

Sorption and Diffusion of Non-radioactive Isotopes under Oxidizing Disposal Environments

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1. Introduction

Deep geological storage is widely considered as the most safe and realistic solution for high-level radioactive waste. The geological repository utilizes a multi-barrier system comprising engineering (e.g., buffer and concrete) and natural barriers (e.g., granitic rock) to mitigate the release of radionuclides into the terrestrial ecosystem. The primary mechanisms governing the behavior of radionuclides in disposal sites include dissolution, diffusion, and sorption. This study investigates the sorption and diffusion of several non-radioactive nuclides surrogate for major concerns of radionuclides in repository using bentonite and granitic rock matrices in oxidizing groundwater conditions and provides a comprehensive understanding of the transport behavior of radionuclides within disposal environments.

2. Method and Results

2.1 Materials

Ca-bentonite (Bentonil-WRK) and Granitic rock obtained from DB-2 were selected as a representative buffer and as a natural barrier. Radionuclides that may be present in the deep disposal of spent nuclear fuel were investigated for sorption and diffusion including Cs, Nb, Ni, Tc, Zr, C, Cl, I, Se, and Sn. The individual target nuclide was spiked in simulant KAERI Underground Research Tunnel (KURT) groundwater obtained from DB-3 with a certain concentration (Table 1).

2.2 Sorption

Both bentonite and granitic rock were allowed to react with synthetic groundwater spiked with the target nuclide for more than 3 days to reach equilibrium. Considering the sorption capacity of each nuclide, the optimized solid/liquid ratios and initial concentration were selected for better performance (Table 1). The sorption distribution coefficient (K_d) was calculated according to the following equation (1). Herein, C_0 and C_{eq} is initial and equilibrated concentration of nuclide in solution, respectively. V and M represents the volume of the solution and mass of the solid.

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \frac{V}{M} \quad (1)$$

Table 1. Experimental methods of sorption and diffusion test

Nuclides	Sorption test		Diffusion test
	Initial conc. (M)	s/s ratio* (g/L)	Initial conc. (M)
Cs	7×10^{-5}	5 / 50*	5×10^{-4}
Nb	5×10^{-8}	50	5×10^{-8}
Ni	3×10^{-7}	1	3×10^{-7}
Pd	3×10^{-8}	5	3×10^{-8}
Tc	2×10^{-7}	100	2×10^{-7}
Zr	1×10^{-7}	5	1×10^{-7}
C	1×10^{-2}	50	1×10^{-2}
Cl	3×10^{-3}	10	3×10^{-3}
I	6×10^{-8}	5	4×10^{-4}
Se	4×10^{-5}	5 / 50*	4×10^{-5}
Sn	3×10^{-8}	1	3×10^{-8}

*solid to solution ratio for Cs and Se experiment were set at 5 for WRK bentonite and 50 for granitic rock to ensure reliable analysis.

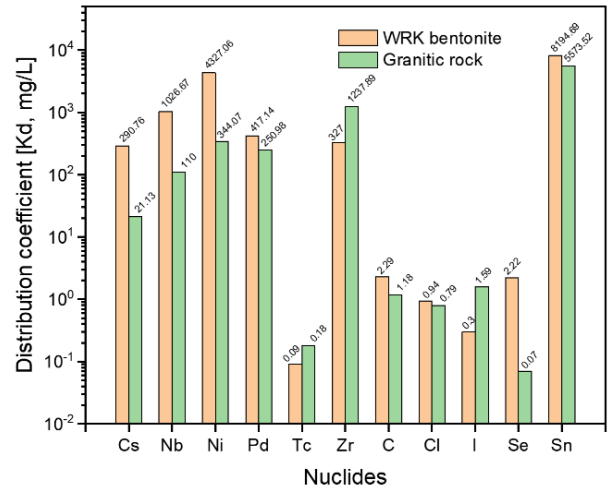


Figure 1. Distribution coefficients of nuclides in oxidizing groundwater condition on bentonite and rock material

Under typical natural conditions, clay or rock surfaces generally carry a negative charge, leading to repulsion to anions and preferred attraction to cations. Therefore, the nuclides of Sn, Ni, Zr, Nb, Pd, and Cs indicated high K_d values, while anionic nuclides: I, C, Cl, and Tc showed low K_d values on both granitic rock and bentonite. Moreover, WRK bentonite showed higher sorption capacity than granitic rock for most tested nuclides except Tc, I, and Zr (Figure 1), because of the larger cation exchange capacity and surface area of bentonite.

2.3 Diffusion

The compacted bentonite specimen (thickness 7mm) and sliced granitic rock core sample (thickness 3mm) were sealed between two reservoirs filled with groundwater. The target nuclide with a concentration below its solubility (Table 1) was spiked in the large volume reservoir to diffuse across the specimen toward the opposite reservoir. Then, the diffused amount of target nuclide was monitored until steady-state diffusion was observed. The diffusion coefficient of each nuclide was evaluated using the time-lag method [1].

Before nuclide injection, pore diffusion coefficients (D_p) of all tested specimens were measured using non-reactive tracer Br⁻. The D_p characterizes the extent of physical retardation of non-reactive tracer within a porous medium, primarily influenced by the medium's porosity and pore connectivity. Granitic rock exhibited D_p values ranging from 6.09×10^{-12} to 8.32×10^{-11} m²/s, while D_p measured for bentonite were almost 2 orders of magnitude higher than granite, which falls in range from 1.34×10^{-9} to 7.16×10^{-9} m²/s. This demonstrates that pore structure of granitic rock is more effective diffusion barrier than that of bentonite for impeding the radionuclide transport (Table 2). With significantly lower porosity compared to bentonite, granite may reduce the diffusion flux by limiting the diffusion area outside of pores and also increase the diffusion length due to pore complexity and high tortuosity.

Table 2. Pore characteristics of diffusing mediums

Material	Porosity (%)	Density (g/cm ³)	Pore diffusivity (D_p , m ² /s)
Bentonite	37	1.6	4.09×10^{-9}
Granite	0.2	2.6	2.86×10^{-11}

Table 3. Diffusion coefficients evaluated by calculation and experiments for bentonite and rock materials

Nuclides	Diffusion coefficient (D_a , m ² /s)			
	WRK bentonite		Granitic rock	
	experiment	calculated	experiment	calculated
Cs	N.D	5.13×10^{-12}	9.77×10^{-13}	3.46×10^{-16}
Nb	N.D	4.66×10^{-13}	N.D	5.65×10^{-16}
Ni	N.D	2.21×10^{-13}	N.D	5.20×10^{-17}
Pd	N.D	1.9×10^{-12}	N.D	2.93×10^{-16}
Tc	4.73×10^{-9}	2.90×10^{-9}	3.60×10^{-11}	1.05×10^{-11}
Zr	N.D	5.60×10^{-12}	N.D	3.64×10^{-17}
C	7.42×10^{-10}	4.64×10^{-9}	6.18×10^{-12}	2.73×10^{-14}
Cl	1.59×10^{-9}	1.34×10^{-9}	2.35×10^{-11}	1.25×10^{-11}
I	4.47×10^{-9}	7.16×10^{-9}	2.74×10^{-11}	6.90×10^{-12}
Se	N.D	1.43×10^{-10}	3.71×10^{-12}	3.71×10^{-12}
Sn	N.D	8.30×10^{-14}	N.D	2.27×10^{-18}

Not only retardation by pore structure, diffusing species through a porous medium may partition to solid by chemical reactions like adsorption/ion-exchange, and it directly influences the local concentration gradient, thereby reducing diffusion flux. The apparent diffusion coefficient (D_a) is a comprehensive measure of these overall retardation capability of each nuclide. Weakly sorbing anionic nuclides such as I, Cl, Tc, and C

exhibited high D_a values, similar to the D_p . However, steady-state diffusion of Cs, Ni, Zr, Pd, and Nb was hardly observed due to their pronounced tendency for sorption. Moreover, Zr, Pd, and Nb were less soluble in tested groundwater conditions, therefore initial concentration gradient was too small to induce steady-state diffusion even after several months.

Therefore, the theoretically calculated D_a values are also presented in Table 3. The D_a of each nuclide was calculated by dividing D_p with retardation factor (2). Here, ρ_b and θ represent bulk density and porosity of tested compacted bentonite and sliced granitic rock specimen used for diffusion experiments. The value K_d obtained from sorption experiment was used (Figure 1).

$$D_a = \frac{D_p}{(1 + \frac{\rho_b K_d}{\theta})} \quad (2)$$

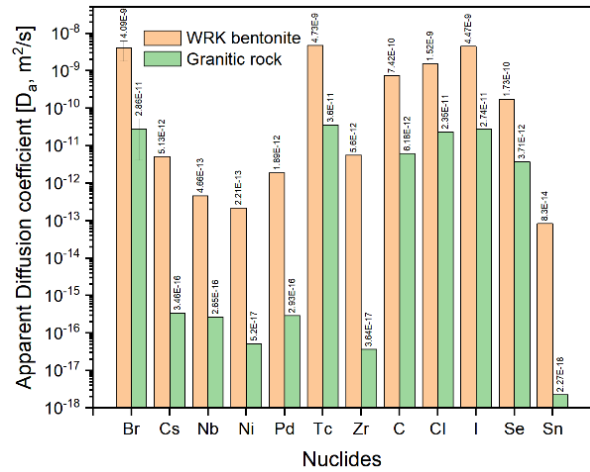


Figure 2. Diffusion coefficients of nuclides in oxidizing groundwater condition through bentonite and rock material

All tested nuclides showed significantly lower diffusion flux through granitic rock compared to bentonite (Figure 2). The difference can be attributed to the low porosity and corresponding pore-connectivity of granitic rock (Table 2). Even though granite showed poor sorption capacity than bentonite for most tested nuclides (Figure 1), the impact of granite's compact structures on nuclide migration demonstrated superior comprehensive retardation. This result highlights the importance of the diffusion barrier provided by complex pore structures as a retardation mechanism in high-level radioactive waste repository.

4. Conclusion

WRK bentonite showed higher sorption capacity than granitic rock for most tested nuclides, however, comprehensive retardation was more efficient in granite, which provides a high physical diffusion barrier to nuclide migration. The effect of diffusion was particularly important for anionic species because they

exhibit minimum sorption interaction with both bentonite and rock material.

REFERENCES

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