Effect of colloids on radionuclide migration for performance assessment of HLW disposal in Japan*

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Abstract: Colloidal effect is one of the major factors to enhance the migration of radionuclides in groundwater. The experimental and theoretical studies of colloid mobility and colloid-facilitated radionuclide transport for the performance assessment of high-level radioactive waste (HLW) geological disposal is presented in this paper. The major aims of the study are (1) to study the filtration effect on colloids by the engineered barrier system, (2) to study bentonite colloid generation by erosion of the engineered barrier system, and (3) to calculate radionuclide migration with groundwater colloids through fractured rock systems.

INTRODUCTION

HLW in Japan refers to the waste resulting from reprocessing of the spent nuclear fuel to recover uranium and plutonium. After reprocessing, the HLW is melted with a glass material, sealed in a metal canister, and stored in a solid form. The baseline policy of Japan with regard to the treatment and disposal of HLW calls for solidification into a stable form and interim storage for 30 to 50 years for cooling, followed by disposal into geological formation at more than several hundred meters underground to further ensure the long-term safety of humans and the environment.

The most important point concerning the safety of geological disposal is to maintain and evaluate safety measures to counteract the possibility of radionuclides affecting humans and the environment through groundwater. The principle is to take necessary measures in advance to prevent this from occurring, and further evaluate and confirm that the influence on humans and the environment will not be significant in all reasonably foreseeable circumstances. This principle conforms to that of multiple protections for nuclear safety.

The performance assessment study centers on the radionuclide transport, as it is an important aspect with respect to the safety of geological disposal. In order to assess the performance of the geological disposal system, it is important to analyze the consequence of the scenario where radionuclides dissolved from the HLW will be transported by the groundwater and enter the human living environment. Accordingly, it is necessary to elucidate the transport characteristics of radioactive species in the engineered barrier and the rock system for the performance assessment of HLW disposal. In this field, the influence of fine particles, such as colloidal particles, on radionuclide transport has received much attention.

Colloidal effect is one of the major factors to enhance the migration of radionuclides in groundwater. At the nuclear test site in Nevada, USA, it has been reported that radionuclides were detected in a well-located 1.3 km from the test site. This cannot be understood in terms of migration of solutes in

groundwater, because the radionuclides would be related by sorption. However, the enhanced migration could potentially be due to colloids, and thus, it is important to consider their potential impact on repository safety.

This paper presents experimental and theoretical studies of colloid mobility and colloid-facilitated radionuclide transport for the performance assessment of HLW geological disposal. The major aims of the study are (1) to study the filtration effect on colloids by the engineered barrier system, (2) to study the bentonite colloid generation by the erosion of the engineered barrier system, and (3) to calculate radionuclide migration with groundwater colloids through fractured rock systems.

GEOLOGICAL DISPOSAL CONCEPT IN JAPAN

Figure 1 shows the HLW geological disposal system in Japan [1]. The HLW is melted with glass materials, sealed in a metal canister, and stored in a solid form as a vitrified waste. The HLW is then sealed into a container called "overpack" and disposed of deep underground. The space between the host rock and the overpack is filled with backfilling material, that is, engineered barrier such as clay. The geological disposal system is based on the complementary nature of an engineered barrier for waste confinement and natural geological environment that have various natural functions favorable to ensure the protection of humans and the environment. The designed function of the engineered barrier is to prevent groundwater from contacting with the HLW owing to the physical and chemical characteristics. Should groundwater come into contact with the HLW, the engineered barrier reduced the dissolution rate and migration of radionuclides from the waste. The natural barrier (host rock) is expected to retain the dissolved radionuclides in the geological environment for a long time by adsorption capacity of the minerals, along with the dispersion and dilution of the radionuclides in the groundwater.

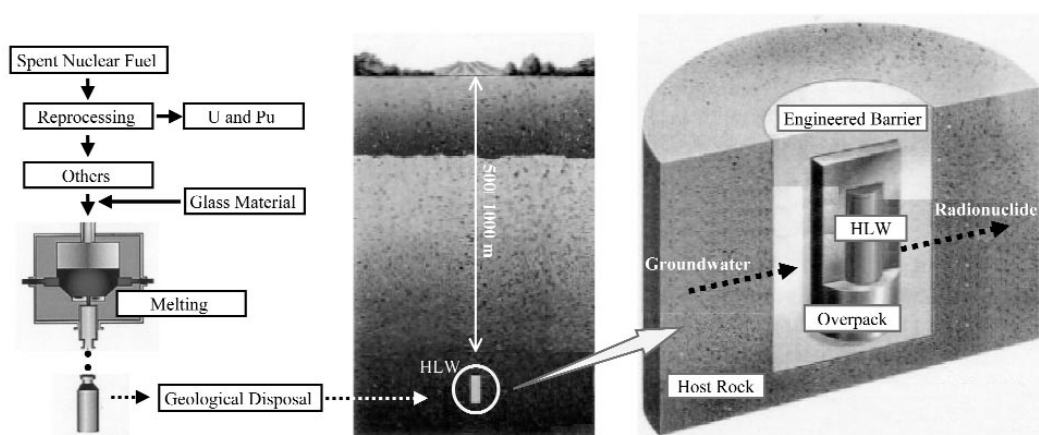**Fig. 1** HLW geological disposal concept in Japan.

FILTRATION EFFECT ON COLLOIDS BY ENGINEERED BARRIER SYSTEM

Bentonite, which has low permeability, high swelling capability, and high adsorption capacity, was examined as the preferred material for the engineered barrier considering required functions such as buffering chemical conditions, dissipating decay heat, supporting overpack, and buffering external stress over a long period of time. The compacted bentonite surrounding the waste of Japanese concept is considered to behave as a filter to trap colloids owing to its microstructure. However, the shape of the

microstructure depends on the degree of compaction and the swelling properties of bentonite. Therefore, column experiments were performed to investigate the transport behavior of colloids through the microstructure of the compacted bentonite and sand–bentonite mixtures, which are expected the engineered barrier.

Experiment

Figure 2 shows the experimental setup [2]. The bentonite used was sodium-type bentonite (Kunigel-V1, Japan). The sand–bentonite mixture was prepared by mixing silica sand with the bentonite. The silica sand used was 0.9–1.2 mm in diameter and was mixed at a ratio of 30 to 90 wt.% with the bentonite. The bentonite and the sand–bentonite mixture were packed into columns at dry densities of 1000, 1400, 1600, and 1800 kg/m^3 and then saturated with distilled water. Tracer solution with the colloidal gold was used to simulate mobile colloids because it was well characterized and dispersivity was controlled. Gold colloid was 15 nm in diameter and was mono dispersed. To maintain colloidal stability, ethanol and plyoxyethylene hydrogenated caster oil were added as surface-active agents [3]. The pH value of tracer solution was 6.6, and the surface potential of the gold colloid was –6.6 mV.

Also in this experiment, ultrafilters with effective 10 000 molecular-weight cutoff (MWCO), equivalent to approximately 1.5 nm pore size [4], were used to separate the colloids from the effluent solutions. The concentrations of gold in the filtered and unfiltered effluents were measured by inductively coupled plasma-mass spectrometry with a detection limit of 5×10^{-11} mol/L. If concentration of gold in filtered effluent was the same as in unfiltered effluent, this means that no measurable colloidal gold transport occurs through the engineered barrier. That is, the difference in the gold concentration between filtered and unfiltered effluents directly corresponds to the concentration of the colloid passing through the compacted bentonite and sand–bentonite mixture. The distribution of colloidal gold in the bentonite samples were observed by using electron probe micro analysis (EPMA) after the column experiments.
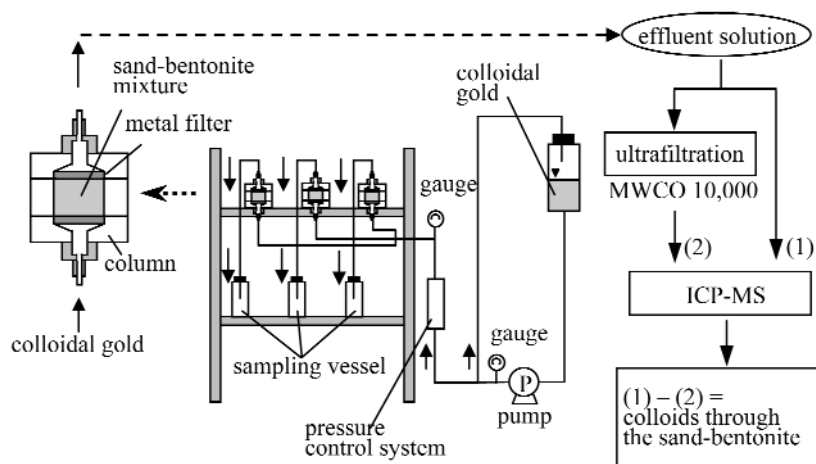

Fig. 2 Schematic view of colloidal transport test equipment.

Results and discussions

Figure 3 shows the results of colloidal transport experiments through compacted sand–bentonite mixture [2]. On the engineered barrier samples of a, b, and c, small amounts (C/C_0 : 0.1) of the colloid's breakthrough were observed in the effluent. On the other hand, on the engineered barrier samples of d and e, no measurable colloidal gold transport occurs through the engineered barrier.
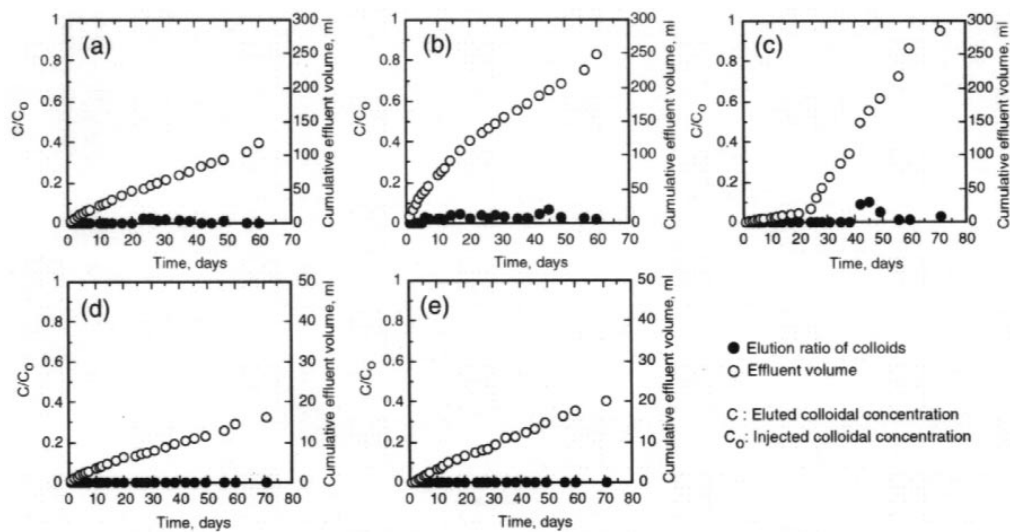
Fig. 3 Results of colloidal transport test through compacted sand–bentonite mixture at dry densities of 1400, 1600, and 1800 kg/m^3: (a) 1400 kg/m^3 with 80 wt.% silica sand, (b) 1600 kg/m^3 with 90 wt.% silica sand, (c) 1600 kg/m^3 with 80 wt.% silica sand, (d) 1600 kg/m^3 with 70 wt.% silica sand, (e) 1800 kg/m^3 with 80 wt.% silica sand.

Figure 4a shows the relation between the possibility of colloid filtration and practical density of bentonite in the engineered barrier based on experimental results [2]. In this figure, the horizontal axis means compacted dry densities of the engineered barrier, and the vertical axis means the content of the silica sand. The broken line in Fig. 4 indicates the bentonite gel density, that is, practical density of bentonite 800 kg/m^3 in the engineered barrier. The experimental results indicate that the possibility of colloid transport or filtration depends on practical density of bentonite. The practical density of bentonite 800 kg/m^3 is considered as the upper-limit density for the colloid transport through the engineered barrier. Also, Fig. 4b shows a photograph of colloids within the engineered barrier, which was obtained by EPMA after the column experiment [5]. The concentration of gold (Au) was found to be rich on the surface of the engineered barrier. This result indicates that the colloids were readily filtered on the surface layer of the engineered barrier.
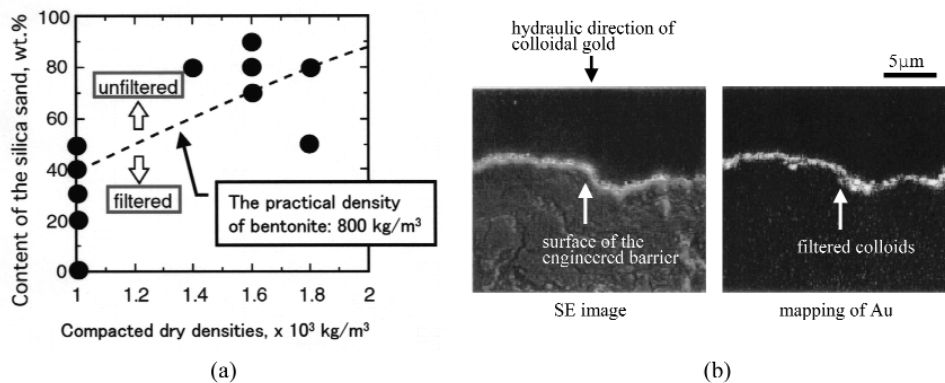

Fig. 4 Colloid filtration by the enginireed barrier: (a) the relation between the possibility of colloid filtration and practical density of bentonite, (b) distribution of colloidal gold in compacted sand–bentonite mixture.

Accordingly, it is estimated based on this study that the engineered barrier should be designed to have the practical density of bentonite more than 800 kg/m^3 to eliminate the effect of colloid transport.

BENTONITE COLLOID GENERATION BY EROSION OF THE ENGINEERED BARRIER

Bentonite, used as a radionuclide transport barrier for HLW geological disposal, can absorb groundwater and expand into fracture in surrounding. In a typical disposal environment, the front of the expanded bentonite is a type of clay gel. Groundwater flow contacting this bentonite front could potentially erode bentonite, generating and dispersing colloidal particles of bentonite. This information is required to determine the long-term stability of bentonite as engineered barrier and the potential influence of bentonite colloidal particles on radionuclide transport. To determine the required information, this experimental study was performed from the point of view of generation of colloids via groundwater-flow shear force.
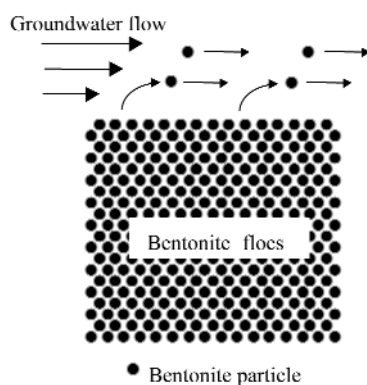

Fig. 5 Concept of typical erosion pattern caused by groundwater.

Experiment

In this study, it is considered that the minimum groundwater velocity required to erode particles from bentonite surface in contact with groundwater is derived from shear forces of aqueous bentonite gel suspension, as determined by viscometer test that refers to the studies of Pusch [6,7]. Fig. 5 shows the concept of typical erosion pattern caused by groundwater.

Flowing water imposes a shear force τ_f on the particle–particle bonds in gel-shaped bentonite. This shear force is related to the flow velocity by Stoke's law. Assuming that the bentonite particles are spherical by applying the assumption of Pusch [6], the following Stoke's equation is obtained:

$$\tau_f = 6\pi\eta aU$$

where η is the viscosity of groundwater, a is the Stoke's particle diameter, and U is the groundwater flow velocity.

In this experiment, a rotational viscometer was used to determine shear forces at 295 K for aqueous suspension of bentonite powder. The bentonite used was sodium-type bentonite, Kunigel-V1. The proper water–bentonite ratios needed to make the desired clay gel were determined in preliminary experiments. As a result, water content was determined at 700%. Two types of water solutions were used to prepare the bentonite suspensions. The first solution simulated typical groundwater at various

Table 1 Conditions of the viscometer test and the test results.

Clay	Water content	Solution		τ_f	U
	%	pH	NaCl mol/l	N	m/s
		6	0.01	5.5×10^{-13}	4.4×10^{-4}
			0.1	4.4×10^{-13}	3.6×10^{-4}
			0.5	3.2×10^{-13}	2.6×10^{-4}
		9	0.01	5.4×10^{-13}	4.4×10^{-4}
Na-bentonite	700		0.1	2.8×10^{-13}	2.3×10^{-4}
(Kunigel-V1)			0.5	2.6×10^{-13}	2.1×10^{-4}
		12	0.01	1.1×10^{-13}	8.9×10^{-5}
			0.1	1.1×10^{-13}	8.9×10^{-5}
			0.5	7.9×10^{-14}	6.4×10^{-5}
		$Ca(OH)_2$ saturated solution		5.2×10^{-14}	2.1×10^{-5}

pH levels and NaCl content (Table 1). The second solution was calcium hydroxide-saturated solution water, to evaluate the effect of alkaline groundwater plumes arising from cementitious materials.

Results and discussions

Table 1 shows conditions of the viscometer test, results of shear force τ_f measurement obtained by the viscometer test and the flow velocity U calculated from Stoke's equation by using the τ_f values [8]. The shear force τ_f of cohesive particle bond was obtained in a range of about 10^{-14} to 10^{-13} N from the viscometer test. The calculated results based on Stoke's law indicate that erosion of particles of bentonite would be initiated at flow velocities in a range of about 10^{-5} to 10^{-4} m/sec. On the other hand, in the deep geosphere of Japan, groundwater flow velocity is generally known lower than 10^{-5} m/s [9]. Therefore, the possibility of bentonite colloid generation and dispersion in groundwater is considered negligible.

Furthermore, it is generally known that the stability of clay colloids agrees with estimates from DLVO theory. In this study, the stability of bentonite colloids in groundwater was estimated from the total potential, V_T, of the interaction between flat plates of bentonite, based on the DLVO theory as follows [10]:

$$V_T = V_R + V_A = \frac{64nkT\gamma^2}{\kappa}\exp(-2\kappa H) - \frac{A}{48\pi H^2}$$

$$\gamma = \frac{\exp(ze\varphi/2kT)-1}{\exp(ze\varphi/2kT)+1}, \quad \kappa = \sqrt{\frac{8\pi nz^2 e^2}{\varepsilon kT}}$$

where V_R is the double layer force, V_A is the van der Waals force, n is the concentration of ions in the bulk solution, k is the Boltzmann constant, T is the absolute temperature, H is the distance between the colloid particles, A is the Hamaker constant, z is the ionic valency, e is the elementary electric charge, φ is the surface potential of a colloid particle, and ε is the dielectric constant of the fluid.

The transition between a stable and a flocculated system is represented by the concentration of ions that satisfies the stability limiting conditions $V_T = 0$ and $dV_T/dH = 0$, the critical flocculation concentration, C_f. The following equation is derived from above equation for this case [10]:

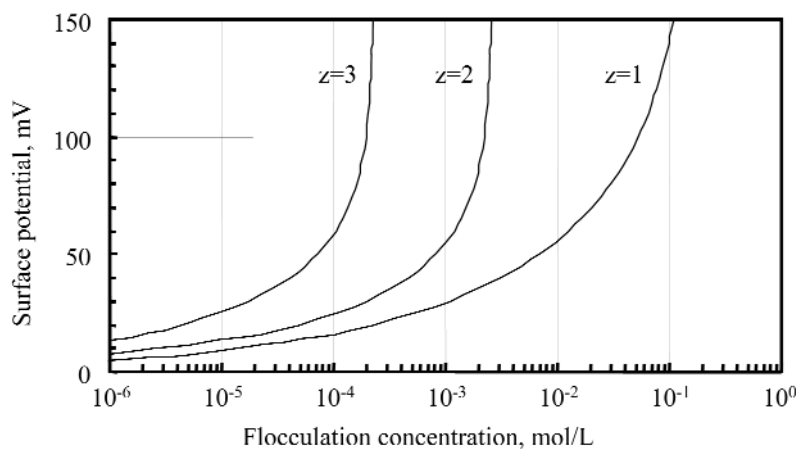$$C_f = 8.10^{-25}\frac{\gamma^4}{A^2 z^6}$$

Fig. 6 Conditions of limiting stability for bentonite colloids having valency, *z*, of 1, 2, and 3, where the Hamaker constant, *A*, is 2×10^{-19} J [12], the left top represents the most stable configuration, the right bottom, the most unstable with respect to flocculation.

C_f was calculated as shown in Fig. 6. Figure 6 shows the relationship between concentration of ion-stability-limiting conditions and surface potential of colloidal bentonite [8]. The measured zeta potentials (surface potentials) were –10 to –40 mV for sodium type bentonite, Kunigel-V1 suspended in the simulated low electrolyte concentration groundwater. The results indicate that at electrolyte concentrations of 10^{-3} mol/L, the monovalent form of the colloid may be flocculated and that di- and trivalent colloidal bentonite forms may be flocculated at even lower electrolyte concentration. On the other hand, even in fresh groundwater with very low concentrations of dissolved ions, the Na^+ concentration is about 7×10^{-3} mol/L in deep underground in Japan [11]. Furthermore, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+,3+}$, Al^{3+}, and other ions are present.

Therefore, the possibility that bentonite colloids will be generated and dispersed by groundwater in this setting is considered negligible. As a result, the effect of colloidal bentonite on radionuclide migration is judged to be negligible for the purpose of performance assessment of HLW disposal.

RADIONUCLIDE MIGRATION WITH GROUNDWATER COLLOIDS THROUGH FRACTURED ROCK SYSTEMS

The sorption of radionuclides on natural colloids in groundwater may significantly modify their transport behavior through fractured media, since radionuclides bonding to colloids may not be subject to the important retardation mechanisms of matrix diffusion and sorption on the pore surface. In this study, theoretical work is aimed at assessing the relevance of colloid-facilitated radionuclide transport to safety analyses of HLW disposal.

Model

In this study, to evaluate the effect of colloids on the radionuclide transport through a fracture in a rock, radionuclide transport was simulated by applying the parallel plane model [13]. In this model, colloid and radionuclide transport are influenced by the advection and dispersion within the fracture flow. Figure 7 indicates other mechanisms of colloid and radionuclide transport in fracture flow, which were considered in the model. Pseudocolloids are generated by radionuclide sorption on the colloids existing

in the groundwater. Radionuclide ions diffuse into the rock matrix. Radionuclide ions and colloid sorption on the pore surfaces of the rock matrix are assumed.

The transport model of radionuclide ions with colloids is described as follows:

$$R\frac{\partial C_1(x,t)}{\partial t} + v\frac{\partial C_1(x,t)}{\partial x} - D\frac{\partial^2 C_1(x,t)}{\partial x^2} + RaC_1(x,t) + \frac{q(x,t)}{\varepsilon_1 b} = 0$$

where $C_1(x,t)$ is the amount of radionuclide ions sorbed on colloid, x is the distance from inlet, t is the time, R is the effective retardation factor of radionuclide ions sorbed on colloids, v is the velocity of radionuclide ions sorbed on colloids, D is the dispersion coefficient radionuclide ions sorbed on colloids, a is the decay constant of radionuclide, ε_1 is the porosity of the fracture fillings, b is the fracture half-aperture and $q(x,t)$ is the diffusive radionuclide ions flux into the rock matrix. In the model, v, D, and R are given by following:

$$v = v_1\left(\xi_1 + \frac{v_2}{Kd_3 v_1}\right) \quad D = D_1\left(\xi_1 + \frac{D_2}{D_1 Kd_3}\right) \quad R = \xi_1\left(1 + \frac{1-\varepsilon_1}{\varepsilon_1}Kd_1\right) + \left(1 + \frac{1-\varepsilon_1}{\varepsilon_1}Kd_2\right)\frac{1}{Kd_3}$$

where D_1 is the colloid longitudinal dispersion coefficient, D_2 is the radionuclide ion longitudinal dispersion coefficient, v_1 is the velocity of colloids, v_2 is the velocity of groundwater, and ξ_1 is the constant volume fraction of colloids in fracture fluid. Furthermore, these equations are considered radionuclide ion–colloid–rock interaction, that is kd's concept. Kd_1 is the colloid sorption on the rock. Kd_2 is the radionuclide ion sorption on the rock. Kd_3 is the radionuclide ion sorption on the colloids.

We can obtain the equation for C_1 as follows:

$$\frac{C_1}{C_0} = \frac{2Kd_3}{\sqrt{\pi}}\int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left(-\frac{\sqrt{v^2 + 4RaD} - v}{2D}x\right)$$

$$\times erfc\left\{\frac{x^2\varepsilon_p\sqrt{D_p R_p}}{8D\varepsilon_1\eta^2 b\sqrt{t - Rx^2/(4D\eta^2)Kd_3}}\right\}\exp\left\{-\left(\eta - \frac{xv}{4D\eta}\right)^2\right\}d\eta$$

where C_0 is the inlet radionuclide ions concentration, ε_p is the rock matrix porosity, D_p is the diffusion coefficient in porewater, and R_p is the radionuclide ion retardation coefficient in the matrix.
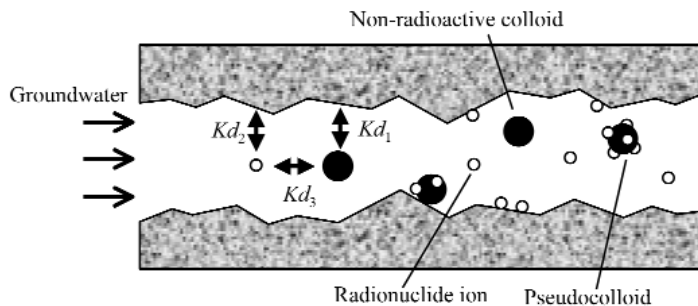

Fig. 7 Colloids and radionuclide ions transport through a fracture in a rock, Kd_1 the colloids sorption on the rock, Kd_2 the radionuclide ions sorption on the rock, and Kd_3 the radionuclide ions sorption on the colloids.

We calculated the transport of radionuclide ions with colloids by using the equation. Table 2 shows input data for the radionuclide transport analyses. These data have referred to "the input data for performance assessment in geosphere" discussed in the Japan Nuclear Cycle Development Institute (JNC) to estimate radionuclide transport behavior [14]. In this study, key radionuclides were considered in advance to analyze the interactive transport of colloids and radionuclide ions in fractured rock. Bentonite colloids assumed as source, because natural colloids characteristics are known. Colloid sorption onto the fracture surface (Kd_1) is conservatively neglected according as hydrodynamic chromatography (HDC) theory [15]. Radionuclide ion distribution coefficient on the rock (Kd_2) was cited from JNC data. Radionuclide ion distribution coefficient on colloids (Kd_3) was selected from batch experiment of bentonite (Kunigel-V1). However, in this analysis, the decay constant a is considered as $a = 0$.

Table 2 Input data for radionuclide migration analyses.

Parameter	Data	Radionuclide	Kd_2	Kd_3
			m^3/kg	
Kd_1	0 m^3/kg			
Kd_2 ⎫		Am	0.5	5.0
Kd_3 ⎭		Pu	0.5	1.0
D_1	0.35 m/yr	U	1.0	10.0
D_2	0.33 m/yr	Np	0.5	1.0
ε	0.99	Th	0.5	1.0
b	0.02 m	Cs	0.01	0.01
ε_p	0.02	Sn	1.0	5.0
D_p	1.6×10^{-7} m^2/yr	Pd	0.1	0.01
R_p	$1 + (1 - \varepsilon_p)pKd_2/\varepsilon p$	Tc	0.1	0.5
v_1	$1.2\,v_2$	Zr	0.01	1.0
v_1	3.2×10^{-2} m/yr			
f	1.0×10^{-6}			

ξ_1 (density of rock) = 2700 kg/m^3

Results and discussions

Figure 8 shows americium, plutonium, and uranium breakthrough curves in fractured rock system as the typical calculated results of radionuclide transport with colloids, as examples. As a result, transport of radionuclides, which have low distribution coefficient on the colloids (Kd_3), are almost not enhanced
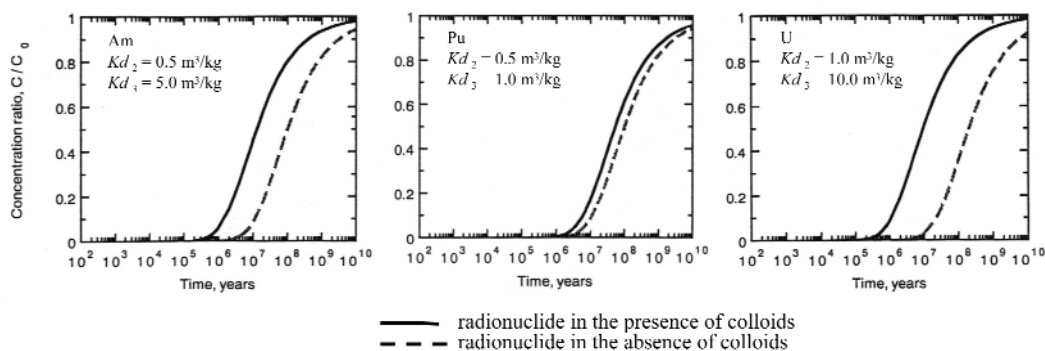

Fig. 8 Radionuclide breakthrough curves within fracture flow, x (distance from inlet) = 100 m.
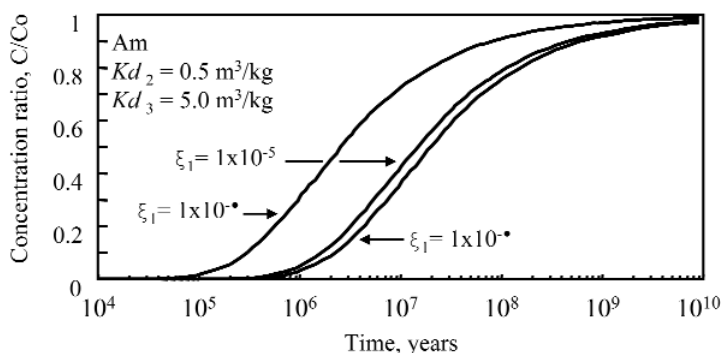
Fig. 9 Radionuclide breakthrough curves dependent on volume fraction of colloids, $x = 100$ m.

by the colloid presence. On the other hand, the transports of radionuclides, which have high Kd_3, are accelerated by pseudocolloid formation. That is, breakthrough curve is advanced. However, the colloid-facilitated radionuclide ions transport may not be one order of magnitude faster than that of radionuclide transport without colloid. Also, based on the result of uranium, the transports of radionuclides, which are dependent on high distribution coefficient on the rock Kd_2, are not particularly retarded in the fracture.

Furthermore, we analyzed the radionuclide transport behavior in fractured media by considering radionuclides–colloids–rock interraction, and extracted the important factors that influence the transport behavior. Figure 9 shows breakthrough curves of radionuclide dependent on volume fraction of colloids. The results of calculation indicate that volume fraction of colloids in groundwater enhances radionuclide transport by increasing total amount of the radionuclide sorption on colloids.

CONCLUSIONS

The experimental and theoretical studies were carried out to evaluate the effect of migration of colloids for the performance assessment of HLW geological disposal. The conclusions of this study are summarized as follows:

The experimental results indicated that the engineered barrier designed to have the practical density bentonite more than 800 kg/m^3 had enough property to eliminate the colloid transport through the engineered barrier.

The experimental and theoretical studies indicated that the possibility of bentonite colloid generation and dispersion by groundwater depended on the velocity of groundwater, and the generation is negligible at the velocity lower than 10^{-5}–10^{-4} m/s.

The transport of radionuclides is enhanced by colloids in the groundwater. The main parameter of the colloids is the distribution coefficient and concentration. Further research to characterize colloid behavior in groundwater is necessary to evaluate the HLW repository safety.

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