# Sorption of Uranium onto a Fracture-Filling Material (Laumontite) of Granite

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## 1. Introduction

One of the major tasks in safety assessments of radioactive waste repositories is the prediction of radionuclide migration behaviors in a groundwater which takes into account the sorption characteristics of various radionuclides onto geological media [1]. In general, actinides show very complex geochemical behaviors which are influenced by changes of the redox states of the elements, a complexation with groundwater constituents and a stable colloid formation [2].

In this study, a batch sorption experiment has been conducted in order to investigate the sorption properties of a fracture-filling material of granite taken from the KURT (KAERI Underground Research Tunnel) located within the KAERI (Korea Atomic Energy Research Institute) research area. Our result will be utilized in analyzing the retardation processes of uranium through a fractured rock in subsurface environments.

## 2. Materials and Methods

### 2.1 Materials

The granite used in the sorption experiments was taken from KURT (KAERI Underground Research Tunnel). The granite was mainly composed of quarts, chlorite, albite, K-feldspar, biotite, and vermiculite. It was found that a number of fractures of the granite cores sampled from the KURT were found to be filled with various secondary minerals such as illite, smectite, calcite, goethite, and laumontite. The fracture of the granite core used in this study was identified to be filled with laumontite which is a kind of natural zeolite by using X-ray diffraction (XRD: Philips, MPD) and Scanning Electron Microscopy (SEM; LEO 1455VP).

In this study, a natural groundwater was used to investigate the sorption behavior of uranium a natural deep groundwater condition. A synthetic groundwater made of distilled water was also used to investigate the effect of pH on the sorption behavior of uranium. The natural groundwater was sampled from a borehole (YS-01) at 457.5 m depth from the surface [3]. Details for the granite and the groundwater are given in elsewhere [3].

### 2.2 Sorption Experiment

The sorption of uranium on the fracture-filling material (laumontite) was carried out using a batch procedure in a glove box and highly pure (99.999%) $N_2$ gas was used as an inert gas. 0.5 g of the crushed fracture-filling material was transferred to a 20 mL PP (polypropylene) bottle and contacted with 10 mL of $NaClO_4$ solution with an appropriate concentration. The pH of each solution was adjusted by NaOH and $HClO_4$, and measured by Ion Analyzer EA-940 (ORION). When the solution 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 $2 \times 10^{-6}$ M. Almost the same procedure was applied to the sorption experiment of uranium for the natural groundwater except adjusting the pH of the solution.

### 2.3 X-ray Image Mapping

In this study, X-ray image mapping was used to investigate the uranium distribution on the granite core surface. A granite surface with the same natural fracture as the granite core used in the migration experiment was chosen and a specimen was prepared for the X-ray image mapping by using EPMA (Electron Probe Micro-Analyzer: EPMA1600, Shimadzu). The same technique previously applied for other granite surfaces was used for the X-ray image mapping [4].

## 3. Results and Discussion

### 3.1 Distribution Coefficient, $K_d$

The sorption coefficient of the uranium sorbed onto the fracture filling material can be presented as a distribution coefficient which is generally obtained by:

$$K_d = \frac{[U]_s}{[U]_c} \cdot \frac{V}{M} = \frac{[U]_0 - [U]_c}{[U]_c} \cdot \frac{V}{M}$$

where $K_d$ is the distribution coefficient of the uranium (mL/g), $[U]_c$ is the concentration of the uranium in the solution (mol/L), $[U]_s$ is the concentration of the uranium sorbed onto solid (mol/g), $[U]_0$ is the initial concentration of the uranium used (mol/L), $M$ is the amount of solid used (g), and $V$ is the volume of the solution (mL).

### 3.2 Sorption Results

The result of the batch sorption experiment for uranium sorebd onto the laumontite showed a distribution coefficient ($K_d$) of 2.3±0.5 mL/g. This low $K_d$ value agrees well with the result from the uranium migration experiment using a fractured granite core with a fracture filled with laumontite [3]. This low $K_d$ value also can be elicited from the fact that uranium exists as

anionic complexes such as uranyl hydroxides ($UO_2(OH)_4^{2-}$ and $UO_2(OH)_6^{4-}$) or uranyl carbonates ($UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$) in the given groundwater condition [4].

Fig. 1 shows the result of the uranium sorption in the synthetic groundwater as a function of pH. The percentages and the $K_d$ values of uranium sorption are relatively low in a lower pH less than 9.0 and then start to increase abruptly after pH 9.5. The higher $K_d$ of uranium in the synthetic groundwater comparing to the $K_d$ in the natural groundwater may be due to the formation of non-sorbing anionic carbonate complexes of uranium by the carbonates present in the natural groundwater.
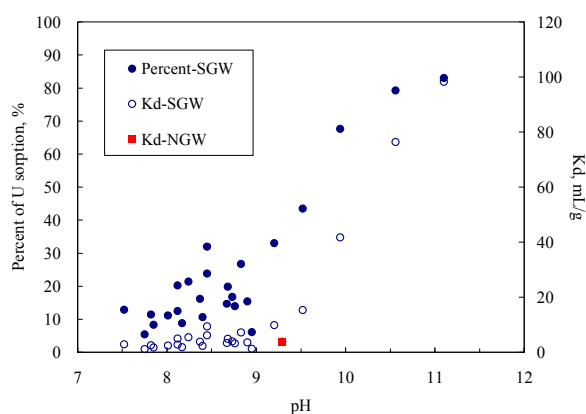


Figure 1. Result of the uranium sorption of uranium onto the fracture-filling material in the synthetic groundwater as a function of pH (SGW: synthetic groundwater; NGW: natural groundwater)

*3.3 Result of X-ray Image Mapping*

In this study, X-ray image mapping was used to investigate the uranium distribution on the granite core surface. A granite surface with the same natural fracture as the granite core used in the migration experiment was chosen and a specimen was prepared for the X-ray image mapping by using EPMA (Electron Probe Micro-Analyzer: EPMA1600, Shimadzu) [5].

Fig. 2 shows the distributions of Ca, Al, U on the granite surface with a natural fracture. For the distribution of uranium, the region of the fracture reveals a relatively lower content of uranium when compared to the surrounding surface. Thus, this EPMA result supports the lower values of $K_d$.

In general, it is known that laumontite, a Ca-rich natural zeolite, has a very high cation exchange capacity (CEC). For example, the potential CEC for laumontite was calculated to be 420 mmol/100g (Boettinger and Ming, 2002). For our natural laumontite, however, the CEC measured by an ammonia acetate method was measured to be less than 5 mmol/100g. The specific surface area of our crushed laumontite sample was also found to be as low as 2.63 $m^2$/g by using the BET method with $N_2$ gas (Asap 2010, Micrometrtics). These small values of BET and CEC for the fracture-filling material also explain the low sorption coefficient of uranium for the fracture-filling material of laumontite in the given reducing environment.
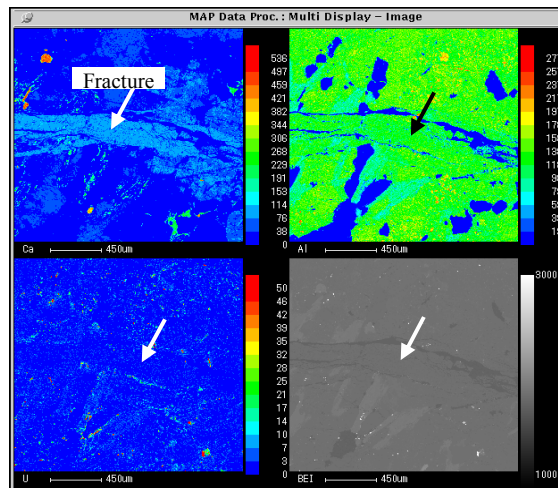


Figure 2. X-ray image mapping showing the distributions of Ca, Al, U on the granite surface with a natural fracture. Arrows indicate the fracture region.

## 4. Conclusion

In this study, the sorption of uranium onto fracture-filling material of granite has been investigated. The lower values of the distribution coefficient $K_d$ for uranium obtained from the batch sorption experiments were directly explained by the result of X-ray image mapping, which showed a lower content of uranium over the fracture region. This result was also supported by the results from a batch sorption experiment, and the CEC and BET measurements for the fracture-filling material of laumontite.

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