. Other studies have documented U(VI) sorption under certain conditions for granite [10, 11] and for primary and secondary minerals [12-16].

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

2. Experiment

2.1. 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 smaller than 0.3 mm but bigger than 0.15 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. Table 1 summarizes the mineralogical composition of the crushed granite rock. The crushed granite was mainly composed of quartz, plagioclase, K-feldspar, biotite, hornblende, and a small amount

Table 1. Mineralogical Composition of the Granite Particles (volume %)

Minerals	Composition (%)
Quartz	44.2
Plagioclase	25.4
K-feldspar	11.5
Biotite	14.7
Hornblende	2.1
Sphene	0.8
Opaque phases	1.3
Total	100.0

of sphere and opaque phases.

The surface area of the crushed granite particles in the size range of $0.15 \leq \phi_p < 0.3$ was measured by the Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Co.). For this measurement, Krypton gas was used as a sorbate instead of common nitrogen gas due to the low surface area of the crushed granite particles. The BET specific surface area of the crushed granite particles was measured as $0.0846 \text{ m}^2/\text{g}$. In this study, U(VI) in the nitrate form ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used, and the concentration of the uranium was measured by ICP-MS (Varian, Ultramass 700).

2.2. Experimental Method

The sorption of U(VI) on the crushed domestic granite particles was studied as a function of contact time, solution-solid ratio, ionic strength, and pH using a batch procedure. The experiments were performed at about $25 \pm 2^\circ\text{C}$ under an ambient condition. All solutions used were made of AR grade reagents and high purity water with the resistivity of $18.3 \text{ M}\Omega\text{-cm}$ (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. Two gram of the crushed granite was transferred to 30 mL PP (polypropylene) bottle and contacted with 20 mL of 0.01 M NaClO_4 solution. The bottle was adjusted to a desired pH using 0.1 and 1.0 M NaOH or HClO_4 solutions, respectively. When the pH was stabilized, 0.01 M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ stock solution (at pH 3) was added to the bottle to achieve an initial uranium concentration of 10^{-5} M . Water-saturated air was bubbled through the solutions in order to maintain an equilibrium with atmospheric CO_2 .

The bottle was loosely sealed, placed in an automatic temperature-controlled shaker to maintain the temperature at 25°C , and gently

shaken at 100 rpm during an equilibrium period of two weeks. After measuring the final pH of the solution, 5 mL of aliquot was sampled after two weeks. The sampled aliquot was filtered with a syringe filter of $0.22 \mu\text{m}$ pore size and stored for the analysis of uranium concentration by ICP-MS. We also conducted kinetic sorption experiments to determine the change of U(VI) sorbed over time using the same electrolyte and pH values as the equilibrium sorption experiment. Blank tests without solid phase were also performed to quantify uranium losses on bottle walls for all sorption experiments. Uncertainties arising from uranium losses on bottle walls were taken into account in the error estimate for the percentage of U(VI) sorbed on granite particles. Separate experiments were also carried out to measure U(VI) retention on the filters as a function of pH. In this study, duplicate experiments were performed for all sorption experiments and an arithmetic mean of the duplicate data was taken.

3. Results and Discussions

3.1. 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:

$$K_d = \frac{C_s}{C_q} \quad (1)$$

where C_s (mol/g) and C_q (mol/mL) are the concentration of the solute in the solid phase and in the solution phase, respectively.

The concentration of U(VI) in the solid phase, C_s , is calculated using the following equation:

$$C_s = (C_0 - C_q) \cdot \frac{V}{M} \quad (2)$$

where C_0 (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 mass of the crushed granite particles used.

Thus distribution coefficient K_d can be therefore expressed as:

$$K_d = \frac{(C_0 - C_q)}{C_q} \cdot \frac{V}{M} \quad (3)$$

3.2. Uranium Losses

Figure 1 shows the results for sorption experiments which determine the amount of uranium lost by adsorption onto the bottle walls. Furthermore, the amount of uranium lost by filtration was investigated and the result is also shown in Fig. 1. Blank tests with PP bottles in the absence of the crushed granite particles show that the maximum uranium uptake on the bottle walls reaches about 10-16 % at pHs between 6 and 7. However, in the pH range other than 6-7, the uptake of uranium on the bottle walls is estimated to be less than 10 %. It is also shown in Fig. 1 that the loss of uranium by filtration with 0.22 μm filter is negligibly small and thus precipitation or colloid

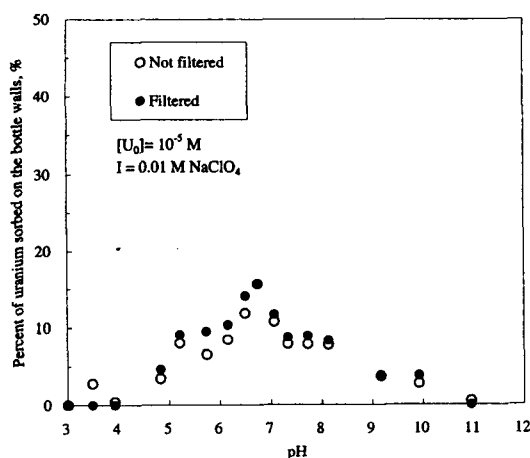


Fig. 1. The Percent of U(VI) Sorbed on the Reaction Bottle Wall and the Effect of Filtration

generation with larger size than 0.22 μm is not expected to occur significantly in our sorption experiment.

3.3. Effect of Contact Time

We conducted kinetic sorption experiments to determine the change of U(VI) sorbed over time at 0.01 M NaClO_4 and pH 7 ± 0.1 . The experimental result is shown in Fig. 2. The experimental time scale in a sorption experiment should be sufficiently long for a steady state to be achieved. It was suggested that distribution ratios for many radiotracers reach constant values within about a week [17]. Fig. 2 indicates that it takes over 4 days to reach a steady state (or an equilibrium). The time needed for the equilibrium of the uranium sorption onto granite is relatively longer than that of the other geological minerals [18]. In some instances, however, even longer timescales have been required for equilibrium [18]. This longer time needed for equilibrium may be due to the composite mineralogical composition of the granite particles.

Hsi and Langmuir [19] concluded that uranium adsorption occurs in two steps. A rapid first step,

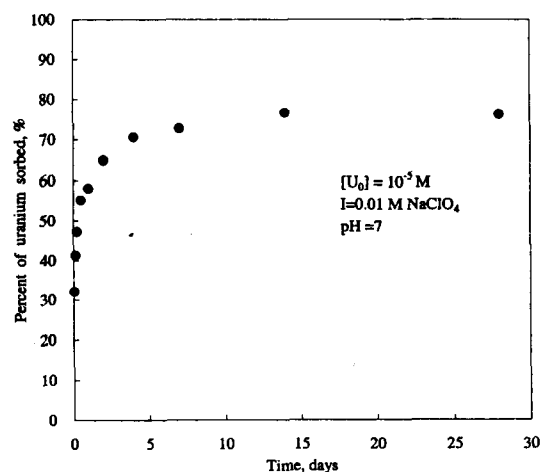
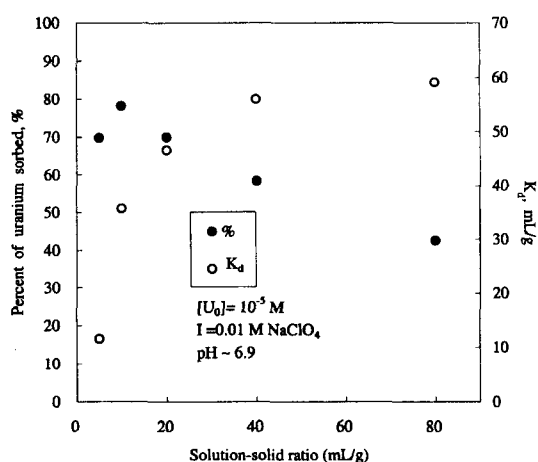


Fig. 2. The Effect of Contact Time on the Sorption of U(VI) onto the Crushed Granite Particles

Table 2. Experimental Conditions Used for the Sorption of U(VI) onto Crushed Granite

Parameters	Range of Values	Reference Conditions
pH	3-11	~ 7
Ionic strength (I)	0.001-0.1 M	0.01 M
Solution-solid ratio (V/M)	5-80 mL/g (20 mL / 4-0.25 g)	10 mL/g (20 mL / 2 g)
Contact time (t)	3h - 4 weeks	2 weeks
Carbonate condition	-	Aerobic ($P_{CO_2} = 10^{-3.5}$ atm)
Initial uranium concentration [U_0]	-	10^{-5} M

**Fig. 3. The Effect of the Solution-Solid Ratio on the Sorption of U(VI) onto the Crushed Granite Particles**

complete within a few minutes is followed by a slower one which lasts for several days. This second step may be due to diffusion of uranium into the sorbent matrix or alteration of adsorbent characteristics. It is shown in Fig. 2 that the sorption of U(VI) onto granite particles also follows the two-step kinetic sorption process.

3.4. Effect of Solution-Solid Ratio

The effect of the ratio of solution volume (mL)

and solid amount (g) on the percentage (%) and K_d of the U(VI) sorbed onto granite particles, respectively, is shown in Fig. 3. The percentage (%) of the U(VI) sorbed have a maximum value at the solution-solid ratio of 10 mL/g. However, the K_d increases continuously until 40 mL/g of solution-solid ratio, and starts to saturate to a constant value with increasing solution-solid ratio over 40 mL/g. This may be due to the limitation of surface sites of the granite particles available for the sorption with increasing solution-solid ratio. In this study, the solution-solid ratio of 10 mL/g was chosen for other sorption experiments as a standard condition as shown in Table 2.

3.5. Effect of Ionic Strength

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 $NaClO_4$. The results are shown in Fig. 4. As shown in Fig. 4, the percentage of uranium sorbed onto the crushed granite at all pHs are slightly decreased as the concentration of $NaClO_4$ increases. This can be explained by the fact that

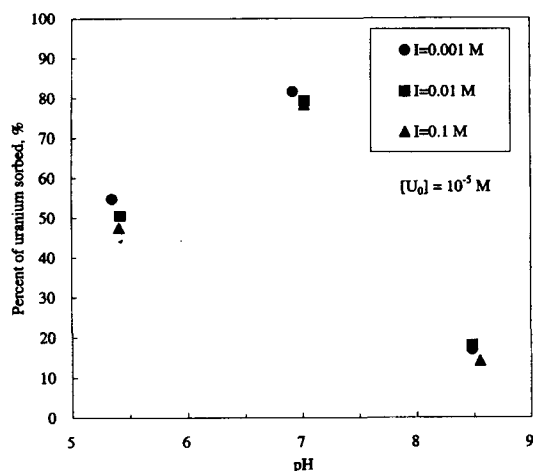


Fig. 4. The Effect of Ionic Strength on the Sorption of U(VI) onto Crushed Granite Particles

the thickness of the electric double layer is reduced and the affinity of uranyl ions for surface sites is finally reduced when the ionic strength of the

solution is increased [20].

3.6. U(VI) Speciation

It is very useful to compare the pH dependence of U(VI) sorption with its aqueous speciation. Thus the chemical speciation of uranium was calculated by the chemical code MINTQA2 [24] with the thermodynamic data from Table 3 [9, 21, 25, 26] in order to provide information on the probable uranium speciation in solutions.

The distribution of the aqueous species for a 10^{-5} M U(VI) system in 0.01 M NaClO₄ solution equilibrated with air ($P_{\text{CO}_2} = 10^{-3.5}$ atm) at 25°C is given in Fig. 5. Free uranyl ion UO_2^{2+} is the dominant species in the acidic pH range up to 5. $\text{UO}_2(\text{OH})^+$ and $(\text{UO}_2)_3(\text{OH})_5^+$ are the dominant species in the pH up to 6 and then the ternary anionic complex $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ in the pH range of 6 to 8. In the alkaline pH range over 8,

Table 3. Formation Constants for Aqueous Speciation of U(VI)

Reaction	$\log\beta(I=0)^*$
$\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.20
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_2^0 + 2\text{H}^+$	-11.5 [21]
$\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{OH}_3^- + 3\text{H}^+$	-20.00 [25]
$\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{UO}_2(\text{OH})_4^{2-} + 4\text{H}^+$	-33.0
$2\text{UO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{OH}^{3+} + \text{H}^+$	-2.70
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62
$3\text{UO}_2^{2+} + 4\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_4^{2+} + 4\text{H}^+$	-11.90
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55
$3\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{OH})_7^- + 7\text{H}^+$	-31.00
$4\text{UO}_2^{2+} + 7\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-21.9
$\text{UO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{UO}_2\text{CO}_3^0$	9.67 [26]
$\text{UO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_2^{2-}$	16.94
$\text{UO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{CO}_3)_3^{4-}$	21.60
$2\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{CO}_3)(\text{OH})_3^- + 3\text{H}^+$	-0.86
$2\text{UO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)(\text{OH})_3^+ + 3\text{H}^+$	0.66
$\text{UO}_2^{2+} + \text{ClO}_4^- \rightleftharpoons \text{UO}_2\text{ClO}_4^+$	0.26
$\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$	10.329
$2\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{H}_2\text{CO}_3$	16.683
$2\text{H}^+ + \text{CO}_3^{2-} - \text{H}_2\text{O} \rightleftharpoons \text{CO}_2(\text{g})$	21.66

*) Values from Grenthe [9], otherwise indicated

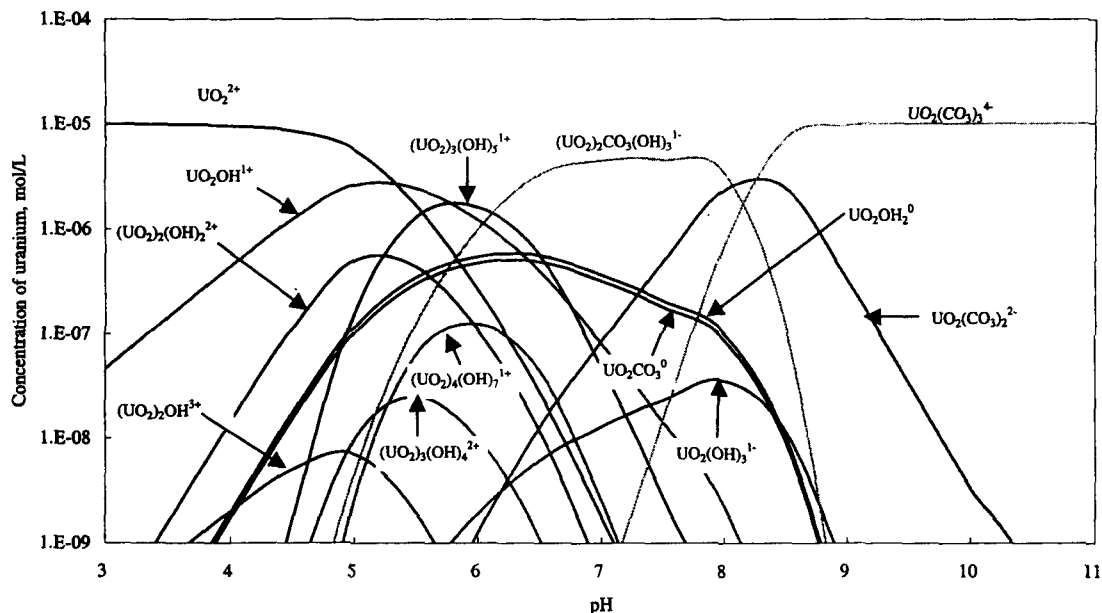


Fig. 5. Dissolved Speciation of U(VI) as a Function of pH in an Open Atmosphere Equilibrated with a Partial Pressure of CO_2 of $10^{-3.5}$ atm. $[\text{U}_0] = 10^{-5}$ M; $I = 0.01$ M 0.01M NaClO_4

$(\text{UO}_2)_2\text{CO}_3^{4-}$ is the dominant species.

3.7. Effect of pH

Fig. 6 shows the retention of uranium on crushed granite (expressed as the percentage of retention) as a function of pH. Under given experimental conditions, K_d values were calculated by using Eq. (2). As shown in Fig. 6, the percent of uranium sorbed and K_d are greatly dependent upon pH.

The distribution coefficient K_d increases from pH 3 continuously to a maximum value of about 75 mL/g at pH ~6.8. The increase of U(VI) sorption has to be related with the uranium speciation, which shows successively different cationic species, namely UO_2^{2+} , $\text{UO}_2(\text{OH})^+$ and $(\text{UO}_2)_3(\text{OH})_5^+$ (see Fig. 5). It has been known that U(VI) sorption occurs in the pH range where U(VI) hydroxyl complexes are predominant [27].

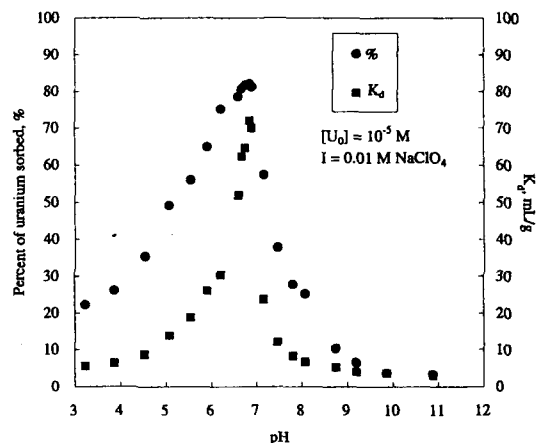


Fig. 6. The Effect of pH on the Sorption of U(VI) onto Crushed Granite Particles

However, uranium speciation can not explain the whole sorption curve. Above pH 6, uranium is present in anionic forms, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$,

whereas the U(VI) sorption still increases up to pH 7. A possible explanation of this phenomena could be the formation of an U(VI)-carbonato ternary surface complex [23]. However, when pH increased above 7, K_d greatly decreased. The decreased sorption of U(VI) sorbed at alkaline pH and atmospheric conditions has been correlated to the increased importance of the anionic U(VI)-carbonato aqueous complexes [28, 29].

4. Conclusions

In this study, sorption experiments of U(VI) onto granite particles were carried out and the effects of the parameters such as contact time, solution-solid ratio, ionic strength, and pH were investigated. From this experimental sorption study, the following conclusions were made:

- The distribution coefficients of U(VI) for granite particles are about 1-100 mL/g depending on the experimental conditions.
- The sorption of U(VI) onto granite particles is greatly dependent on the contact time, solution-solid ratio and pH, but little on the ionic strength.
- It is noticed that the sorption of U(VI) onto granite particles follows the two-step kinetic sorption process.
- A possible formation of a U(VI)-carbonato ternary surface complex is predicted from the result that the uranium uptake still increases up to pH 7 although uranium is present as anionic complexes in the aqueous solution above pH 6.
- In the alkaline range of pH above 7, U(VI) sorption was greatly decreased and this was explained by the formation of anionic U(VI)-carbonato aqueous complexes.

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