

Effects of Geochemical Conditions on the Sorption of Radionuclides onto Granitic Rock

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1. Introduction

The geochemical behaviors of radionuclides released from the radioactive waste repository are affected by various physical or chemical factors such as advection, dispersion, diffusion, sorption, precipitation, filtration, etc. The sorption of radionuclides onto minerals is a main mechanism to retard the migration of radionuclides in a deep geological environment [1]. The sorption of radionuclides in the underground environment is highly sensitive to geochemical conditions such as concentration of radionuclides, composition of groundwater, pH, redox potential and mineral composition. The distribution coefficient (Kd) is commonly used as one of the main input parameters for the safety assessment of the repository.

Therefore, it is necessary to evaluate the effects of geochemical conditions on the sorption of radionuclides onto minerals. In this study, we collected, compared and evaluated the Kd data of radionuclides according to the pH, redox potential and carbonate concentration of groundwater.

2. Evaluation criteria of sorption data

The selection of the sorption data (Kd) for the evaluation of sorption of radionuclides was carried out under the following criteria.

- Radionuclides to be evaluated are technetium (Tc), cesium (Cs), strontium (Sr), nickel (Ni), americium (Am), and the target mineral is granite or granodiorite.
- Sorption databases (KAERI-SDB [2] and JAEA-SDB [3]) are used for the selection of Kd. Data not available in the database are referenced in the existing literatures.
- pH, redox potential, and carbonate concentration are considered as the main factors affecting the sorption of radionuclides. We compare and evaluate the Kd data under similar experimental conditions.
- A range of influencing factors for sorption is as follows; pH = 4~12, Eh = -400~+400 mV, $[\text{CO}_3^{2-}] = 0.2\sim 200$ mM
- Evaluation results are expressed by the range of Kd and the average Kd values. If the data are not sufficient, they may be presented as a single value.

3. Results and discussion

3.1 Sorption data of Tc

The Kd values of Tc tend to decrease with increasing pH (Table 1). Since Tc is mainly sorbed by surface complex formation, the formation of anionic species with increasing pH results in a decrease in Kd. The Kd value of Tc in the reducing condition was estimated to be about 10 times higher than the oxidizing condition. However, the aqueous carbonate concentration didn't affect the sorption of Tc. The Tc species changed from Tc(VII) to Tc(IV) when the redox condition changes from oxidizing condition to reducing condition. On the other hand, the carbonates do not affect the distribution of species of Tc and therefore do not affect the Kd of Tc.

Table 1. Effect of Geochemical Conditions on Kd of Tc

Geochemical conditions		Kd (m ³ /kg)	
		Range	Average
pH	3-5	$2.0 \times 10^{-3} \sim 1.0 \times 10^{-2}$	$(5.8 \pm 4.1) \times 10^{-3}$
	5-7	$3.7 \times 10^{-3} \sim 6.0 \times 10^{-3}$	$(4.8 \pm 1.2) \times 10^{-3}$
	7-9	$1.1 \times 10^{-3} \sim 6.8 \times 10^{-3}$	$(3.0 \pm 3.3) \times 10^{-3}$
Eh	Oxic	$1.1 \times 10^{-3} \sim 6.8 \times 10^{-3}$	$(3.0 \pm 3.3) \times 10^{-3}$
	Reducing	$2.4 \times 10^{-2} \sim 3.6 \times 10^{-2}$	$(3.1 \pm 5.9) \times 10^{-2}$

3.2 Sorption data of Cs

Table 2 shows the effect of pH and Eh on the Kd values of Cs. The sorption of Cs was evaluated to be independent of pH because ion exchange is the main mechanism of sorption which is less influenced by pH. The Kd distribution of Cs is not significantly affected by the change in redox condition. However, the sorption of Cs is highly dependent on the aqueous carbonate concentration. The increase of ionic strength accompanied by the increase of carbonate concentration results in an increase of competitive ions, which inhibit the ion exchange of Cs.

Table 2. Effect of Geochemical Conditions on Kd of Cs

Geochemical Conditions		Kd (m ³ /kg)	
		Range	Average
pH	3~7	$8.9 \times 10^{-2} \sim 2.6 \times 10^{-1}$	$(1.5 \pm 1.0) \times 10^{-1}$
	7~9	$4.3 \times 10^{-2} \sim 3.8 \times 10^{-1}$	$(2.2 \pm 1.5) \times 10^{-1}$
	9~11	$8.3 \times 10^{-2} \sim 6.4 \times 10^{-1}$	$(2.9 \pm 3.0) \times 10^{-1}$
Eh	Oxic	$4.3 \times 10^{-2} \sim 3.8 \times 10^{-1}$	$(2.2 \pm 1.5) \times 10^{-1}$
	Reducing	$4.9 \times 10^{-2} \sim 7.2 \times 10^{-1}$	1.8×10^{-1}

3.3 Sorption data of Sr

The Kd of Sr according to pH was not significant in the range of pH 3~9, but the Kd values tended to increase above pH 9 (Table 3). The Kd of Sr was reported to be 1.3×10^{-2} m³/kg under reducing conditions [4]. Since the sorption of Sr is hardly affected by the redox conditions, the Kd of the oxidizing condition is expected to be similar to that of the reducing condition. As the carbonate concentration increases, Kd tends to decrease slightly. This is due to the formation of Sr-carbonate complexes in the presence of carbonate. In addition, the increase in ionic strength with increasing carbonate concentration is considered to be due to the competing of cations with ion exchange with Sr.

Table 3. Effect of Geochemical Conditions on Kd of Sr

Geochemical Conditions		Kd (m ³ /kg)	
		Range	Average
pH	3~5	$1.0 \times 10^{-3} \sim 1.5 \times 10^{-3}$	$(1.2 \pm 0.3) \times 10^{-3}$
	5~7	$2.5 \times 10^{-3} \sim 5.5 \times 10^{-3}$	$(3.9 \pm 1.2) \times 10^{-3}$
	7~9	$4.2 \times 10^{-3} \sim 6.5 \times 10^{-3}$	$(2.3 \pm 0.5) \times 10^{-3}$
	9~12	$2.9 \times 10^{-3} \sim 1.7 \times 10^{-2}$	$(1.0 \pm 0.4) \times 10^{-2}$
Eh	Oxic	N.A	N.A
	Reducing	$1.0 \times 10^{-3} \sim 6.1 \times 10^{-1}$	1.3×10^{-2}

3.4 Sorption data of Ni

When the pH is increased, the Kd value of Ni increased almost 10 times (Table 4). Since sorption of Ni is not sensitive to redox conditions, Kd value was reported to be the same at 1.0×10^{-1} m³/kg under oxidation and reduction condition [5]. Since there are little data on the effect of carbonate on Kd of Ni for granite or granodiorite, it is difficult to directly evaluate the effect of carbonate. However, the sorption of Ni to SiO₂, which is one of the main components of granite, is not affected by carbonate [6]. Therefore, it is cautiously concluded that the effect of carbonate on the Kd of Ni is scarce.

Table 4. Effect of Geochemical Conditions on Kd of Ni

Geochemical Conditions		Kd (m ³ /kg)	
		Range	Average
pH	5~6	$8.0 \times 10^{-3} \sim 5.9 \times 10^{-3}$	$(6.9 \pm 1.5) \times 10^{-3}$
	7~8	$3.3 \times 10^{-2} \sim 7.6 \times 10^{-2}$	$(5.4 \pm 1.8) \times 10^{-2}$
	10~12	$1.7 \times 10^{-1} \sim 7.1 \times 10^{-1}$	$(4.1 \pm 2.7) \times 10^{-1}$
Eh	Oxic	$1.0 \times 10^{-3} \sim 5.0 \times 10^{-1}$	1.0×10^{-1}
	Reducing	$1.0 \times 10^{-3} \sim 5.0 \times 10^{-1}$	1.0×10^{-1}

3.5 Sorption data of Am

The sorption of Am was found to be very sensitive to pH changes. The average Kd value is 0.2 ± 0.4 m³/kg at below pH 5. However, the Kd of Am is more than 30 m³/kg at above pH 5. Kd of Am decreases about 50 % when the carbonate concentration increases (Table 5).

This is due to the formation of Am-carbonate complexes that are less reactive with mineral surfaces.

Table 5. Effect of Geochemical Conditions on Kd of Am

Geochemical Conditions		Kd (m ³ /kg)	
		Range	Average
pH	3~5	$1.4 \times 10^{-2} \sim 1.3$	0.2 ± 0.4
	5~7	$5.5 \times 10^{-1} \sim 68$	33.2 ± 18.2
	7~9	20~48	36.0 ± 12.4
	9~12	28~140	37.5 ± 56.5
Eh	Oxic	20~48	36.0 ± 12.4
	Reducing	>17	17.7 ± 12.4

4. Conclusions

Since the radionuclides released into underground environment behave under the influence of various geochemical factors of groundwater such as pH, redox potential and dissolved ions. Hence the geochemical factors on the behavior of radionuclides should be considered for the safety assessment of radioactive waste disposal. The Kd data for the each five radionuclides (Tc, Cs, Sr, Ni and Am) evaluated in this study cannot be used directly in the safety assessment because the measurement conditions may be different from the geochemical conditions of repository. However, it can be used as supplementary data.

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