Kinetic approach for interactive reactions of radionuclide, bacteria and granitic crushed rock

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1. Introduction

For many radionuclides, sorption is an important phenomenon as their migration rates in groundwater are reduced in both engineered barrier and fractured rock matrix [1]. Sorption of radionuclides is strongly dependent on the chemistry of the surrounding groundwater, such as pH, Eh, ionic strength, etc., by changing their valence states (e.g., [2]). In addition, it is also known that some bacteria can change the mobility and speciation of a radionuclide in groundwater. Biological immobilization mechanisms of radionuclides include precipitation, transformation to less soluble forms and so on [3]. On the other hand, bacteria can also play a role of sorbent for radionuclides [4]. Since bacteria can not only be mobile as a colloid but also be immobile as biofilm in the rock fracture, the bacteria as the sorbents of radionuclides in the groundwater can have both positive and negative effects on the radionuclide migration. In this study, therefore, sorption of radionuclide onto rock surface in the presence of bacteria was investigated via batch experiments. Although sorption equilibrium state can be expected in the transport of weakly sorbing (distribution coefficient, $K_d < \sim 4.6\times10^{-3}$ m^3kg^{-1}) or strongly adsorbing ($K_d > \sim 4.6$ m^3kg^{-1}) nuclides in fractured rock, sorption kinetics needs to be considered in the intermediate range [5]. Therefore, the sorption of radionuclide whose valence state is expected to be changed by biological reduction was evaluated in a kinetic approach.

2. Materials and Methods

The batch experiments were conducted using 120-mL glass serum bottles which were shaken at 120 rpm (30℃) for 7 days. The detailed experimental materials and conditions are followed.

2.1 Radionuclide

Radionuclide used in this study was U(VI) in the form of uranyl dinitrate ($UO_2(NO_3)_2{\cdot}6H_2O$). For the stock solution, 10 mM of uranyl dinitrate was prepared. The concentration of soluble uranium which includes U(VI) and U(IV) was measured using an inductively coupled plasma mass spectrometry (ICP/MS) after filtration with 0.2 μm filter.

2.2 Bacteria

Shewanella putrefaciens strain CN32 (ATCC BAA-1097) was previously cultured aerobically in a 30 g/L tryptic soy broth (TSB) (Difco Laboratories, Detroit, MI). The *Shewanella* cells at mid to late log phase were centrifuged at 6,000 rpm for 10 min. The supernatant was discarded and the cells were washed with autoclaved 30 mM $NaHCO_3$ (pH 7) buffer solution. The washing procedure was repeated for 3 times and the final bacteria solution was purged with N_2 gas for 30 min before the inoculation. The concentration of bacteria was measured by optical density (OD_{562}) at 562 nm wave length, and the OD_{562} of 10^2 times diluted bacteria stock solution was 0.260.

2.3 Granitic crushed rock

The granitic rock core obtained from the KURT (KAERI Underground Research Tunnel) was crushed and sieved to get particles ranged from 150 to 300 μm in diameter. The sieved rock particles were washed with deionized water using sonication and dried at room temperature.

2.4 Batch reactor

Glass serum bottles were initially filled with 100 mL of 30 mM $NaHCO_3$ (pH 7) buffer solution and 2 mL of 500 mM $NaC_3H_5O_3$ as a carbon source. Bottles for Cond. 1, 2 and 4 in Table I were also filled with 10 g of the prepared crushed rock. All bottles were purged with N_2 gas for 30 min before covering up a lid and autoclave. After autoclave, U(VI) and *Shewanella* were injected into the serum bottles using syringe with a needle as shown in Table I. Each experiment was conducted in duplication.

Table I: Experimental conditions

	U(VI)	*Shewanella*	Crushed rock
Cond.	0.1 mM	-	10 g
Cond.	-	1 mL	10 g
Cond.	0.1 mM	1 mL	-
Cond.	0.1 mM	1 mL	10 g

3. Results and Discussion

The total dissolved uranium concentration in Fig. 1 includes both U(VI) which was initially injected and U(IV) which was expected to be generated by bacteria for each experimental condition. When uranium was reacted with only bacteria, total dissolved uranium concentration was kept constant within the standard deviation (Fig. 1) while bacteria concentration significantly increased within 1 day (Fig. 2). This implies that the sorption of uranium onto bacteria cell surface is negligible although U(VI) may be reduced to U(IV).

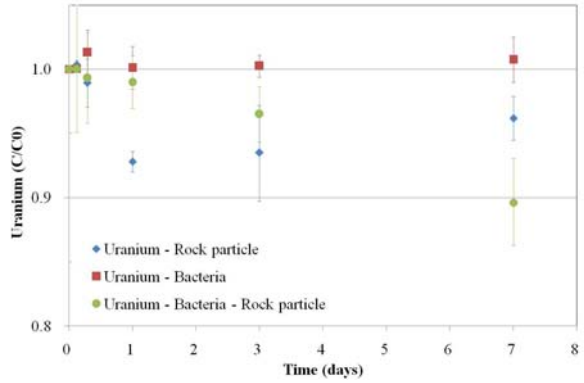

Fig. 1. Temporal distributions of normalized soluble uranium (U(VI)+U(IV)) concentration for each experimental condition.

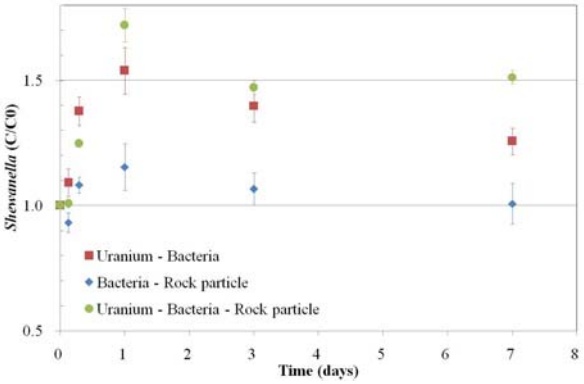

Fig. 2. Temporal distributions of normalized *Shewanella* concentration for each experimental condition.

When uranium was with only crushed rock in which biological reduction of U(VI) was not expected, initial decrease of soluble uranium concentration due to sorption to the crushed rock was observed within 1 day. After 1 day, however, the soluble uranium concentration was started to be recovered presumably due to the following desorption or dissolution. The result is in agreement with the two-step first order kinetic behavior for U(VI) sorption onto granite rock proved by Baik et al. [6]. They explained the slower sorption of U(VI) after 1 day by presumable diffusion-controlled sorption onto the granite surfaces and a mineral dissolution of the surfaces.

When uranium was with both bacteria and crushed rock, soluble uranium concentration was continuously decreased during the experimental period (7 days) and clearly distinguished from other results (Fig. 1). At that time, the bacteria growth was similar to the case that uranium was reacted with only bacteria (Fig. 2). The results can be explained as follows: uranium sorption could be initially hindered by coexisting bacteria, but the following biological reduction of U(VI) to U(IV) could continuously decrease the soluble uranium concentration.

When only bacteria and crushed rock were considered, initial decrease of bacteria concentration was slightly observed which may be due to the bacteria sorption on to the crushed rock. After instant decrease, however, bacteria concentration was little increased again. This is presumably because the bacteria inoculated at the mid to late log phase was still inertially growing.

4. Conclusions

From the multi-conditional batch experiments with uranium, *Shewanella* and granitic crushed rock, bacterial effects on the sorption of radionuclides on the granitic rock were examined in a kinetic approach. Results reveal that the biological reduction of uranium is expected to improve the retardation of uranium transport by enhancing sorption rates while colloidal effects of bacteria on the uranium migration might be negligible due to the insignificant uranium sorption onto the bacteria cells. The results will be needed to be quantitatively and specifically analyzed in the future.

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