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

〈 산화환경 처분장 조건에서 비방사성 동위원소의 수착, 확산 평가 〉

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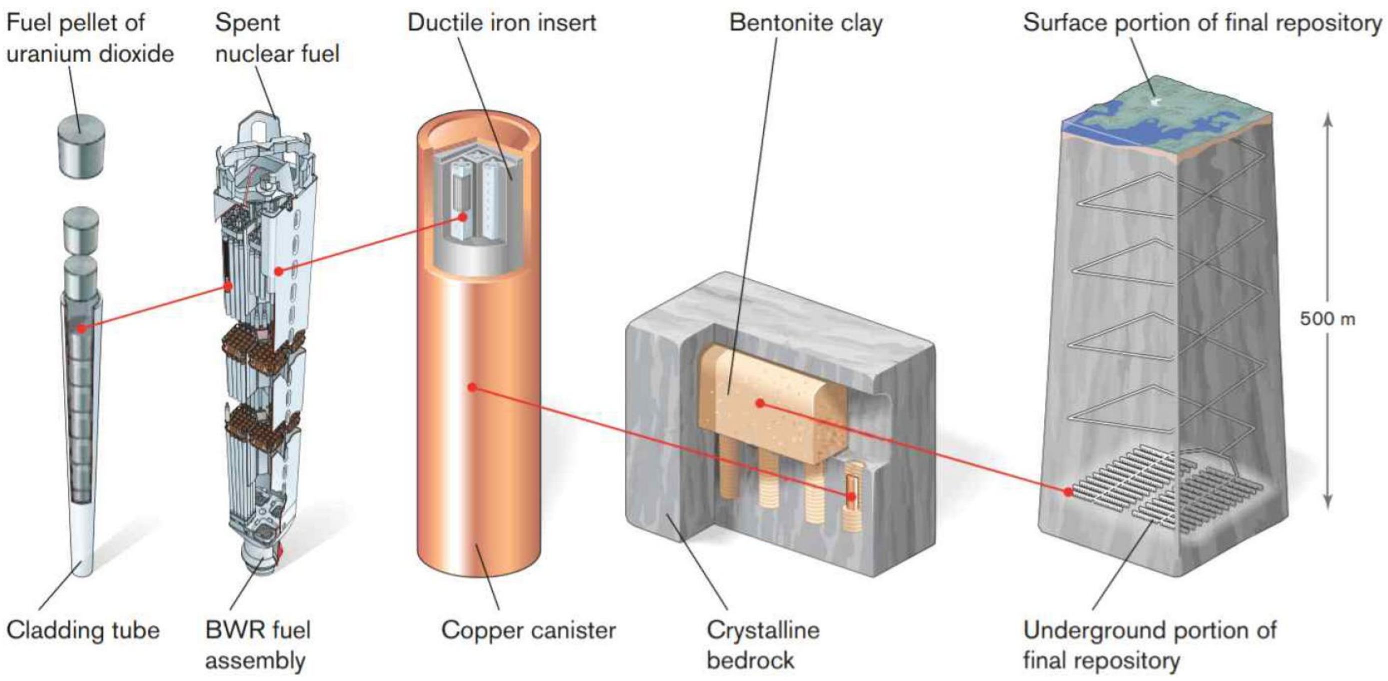
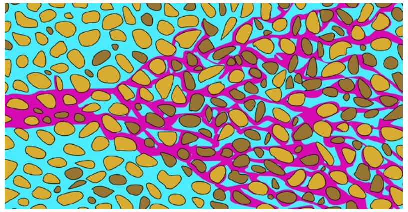
Introduction

01 Deep geological disposal based on multi-barrier design



- Deep geological storage is widely considered as the most safe and realistic solution for high-level radioactive waste.
- Korea has decided to introduce the concept of an multi-barrier system for deep disposal at a depth of 500 m underground.
- 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.
- Therefore, in order to evaluate the safety of deep disposal facilities, understanding of the transport behavior of nuclides in each barrier are critically required.



Distribution & Diffusion coefficient of RN through
- Buffer material : Bentonite
- Natural Barrier : Crystalline bedrock

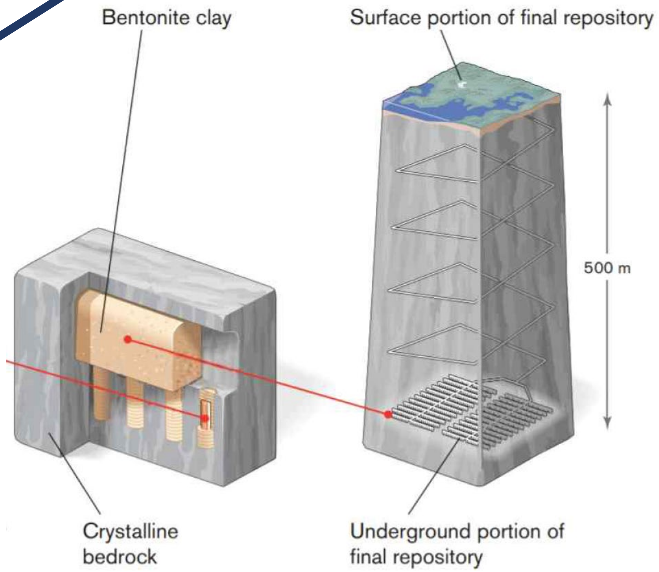
Dissolution
from SNF to groundwater

Sorption
(adsorption, ion-exchange, precipitation, etc.)

Diffusion
through pore structure of natural/engineering barrier

Advection/Dispersion
by flow of groundwater

Transport of Radionuclide
from Repository to Environment



This study investigates..

The sorption and diffusion of several non-radioactive nuclides using bentonite and granitic rock matrices in oxidizing groundwater conditions and provides a comprehensive understanding of the transport behavior of radionuclides within disposal environments.

II

Material & Method

Solid Materials

Solid Materials	Sorption	Diffusion
Ca-bentonite (Bentonil-WRK)	• Used as received (without pre-equilibration)	• Compacted specimen with thickness 7mm • Density 1.6 g/cm^3, Porosity 37 %
Rock from DB-2 (~ 800 m #140)	• Crushed (75~150 μm) & washed • Pre-equilibrated with groundwater (3d)	• sliced core with thickness 3mm • Density 2.61 g/cm^3, Porosity 0.222 %

Groundwater & Target nuclides

Synthetic groundwater

KURT DB-3		Synthetic GW	
Composition	mg/L	Chemicals	mg/L
Na^+	37.9	$Mg(OH)_2$	0.696
Ca^{2+}	5.70	KCl	0.629
K^+	0.33	$Na_2SO_39H_2O$	35.483
Mg^{2+}	0.29	$CaSO_4$	8.220
SiO_2	7.50	NaCl	2.458
HCO_3^-	79.3	$Ca(OH)_2$	6.064
Cl^-	1.79	$NaHCO_3$	109.183
SO_4^{2-}	5.80	NaF	1.402
F^-	8.10	HF	7.380
Temp (℃)	14.8		25
pH	9.05		8.14
Eh (mV)	-438		426
DO (mg/L)	0.05		
EC (μS/cm^2)	196		

KURT and DB-2 borehole locations


box#140

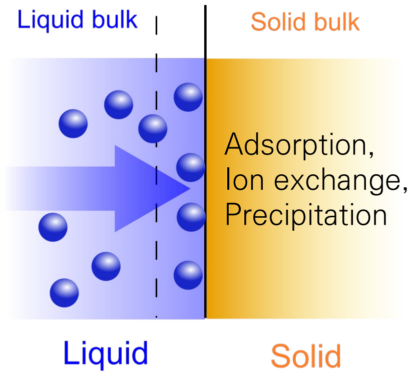
+ Target Nuclides

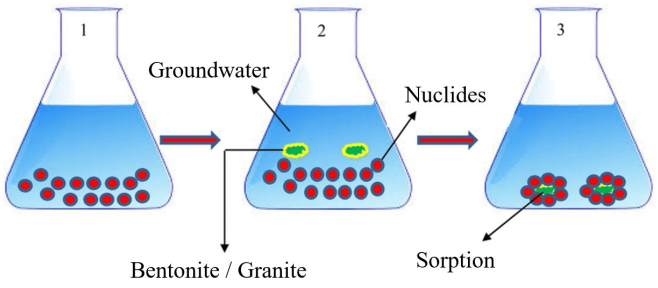
- Cs, Nb, Ni, Pd, Zr, Sn, C, Cl, I, Tc, Se (POSTECH)
- Sr, Ra, Ac, Am, Cm, Np, Pa, Pu, Th, U (KAERI)

Sorption test

Nuclides	Initial conc. (M)		s/s ratio* (g/L)		Analysis
	Bentonite	Granite	Bentonite	Granite	
Cs	7.32×10^{-5} (10 ppm)	7.95×10^{-5} (10 ppm)	5	50	ICP-MS
Ni	3.55×10^{-7} (20 ppb)	1.97×10^{-7} (11 ppb)	1	1	
Zr	1.26×10^{-7} (11 ppb)	1.08×10^{-7} (10 ppb)	5	5	
Pd	3.38×10^{-8} (4 ppb)	3.60×10^{-8} (4 ppb)	5	5	
Sn	3.31×10^{-8} (4 ppb)	2.84×10^{-8} (3ppb)	1	1	
Nb	5.63×10^{-8} (5 ppb)	4.66×10^{-8} (4 ppb)	50	50	
Tc	1.48×10^{-7} (15 ppb)	1.48×10^{-7} (15 ppb)	100	100	
C	1.03×10^{-2} (123 ppm)	9.48×10^{-3} (113 ppm)	50	50	TOC
Cl	2.77×10^{-3} (98 ppm)	2.78×10^{-3} (98 ppm)	10	10	IC
I	6.06×10^{-8} (8 ppb)	5.76×10^{-8} (7 ppb)	5	5	
Se	4.56×10^{-5} (3.8 ppm)	4.72×10^{-5} (3.8 ppm)	5	50	ICP-MS

The solid/liquid ratio and Initial concentration was determine according to the adsorption capacity of the nuclides.





70 rpm at RT for 7 days

Distribution coefficient, K_d

$$K_d = \frac{C_0 - C_{eq}}{C_{eq}} \frac{V}{M}$$

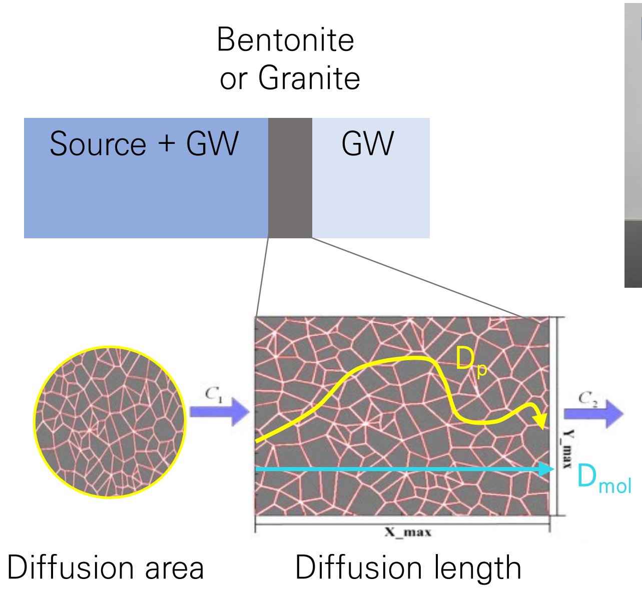
C_0 (mol/m^3 or Bq/m^3): Initial concentration of nuclides

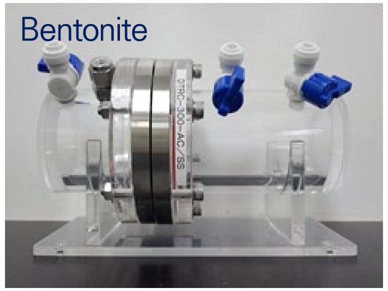
C_{eq} (mol/m^3 or Bq/m^3): equilibrium concentration of nuclides in liquid phase after equilibrated with solid phase

V (mL): volume of groundwater, M (g): mass of solid phase

Experimental Method

Nuclides	Initial conc. (M)	Analysis
Cs	7.52×10^{-4} (100 ppm)	ICP MS
Ni	1.70×10^{-7} (10 ppb)	
Zr	1.10×10^{-7} (10 ppb)	
Pd	4.70×10^{-8} (5 ppb)	
Sn	4.21×10^{-8} (5 ppb)	
Nb	5.38×10^{-8} (5 ppb)	
Tc	1.48×10^{-7} (10 Bq/mL, 15 ppb)	
C	1.64×10^{-3} (100 ppm)	TOC
Cl	2.82×10^{-1} (1000 ppm)	IC
I	7.88×10^{-3} (1000 ppm)	
Se	3.50×10^{-5} (5 ppm)	ICP MS

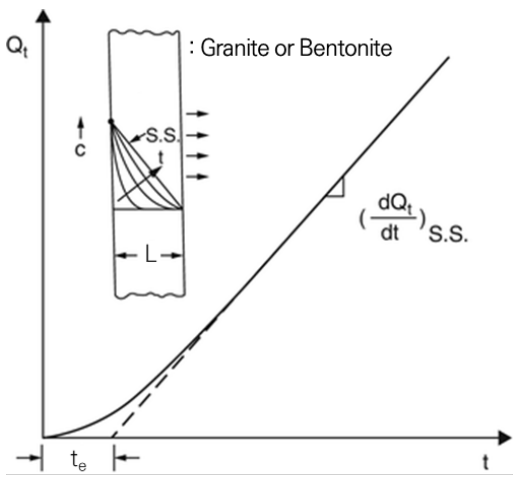




- D_{mol} + effect of porous media = D_p
- D_p + effect of sorption = D_a

Diffusion coefficient

Time Lag method



- D_a : Apparent diffusion coefficient

Fick's 2nd law → $\frac{Q}{A} = \frac{D_a \alpha C_0}{L} t - \frac{\alpha C_0 L}{6}$ $\quad D_a = \frac{L^2}{6t_e}$ $\quad D_a = \frac{D_p}{(1 + \frac{\rho_b K_d}{\theta})}$

Q/A : cumulative ion transmission per unit area of the specimen
C_0 : concentration of nuclide in concentration cell
L : thickness of porous specimen, α : capacity factor, t_e : elapsed time
ρ_b : bulk density, θ : porosity

K_d : distribution coefficient (sorption)
ρ_b : bulk density, θ : porosity

- D_p : Pore diffusion coefficient

$$D_p = \frac{D_{mol}}{G} \qquad D_{mol} = \frac{RT}{F^2}\frac{\frac{1}{n^+} + \frac{1}{n^-}}{\frac{1}{\lambda^+} + \frac{1}{\lambda^-}}$$

(Nernst−Haskell equation)

D_{mol} : molar diffusion coefficient
n : ion charge, λ : ionic conductivity

III

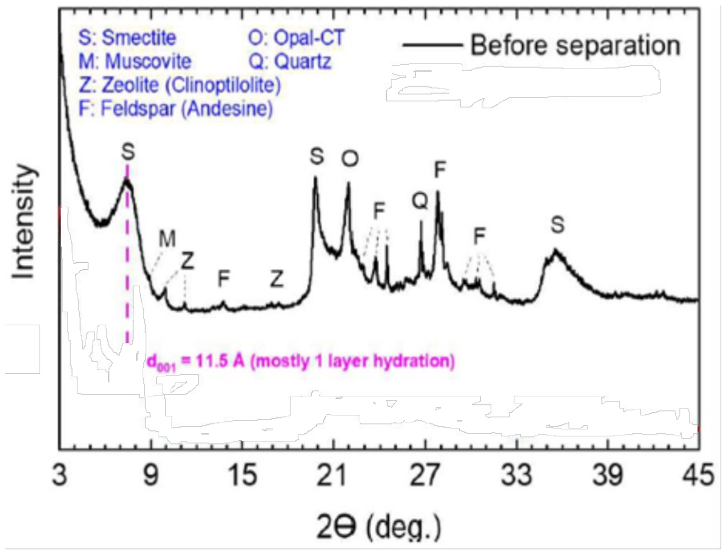
Result & Discussion

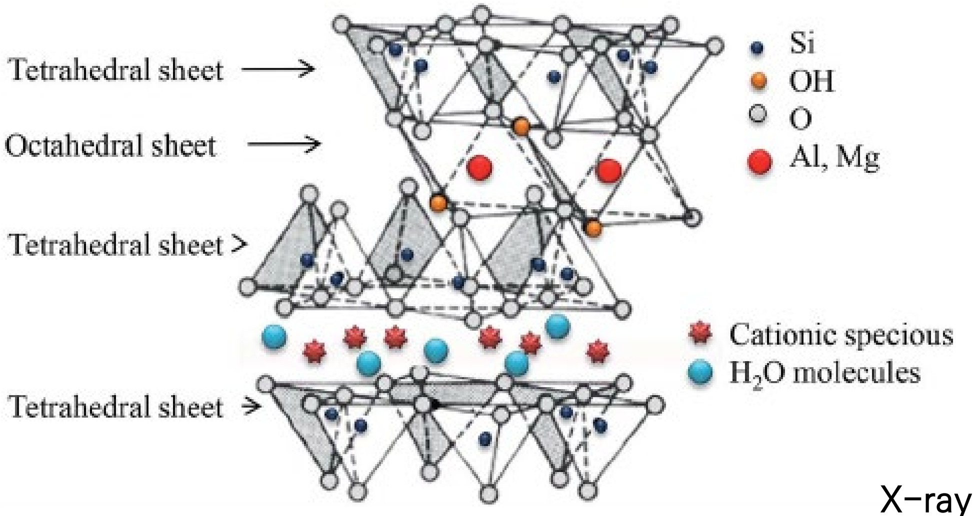
- Characterization
- Retardation by Sorption
- Retardation of RN by Diffusion
- Conclusion

01 Characterization of Bentonite

Mineralogy

X-ray diffraction (XRD)





(wt.%)

Mineral	Smectite	Feldspar	Muscovite	Quartz	Opal-CL	Zeolite	Total
Bentonil WRK	75.1	8.8	5.7	1.7	4.0	4.6	100.2
MX-80	81.4	-	3.4	3.0			

X-ray fluorescence (XRF)

Comp.	Bentonil WRK	MX-80
SiO_2	63.37	67.4
Al_2O_3	16.29	21.2
Fe_2O_3	3.79	4.1
CaO	2.78	1.5
MgO	3.18	2.6
K_2O	0.68	0.6
Na_2O	0.55	2.3
TiO_2	0.52	0.2
MnO	0.09	-
P_2O_5	-	0.1

Ca bentonite ⇦

Density / Porosity / Surface area

Powder		Compacted specimen	
Surface area	Particle density	Bulk density	Porosity
59.1 m^2/g	2.548 g/cm^3	1.6 g/cm^3	37 %

02 Characterization of Granite

Mineralogy

X-ray diffraction analysis (XRD) (wt.%)

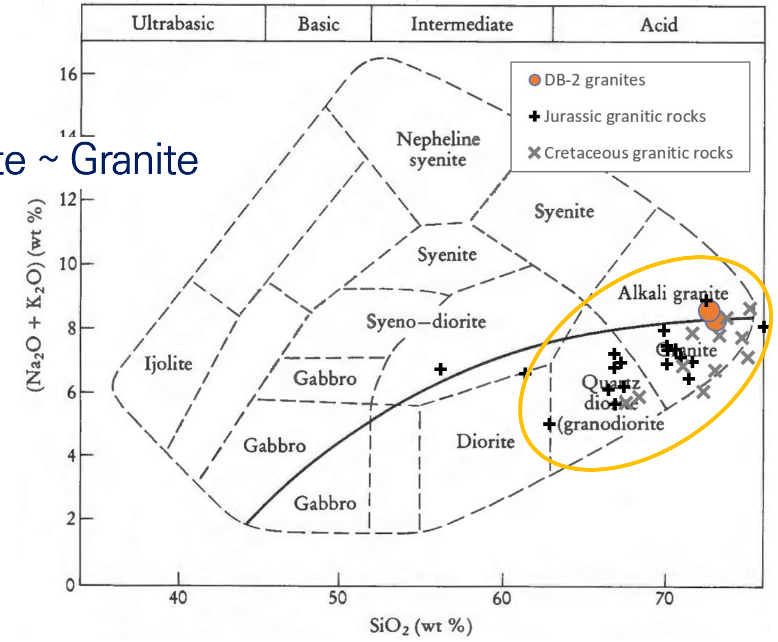
Mineral	Plagioclase	Quartz	K-feldspars	Muscovite	Biotite	Chlorite	Total
Granite	31.3	29.5	26.5	7.2	4.2	1.5	100.2

Elemental composition

X-ray fluorescence analysis (XRF) (wt.%)

SiO_2	71.4	K_2O	5.0
Al_2O_3	14.9	Na_2O	3.3
Fe_2O_3	1.5	TiO_2	0.2
P_2O_5	0.1	MnO	0.1
Loss of ig.	1.1		

Alkali granite ~ Granite



Density / Porosity / Surface area

Crushed rock		Bulk specimen	
Particle size	Surface area	Bulk density	Porosity
75~150	0.2087 m^2/g	2.61 g/cm^3	0.222 %
150~300	0.1616 m^2/g		

Retardation by Sorption

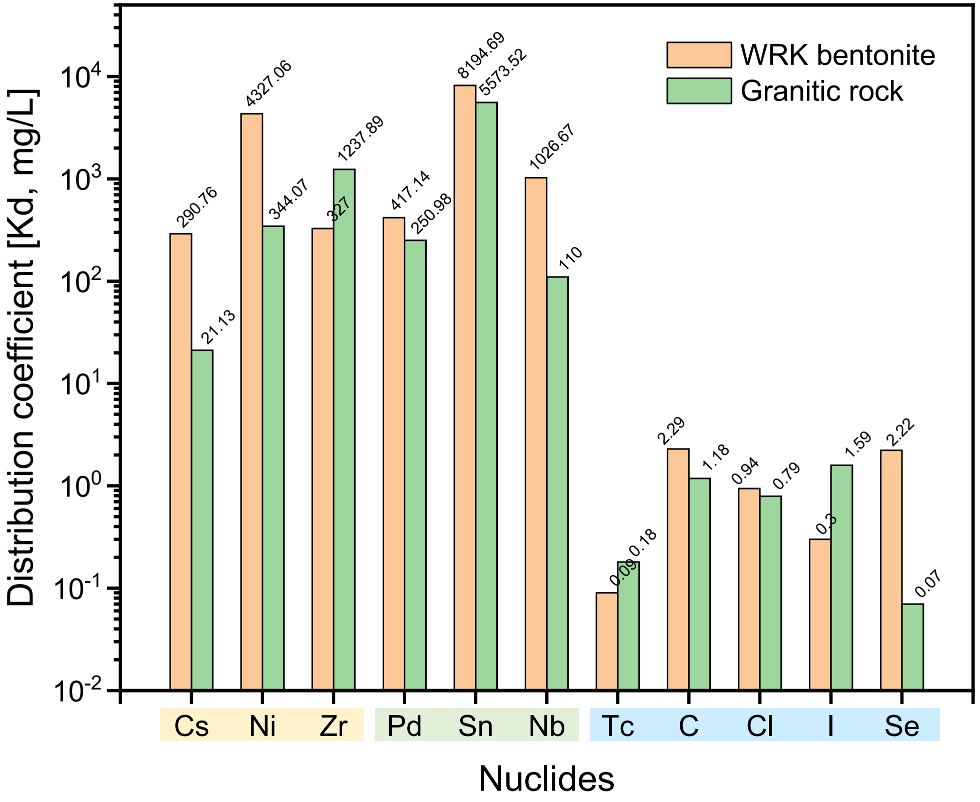
- Under typical natural conditions, clay or rock surfaces generally carry a negative charge, leading to repulsion to anions and preferred attraction to cations.
- Anionic nuclides: I, C, Cl, and Tc showed low Kd values on both granitic rock and bentonite.
- WRK bentonite showed higher sorption capacity than granitic rock for most tested nuclides except Tc, I, and Zr, because of the larger cation exchange capacity and surface area.

Sorption capacity

Bentonite 〉 Granite

- High surface area
- High cation exchange capacity

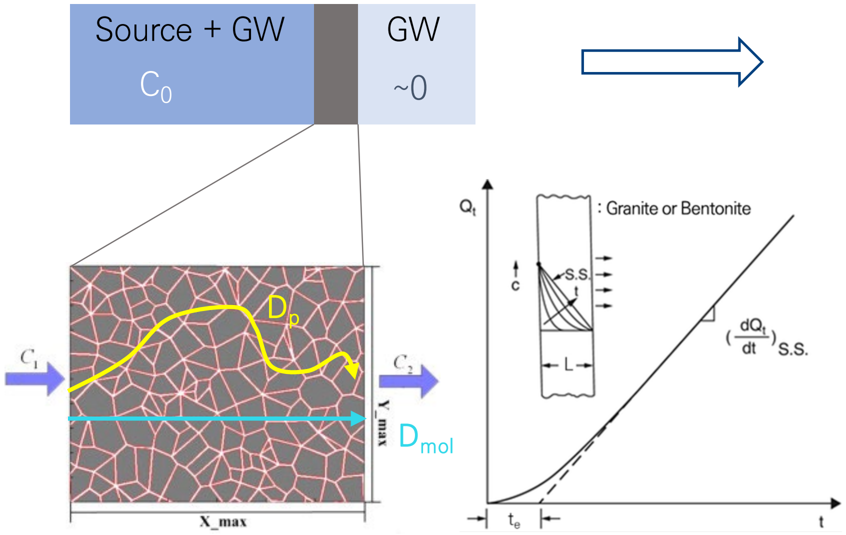
	Speciation in GW		Kd value
Cs	Cationic species	Cs^+	High Kd
Ni		Ni^{2+}	
Zr		Zr(Ⅳ) : Zr^{4+} or $Zr(OH)^{3+}$, $Zr(OH)_2^{2+}$	
Pd	Less soluble	Pd(Ⅱ) : $Pd(OH)_{2(aq)}$	
Sn		Sn(IV) : $SnOCl_2$ / $Sn(OH)_2Cl_2$	
Nb		Nb(Ⅴ) : $Nb(OH)_6^-{}_{(aq)}$, $Nb_2O_{5(aq)}$	
Tc	Anionic species	TcO_4^-	Low Kd
C		HCO_3^-	
Cl		Cl^-	
I		I^-	
Se		SeO_3^{2-}	

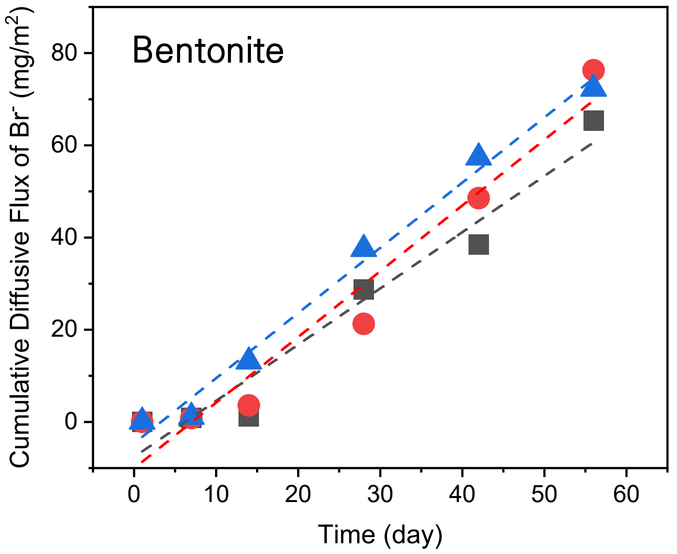


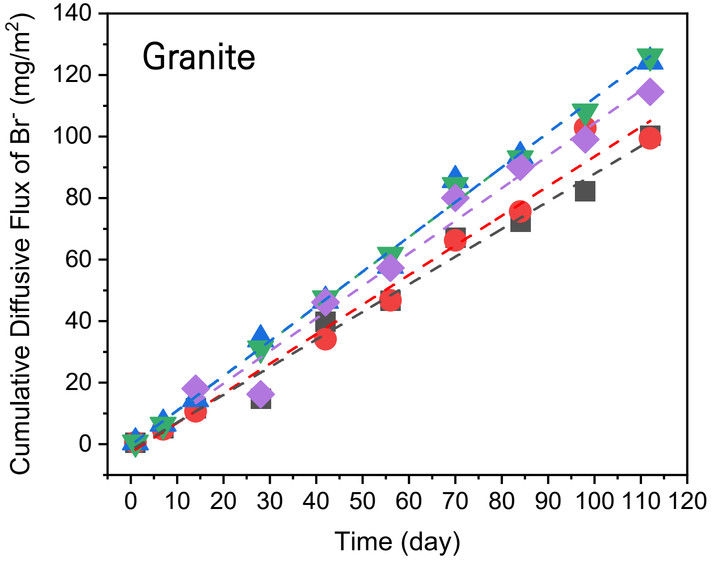
04 Pore diffusion (D_p)

D_{mol} + effect of porous media = D_p

The D_p characterizes the extent of physical retardation within a porous medium, primarily influenced by the medium's porosity and pore connectivity.

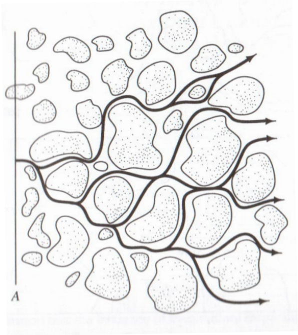






Sample	Thickness (mm)	Diffusion area (mm^2)	Bulk density (g/cm^3)	Porosity (%)	Pore diffusion coefficient (m^2/s)	
					Range	Average
WRK bentonite	7	615.75	1.6	37	1.34×10^{-9} – 7.16×10^{-9}	4.09×10^{-9}
Granitic rock	3	1809.56	2.6	0.2	6.09×10^{-12} – 8.32×10^{-11}	2.86×10^{-11}

- Pore structure of granitic rock is more effective diffusion barrier than that of bentonite for impeding the radionuclide transport.
- 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.



- Not only retardation by pore structure, diffusing species through a porous medium may partition to solid by sorption, 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.

$$D_{mol} = \frac{RT}{F^2}\frac{\frac{1}{n^+}+\frac{1}{n^-}}{\frac{1}{\lambda^+}+\frac{1}{\lambda^-}} \qquad D_p = \frac{D_{mol}}{G} \qquad D_{mol} = \frac{RT}{F^2}\frac{\frac{1}{n^+}+\frac{1}{n^-}}{\frac{1}{\lambda^+}+\frac{1}{\lambda^-}} \qquad D_a = \frac{D_p}{(1+\frac{\rho_b K_d}{\theta})}$$

Cationic species

Cs^+, Ni^{2+}, Zr^{4+}

→ Steady-state diffusion was hardly observed due to their pronounced tendency for sorption.

Less soluble

Pd(II), Sn(IV), Nb(V)

→ Initial concentration gradient was too small to induce steady-state diffusion even after several months

Anionic species

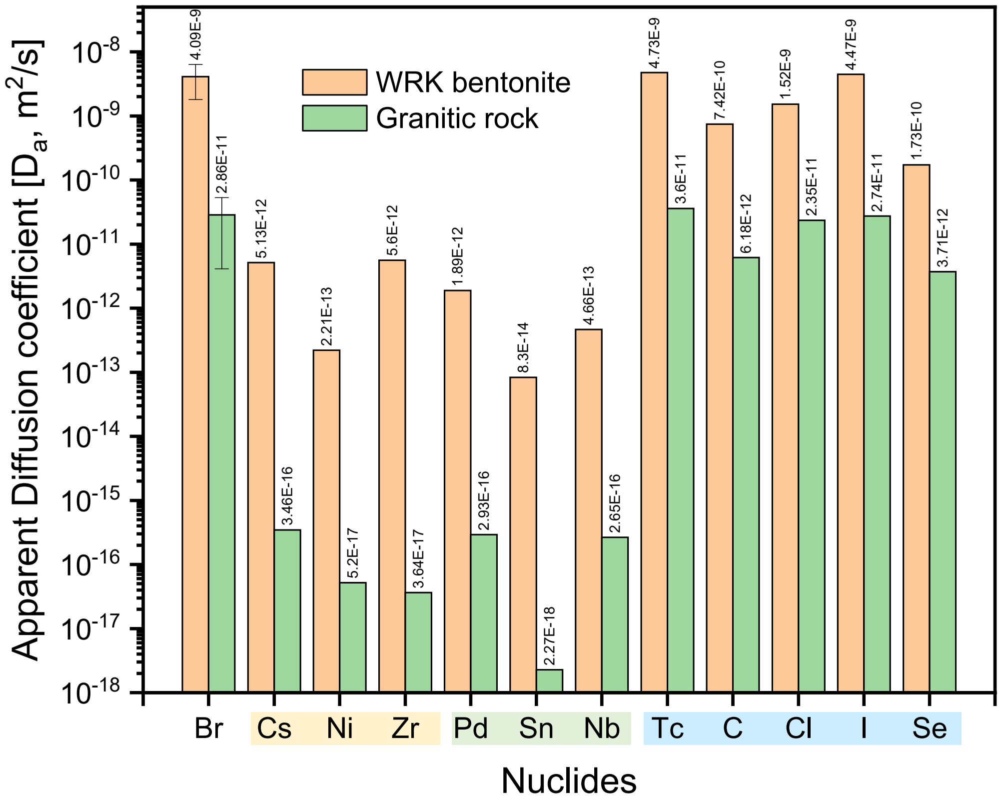
I^-, HCO_3^-, Cl^-, TcO_4^-, SeO_3^{2-}

→ Weakly sorbing nuclides. High D_a values similar to the D_p

Nuclides	Diffusion coefficient (D_a, m^2/s)			
	WRK bentonite		Granitic rock	
	experiment	calculated	experiment	calculated
Cs	N.D	5.13×10^{-12}	N.D	3.46×10^{-16}
Ni	N.D	2.21×10^{-13}	N.D	5.20×10^{-17}
Zr	N.D	5.60×10^{-12}	N.D	3.64×10^{-17}
Pd	N.D	1.90×10^{-12}	N.D	2.93×10^{-16}
Sn	N.D	8.30×10^{-14}	N.D	2.27×10^{-18}
Nb	N.D	4.66×10^{-13}	N.D	5.65×10^{-16}
Tc	4.73×10^{-9}	2.90×10^{-9}	3.60×10^{-11}	1.05×10^{-11}
C	7.42×10^{-10}	4.64×10^{-9}	6.18×10^{-12}	2.73×10^{-13}
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}

06 Apparent Diffusion (D_a)

- All tested nuclides showed significantly lower diffusion flux through granitic rock compared to bentonite.
- The difference can be attributed to the low porosity and corresponding pore−connectivity of granitic rock.
- Even though granite showed poor sorption capacity than bentonite for most tested nuclides, the impact of granite's compact structures on nuclide migration demonstrated superior comprehensive retardation.



Sorption capacity

Bentonite 〉 Granite

- High surface area
- High cation exchange capacity

Diffusion barrier

Bentonite 〈 **Granite**

- Low porosity, pore connectivity
- High density

Sample	Bulk density (g/cm^3)	Porosity (%)	Pore diffusion coefficient (m^2/s)
WRK bentonite	1.6	37	4.09×10^{-9}
Granitic rock	2.6	0.2	2.86×10^{-11}

- Present study investigates the sorption and diffusion characteristics of non-radioactive isotopes (Cs, Ni, Zr, Pd, Nb, Sn, Tc, I, C, Cl, Se) under oxidizing KURT condition.
- Batch sorption, through-diffusion experiment were performed using on-site collected rock sample and simulate solutions (groundwater) and potential engineering barrier materials (bentonil WRK).
- Potential buffer material, WRK bentonite showed high sorption capacity for Cs, Ni, Zr, Pd, Nb, Sn.
- The granite host rock provided good diffusion barrier for anionic species.
- WRK bentonite showed higher sorption capacity than granitic rock for most tested nuclides, however, comprehensive retardation (D_a) was more efficient in granite, which provides a high physical diffusion barrier to nuclide migration.
- This result highlights the importance of the diffusion barrier provided by complex pore structures as a retardation mechanism in high-level radioactive waste repository.
- All the tested parameters can be used as input parameter of safety analysis of radioactive waste repository

Thank you.

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