

## Adsorption/desorption of uranium on iron-bearing soil mineral surface

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**Abstract.** In this study, we evaluated the adsorption/desorption of uranium (U) in pure soil environment using continuous column reactor. We additionally investigated the adsorption/desorption mechanism of U on vivianite surface in molecular scale using quantum calculation. We observed that below 0.1  $\mu\text{M}$  of U was detected after 20 d from U injection (1  $\mu\text{M}$ ) in adsorption test. However, all of absorbed U was detached from vivianite surface in 24 h by injection of CARB solution ( $1.44 \times 10^{-2}$  M  $\text{NaHCO}_3$  and  $2.8 \times 10^{-3}$  M  $\text{Na}_2\text{CO}_3$ ). Based on exchange energy calculation, we found that  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  species have higher repulsive energy than  $\text{UO}_2(\text{OH})_2$  species. The results obtained from this study could be applied to predict the behavior of uranium in contaminated and remediation sites.

**Keywords:** uranium; adsorption/desorption; vivianite; column test; quantum calculation

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### 1. Introduction

Radioactive materials (e.g., nuclear fuel and fission products) generated from nuclear reactor destruction and nuclear weapon launch can severely influence on eco-systems and human beings (Behrens and Holt 2005). There have been many cases (Bikini Atoll, Fukushima Daiichi, Chernobyl, and Mayak) showing the seriousness of radioactive materials (Johnson 2013). The  $\alpha$ ,  $\beta$ ,  $\gamma$ , and X-ray radiated from radioactive materials can cause tissue damage and genetic modification. Recently, it has been estimated that at least fifteen-years are required to remediate the soil and ground water contaminated by radioactive materials. Remediation of sites contaminated by radioactive materials has been emerged as a major challenge to maintain safe environment and reduce the damage and loss from radioactive contamination.

Among the many radioactive compounds, uranium (U) has been highly focused by researchers due to its ubiquitousness and harmfulness. The mobility of uranium (U) is strongly dependent on redox condition. Hexavalent uranium (U(VI)) species are highly soluble while tetravalent uranium (U(IV)) species are sparingly soluble (Wan *et al.* 2005). Therefore, reduction of U(VI) to U(IV) with abiotic and/or biotic reactions and maintain of U as U(IV) for long-term stabilization have been considered as a promising way to treat sites contaminated by U (Sihn *et al.* 2013).

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Reduction of uranium using several materials has been well investigated: (1) Nano-sized zero-valent iron (nZVI) (Fiedor *et al.* 1998, Noubactep *et al.* 2006, Riba *et al.* 2008); (2) electrodes (Gregory and Derek 2005); (3) sulfide minerals (Wersin *et al.* 1994); and (4) iron-bearing soil minerals (Kriegman-King and Reinhard 1994, Butler and Hayes 1998, Lee and Batchelor 2002, Kim and Batchelor 2009, Descostes *et al.* 2010). Iron-bearing soil minerals such as vivianite, maghemite, and green rust showed high reductive capacity to reduce toxic chemicals including radioactive compounds (Lee *et al.* 2000, Zachara *et al.* 2001, Roden *et al.* 2002, Jung *et al.* 2012). It has been known that iron-bearing soil minerals can play an important role to control the immobilization of inorganic compounds in subsurface environment (Bae and Lee 2012). However, there have been few studies dealt with adsorption/desorption of radioactive materials on the surface of iron-bearing soil minerals.

In this study, we: (1) tested adsorption/desorption of U on the surface of soil minerals using continuous column reactor; and (2) investigated the specific adsorption/desorption behavior on the surface of vivianite using quantum calculation. The experimental and computational results could provide fundamental knowledge to treat radioactive chemicals in soil and groundwater environments.

## 2. Methodology

### 2.1 Soil characterization

Soil collected from 30 cm below surface at KAIST campus was used for continuous column test. The soil was sealed up and brought to laboratory then it was dried in natural condition in the shade for 30 d. X-ray diffraction (XRD) analyses (RIGAKU, D/MAX-2500) were conducted to estimate soil composition and to check the presence of crystalline particles (Fig. 1). The soil included SiO<sub>2</sub>: 56.75%, Al<sub>2</sub>O<sub>3</sub>:19.99%, Fe<sub>2</sub>O<sub>3</sub>: 7.78%, K<sub>2</sub>O: 3.1%, MgO: 2.53%, TiO<sub>2</sub>:0.93%, Na<sub>2</sub>O: 0.37%, CaO: 0.36%, P<sub>2</sub>O<sub>5</sub>:0.09%, and MnO: 0.08%. Particle size and surface area of collected soil was also analyzed by particle size analyzer and BET method, respectively (Fig. 2 and Table 1). Over 60% of soil was fine sand, 30% of soil was silt and about 10% of soil was classified as coarse sand (Table 1).

### 2.2 Synthesize of vivianite

Vivianite was synthesized by following the method previously described (Jeon *et al.* 2015). An aqueous solution of Fe(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O (80 g/L) and a solution containing CH<sub>3</sub>OONa (13.33 g/L)

Table 1 Characteristics of collected soil

Particle size	4.5 $\mu\text{m}$ – 435 $\mu\text{m}$ (60% of soil) 75 $\mu\text{m}$ – 305 $\mu\text{m}$ (total)
Surface area	28.6788 m <sup>2</sup> /g
Pore size	8.5 nm
Anion exchange capacity	$3 \times 10^{-6}$ meq/100 g soil
Cation exchange capacity	13.3 $\pm$ 2 meq/100 g soil

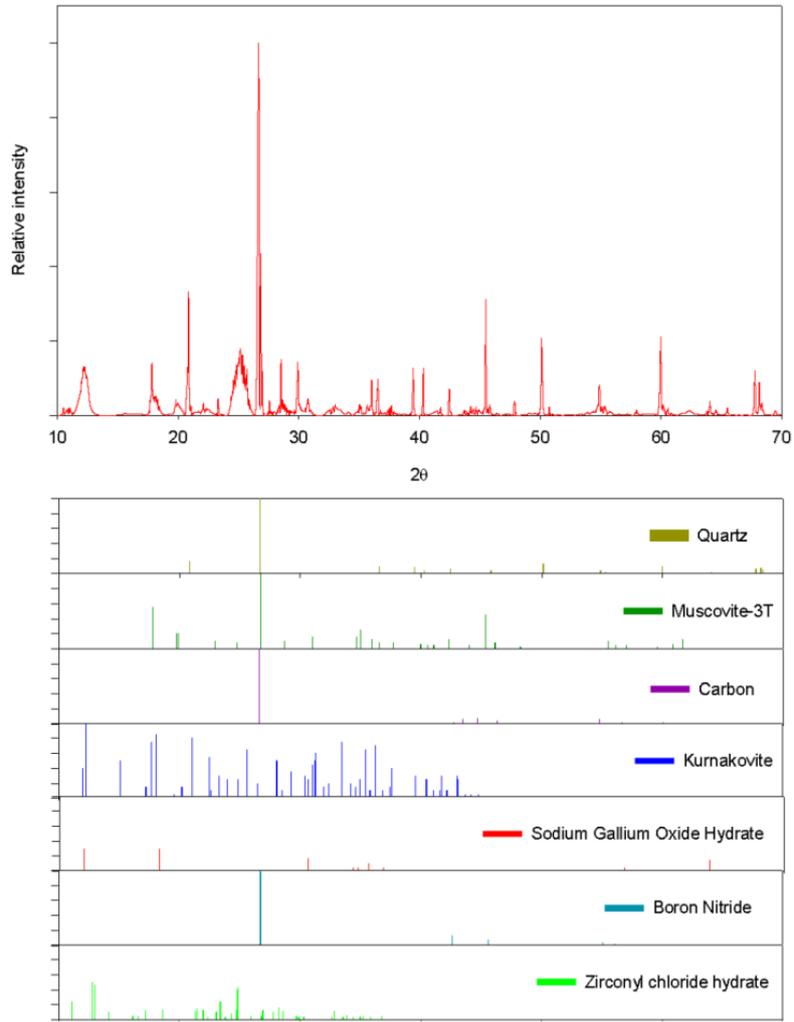


Fig. 1 XRD patterns of collected soil

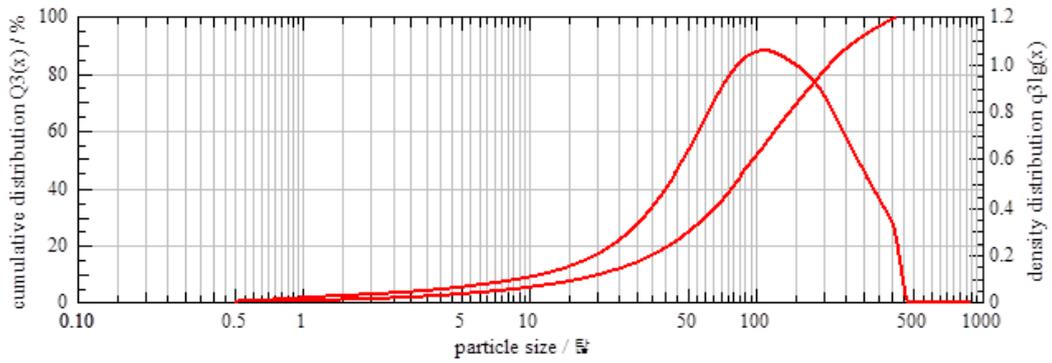


Fig. 2 Particle size distribution

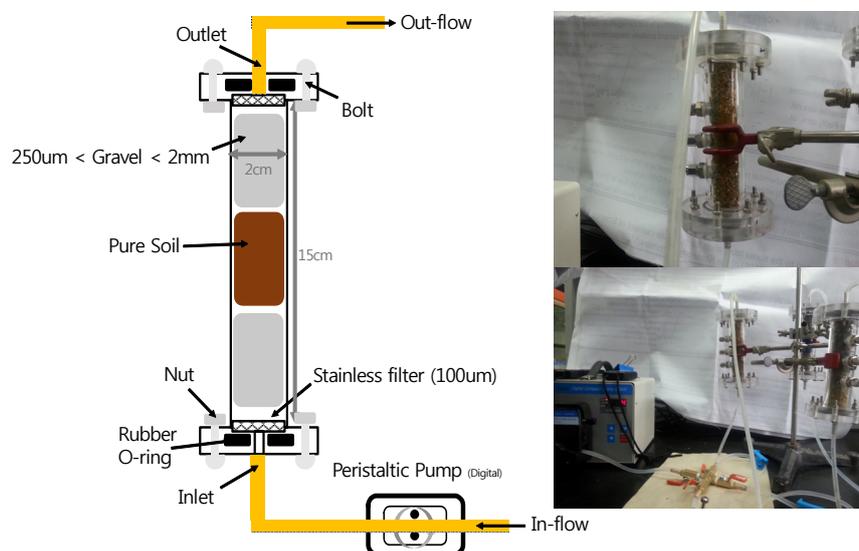


Fig. 3 Scheme of continuous column reactor

and  $\text{Na}_2\text{HPO}_4$  (66.67 g/L) were mixed under continuous stirring for 2 d in an anaerobic chamber (Coy Laboratory Products Inc.). The bluish-gray precipitate was continuously washed with deaerated deionized water (DDW) to remove remnant iron species during its synthesis. The iron contents in the aqueous phase were monitored after each washing process until the supernatant solution was free of iron. The washed vivianite was then centrifuged and dried under anaerobic conditions, after which it was analyzed by XRD. The XRD results of the synthesized vivianite agreed well with the corresponding Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data.

### 2.3 Reactor design

To reduce the reaction between inner part of column and soil with contaminants, cylindrical column reactor was made of acryl with 2 cm internal diameter and 15 cm total length (Fig. 3). Gravel layers located upside and bottom minimized the pressure inside of column and stainless filters (100  $\mu\text{m}$ ) used to prevent leak of soil. Injection of influent and sampling of effluent ran through polyethylene tubes and digital pump are utilized.

### 2.4 Experimental methods

Bromide solution (20 ppm), which is known as conventional tracer, was continuously injected into the soil-filled column with 2 ml/min flow rate. Effluent samples were filtered by 200 nm nylon filters to remove particles. In the same way, 1  $\mu\text{M}$  of uranium, controlled to pH 8 using Tris buffer and aerated with nitrogen gas was continuously injected into column with 2 ml/min flow rate. After filtering with 200 nm nylon filters, each sample was diluted 10 times with 2% nitric acid.

## 2.5 Analytical methods

Concentration change of Br in effluent was analyzed using Ion Chromatography and concentration change of Uranium in effluent was analyzed using Inductively Coupled Plasma-Mass Spectrometry (ELAN DRC II).

## 2.6 Quantum calculation

To find out adsorption characteristic of Uranium oxide to vivianite, Vienna Ab-initio Software Package (VASP) program, one of the quantum mechanics methodologies based on density function theory, is utilized. Water potential is calculated by projective augmented wave (PAW) method and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. To fast screen for Uranium compound, 250 eV of electric velocity cutoff and Gamma K-point are used to calculation. To see though calculation is Uranium compound produced in a number of condition and adsorption characteristic onto  $(\text{UO}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_6, \text{UO}_2(\text{CO}_3)_2\text{Ca}, \text{UO}_2(\text{CO}_3)_2\text{Ca}_2)$  vivianite. Adsorbed location is determined based on the (010) face which is most stable surface at vivianite. Vivianite surface is divided to adsorption location A and B depending on binding type of Fe and O.

Vivianite surface model for quantum calculation expands (010) surface twice in direction of a-axis to situate Uranium oxide on it. Because water is absorbed on the surface of vivianite, it is calculated that Uranium oxide is estimated to occupy the position of water on surface of vivianite on the assumption that uranium oxide combines with iron directly.  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  that produced normally from pH 5 to pH 7 are calculated under the condition of pure distilled water and pH 7 distilled water containing  $\text{UO}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_6$  and carbonic acid.  $\text{UO}_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_6$  is compensated to  $\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  considering symmetry of structure and total charge of uranyl carbonate oxide is revised to zero using cations (Calcium and Hydronium ion).

## 3. Results and discussion

### 3.1 Continuous column test

Ten minutes after bromide injection, 9.7 ppm Br was detected that corresponded to the half of injection concentration (Fig. 4). Forty minutes after injection, 20 ppm Br was detected and the concentration was maintained constantly until 600 min from injection time. From the result, soil in reactor absorbed Br<sup>-</sup> in aqueous solution and lost its reactivity within 40 min. Differently with Br, U was still detected below 0.1  $\mu\text{M}$  after 20 d from injection and this figure is below 20-40 ppb (Fig. 5), the concentration of environmental regulations in Korea. It represents that the field soil has high Uranium absorptivity.

However, because half-life of uranium reaches to hundreds of millions of years, it is important factor to fix uranium in original location for long term. To check this, CARB ( $1.44 \times 10^{-2}$  M  $\text{NaHCO}_3$  and  $2.8 \times 10^{-3}$  M  $\text{Na}_2\text{CO}_3$ ) was injected then concentration of U in effluent was measured. It is known that carbonic acid is prevalent in groundwater. When carbonic acid reacts with Uranium, Uranyl carbonate ion is formed. Accordingly, CARB solution is frequently used to U desorption. Shortly after injection of CARB solution, 1.5  $\mu\text{M}$  of U was discharged and sharply increased up to 3  $\mu\text{M}$  after 4 h from injection. In 24 h, all U that had absorbed to soil finally desorbed in aqueous solution. That means, if groundwater which contains a quantity of carbonic acid passes though U contaminated site, it is estimated that serious U diffusion aspects happen.

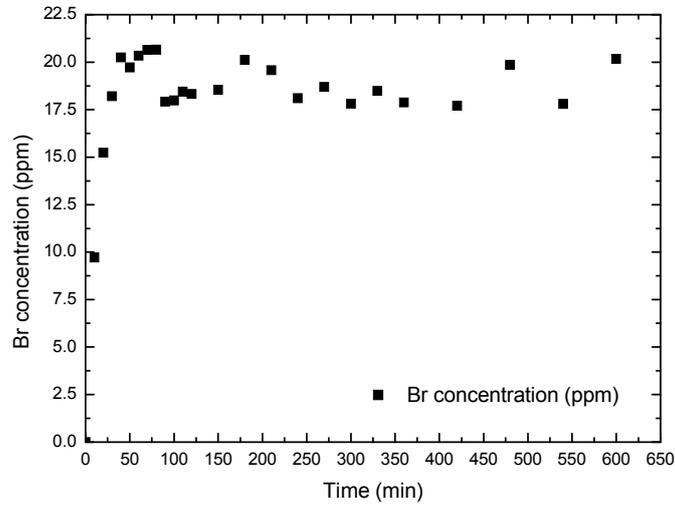


Fig. 4 Br concentration of effluent from column reactor

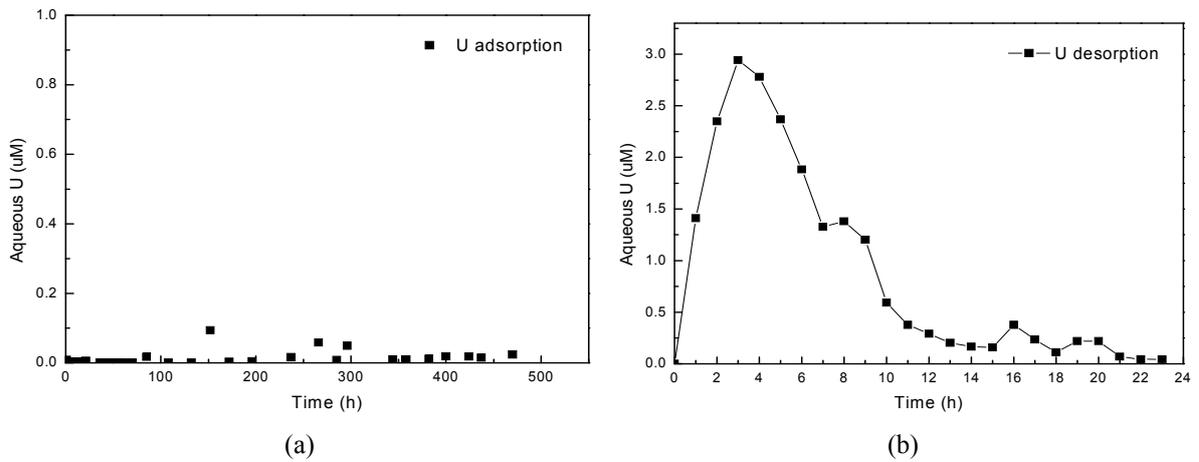
Fig. 5 (a) Adsorption aspect of 1  $\mu\text{M}$  U by pure soil; and (b) desorption aspect after CARB solution injection

Table 2 Exchange energy between vivianite (010) surface and uranium chemical species

Uranium chemical species	Exchange energy (eV)	
	A adsorption position	B adsorption position
$\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	1.01	-0.12
$\text{UO}_2(\text{CO}_3)_2^{2-}(\text{Ca}^{2+})$	-6.33	-7.57
$\text{UO}_2(\text{CO}_3)_2^{2-}(2\text{H}_3\text{O}^+)$	-5.32	-7.66
$\text{UO}_2(\text{CO}_3)_3^{4-}(2\text{Ca}^{2+})$	-6.73	-6.88
$\text{UO}_2(\text{CO}_3)_3^{4-}(4\text{H}_3\text{O}^+)$	-6.02	-6.38

### 3.2 Quantum calculation

Table 2 shows exchange energy between vivianite (010) surface and uranium chemical species. In case of  $\text{UO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  produced in distilled water, 1.4 eV and 1.7 eV of exchange energy are stably shown at A and B position. To see the exchange energy considering removal of hydrated water, it is about 1eV and -0.1 eV and goes to stable reaction. In contrast, in case of  $(\text{UO}_2(\text{CO}_3)_2)^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$  which produced in carbonic acidic condition, it seems to result in bigger repulsive energy than 5eV so that carbonic acid molecular physically resulted in desorption of uranium acid.

### 4. Conclusions

We investigated the adsorption/desorption of U in pure soil environment using continuous column reactor. Additionally, molecular scale adsorption/desorption of U on vivianite surface was elucidated by quantum calculation. Although U was detected below 0.1  $\mu\text{M}$  out of 1  $\mu\text{M}$  after 20 d from injection, it is important factor to fix uranium in soil for long term once spilt because half-life of U reaches to hundreds of millions of years. After injection of CARB solution, 1.5  $\mu\text{M}$  of U was discharged and sharply increased up to 3  $\mu\text{M}$  after 4 h from injection and all U that had absorbed to soil finally desorbed in aqueous solution in 24 h. Vivianite was selected as representative iron-bearing soil mineral and exchange energy between vivianite (010) surface and uranium chemical species was calculated.  $\text{UO}_2(\text{CO}_3)_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_3^{4-}$  produced in carbonic acidic condition seem to result in 5eV higher repulsive energy than pure groundwater condition. This indicates that carbonic acidic condition resulted molecular physically desorption of uranium acid on vivianite. Based on the adsorption and desorption mechanism between vivianite and uranium in neutral and acidic condition, it is expected that behavior of uranium in contaminated site could be monitored and predicted. Furthermore, the results could be applied to remediation technology for the removal of radioactive materials.

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