

## Article

# Numerical simulation of the influence of humic-complexation on the migration of radionuclide through porous media – a consideration of the sensitivity of analytical parameters

Tadao TANAKA\* and Masayuki MUKAI

Nuclear Safety Research Center, Japan Atomic Energy Agency

## Abstract

We numerically and schematically examined the influence of humic-complexation and the sensitivity of certain analytical parameters on migration of cationic radionuclides through porous media, where it was assumed that complexation reactions between radionuclides and natural organics, such as humic acid and fulvic acid, achieve instantaneous equilibrium or are a first-order kinetic reaction. The calculation results revealed that radionuclide migration in the presence of humic substance was predominantly controlled by the relative magnitude of distribution coefficients between the cationic radionuclides and the complexed radionuclides. Radionuclide migration was also affected significantly by the stability of the complexes and the rate constants of the complexation reaction.

## Introduction

To evaluate the safety of radioactive waste disposal into geologic media, it is important to estimate the migration of radionuclides in the geologic environment. The migration of radionuclides depends on their chemical species. Complexation of the radionuclides with organic ligands occurring in groundwater might influence their migration behavior (Robertson et al., 1995; McCarthy et al., 1998). Especially, the possible complexation of radionuclides with humic substances, such as humic acid or fulvic acid which are major organic ligands in the environment, has received considerable attention (Choppin, 1988; McCarthy et al., 1989).

In many geologic media, humic substances contribute greatly to the cation exchange capacity, and increased exchange capacity increases retention of cationic radionuclides (Stevenson, 1985; Bidoglio et al., 1989; Sakamoto et al., 1990). In addition, rapid movement of humic substances through a porous media also has been observed (Gutierrez et al., 1991; Artinger et al., 1998). Thus, mobile humic sub-

stances are believed to enhance the transport of the associated radionuclides through the porous media. Some studies have demonstrated that humic substances are immobilized by some interactions with mineral surfaces (Stevenson, 1985), which impedes the mobility of the associated radionuclides. These results indicate that the migration behavior of radionuclides in geologic environment should be quantitatively evaluated by taking account of the influence of humic substances.

Understanding of the radionuclide migration in porous media may be gained by using a mathematical solute transport model, whose construction requires a plausible quantitative description of the complexation behavior of radionuclides in the geologic environment. The majority of conventional models to evaluate the radionuclide migration are based on simplifying assumptions of linear, instantaneous sorption and homogeneous media (Selim et al., 1977; Carlsen et al., 1989). On the other hand, more generic models describing transport of transformed solutes that consider nonlinearity, heterogeneity, and kinetics are being developed (Randall et

\* Corresponding Author: TEL: +81-29-282-5625, FAX: +81-29-282-6678, E-mail address: tanaka.tadao26@jaea.go.jp

al., 1994; Brusseau, 1995; Schuesser et al., 2000; Tanaka et al., 2004).

This is a theoretical study elucidating the influence of complexation on radionuclide migration in porous media, in which sorption and transformation parameters of radionuclide, such as distribution coefficients, and stability constants and rate constants in the complexation, are numerically investigated.

## Analytical Models

### Solute Transport Model

Radionuclide migration in geologic media is controlled by both groundwater flow characteristics and sorptive interactions of radionuclides with the geologic media. Mass conservation during water flow in porous geologic media results in the following advection-dispersion formula:

$$\frac{\partial C}{\partial t} + \frac{\rho}{fs} \frac{\partial Q}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - V \frac{\partial C}{\partial x}, \quad (1)$$

where  $C$  is the concentration of the radionuclides in question in groundwater ( $\text{mol cm}^{-3}$ ),  $Q$  the concentration of the radionuclides sorbed on geologic media ( $\text{mol g}^{-1}$ ),  $f$  porosity,  $s$  degree of water saturation,  $\rho$  density of geologic media ( $\text{g cm}^{-3}$ ),  $D$  dispersion coefficient ( $\text{cm}^2 \text{min}^{-1}$ ),  $V$  groundwater flow velocity ( $\text{cm min}^{-1}$ ),  $x$  distance (cm), and  $t$  time (min).

This radionuclide migration model assumes linear reaction, instantaneous sorption and homogeneous media. On the assumption that a sorption of radionuclide onto the geologic media follows Henry's type sorption isotherm and that sorption instantaneously achieves equilibrium, the sorptive interaction can be described as follows using the distribution coefficient  $Kd$  ( $\text{cm}^3 \text{g}^{-1}$ ):

$$Q = Kd C. \quad (2)$$

The instantaneous equilibrium sorption model using  $Kd$  has been applied to many migration analyses, on account of its mathematical simplicity. This instantaneous equilibrium sorption model is employed in the present study.

### Sorption Models Taking Account of Chemical Transformation of Solute

In the presence of the humic substance L which is the organic ligand here, cationic radionuclide M forms humic complexes according to the following reversible reaction (Maes et al., 1989; Tanaka et al., 1995b):



where  $n$  refers to the stoichiometric number of ligand groups associating with M in the complex, and here we assume a 1:1 complex ( $n = 1$ ).

#### i) Instantaneous Equilibrium Transformation Model

In the case where the reversible reaction Eq. (3) is sufficiently rapid compared to the mass transfer process, the association and dissociation processes can be regarded as instantaneous equilibrium reactions (Tanaka et al. 1995b, Meas et al. 1988), and the stability constant  $\beta$  is given by

$$\frac{C_{ML}}{C_M C_L} = \beta, \quad (4)$$

in which  $C_M$  is the concentration of cationic radionuclides ( $\text{mol cm}^{-3}$ ),  $C_{ML}$  the concentration of complexed radionuclide ( $\text{mol cm}^{-3}$ ),  $C_L$  the stoichiometric concentration of humic substance ( $\text{mol cm}^{-3}$ ).

On the assumption that the only complex M forms is ML in the present analytical system,  $Kd$  is

$$Kd = \frac{Q}{C_M (1 + \beta C_L)}. \quad (5)$$

The distribution coefficients  $Kd_M$  for M and  $Kd_{ML}$  for ML are here defined by the equations:

$$Kd_M = Q_M / C_M, \quad (6)$$

$$Kd_{ML} = Q_{ML} / C_{ML}, \quad (7)$$

$$C_M + C_{ML} = C, \text{ and} \quad (8)$$

$$Q_M + Q_{ML} = Q, \quad (9)$$

where  $Q_M$  is the concentration of cationic radionuclides sorbed on geologic media ( $\text{mol g}^{-1}$ ), and  $Q_{ML}$  the concentration of complexed radionuclides sorbed on geologic media ( $\text{mol g}^{-1}$ ).

Combination of Eqs.(3) and (5) with (9) leads to

$$Kd = \frac{Kd_M + Kd_{ML} \beta C_L}{1 + \beta C_L}. \quad (10)$$

Thus, the sorption model to be linked with Eq. (2) is

$$Q = \frac{Kd_M + Kd_{ML} \beta C_L}{1 + \beta C_L} C. \quad (11)$$

### ii) Rate-Limited Transformation Model

In the case where the time required for the reactions transforming the radionuclides described by Eq. (3) are not negligible in comparison to the time of the mass transfer process, the kinetics of the association and dissociation processes needs to be considered.

Typically, the humic substance concentration is so much greater than the radionuclide concentration that the reaction rates are independent of  $C_L$ , and  $C_L$  thus may be kept at a constant value in our radionuclide migration system. The relationship between  $C_M$  and  $C_{ML}$  in the radionuclide migration system through porous media must be affected by the initial forms of the introduced radionuclides. When the cationic radionuclide M is introduced into the migration system, the relationship between  $C_M$  and  $C_{ML}$  can be described as a first-order rate-limited reaction:

$$\frac{\partial C_{ML}}{\partial t} = C_L k_1 C_M - k_2 C_{ML} \quad (12)$$

where  $k_1$  ( $\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$ ) is the rate constant of the association process and  $k_2$  ( $\text{min}^{-1}$ ) is the rate constant of the dissociation process.

Combination of Eqs. (12) and (6) with (9) leads to

$$\frac{\partial Q}{\partial t} = Kd_M \frac{\partial C}{\partial t} + (Kd_M k_2 + Kd_{ML} C_L k_1) C - (C_L k_1 + k_2) Q \quad (13)$$

The radionuclide migration can be estimated with consideration given to the kinetics of the chemical transformation by combining Eq. (1) with Eq. (13).

## Calculations

For the numerical simulation, the radionuclide migration through a one-dimensional column system of laboratory experimental scale as seen in Fig. 1 was assumed. The column was 2.5 cm in length, and contained porous media of density  $\rho = 2.5 \text{ g cm}^{-3}$ . The porosity  $f$  was 0.5, and the water saturation  $s$  was

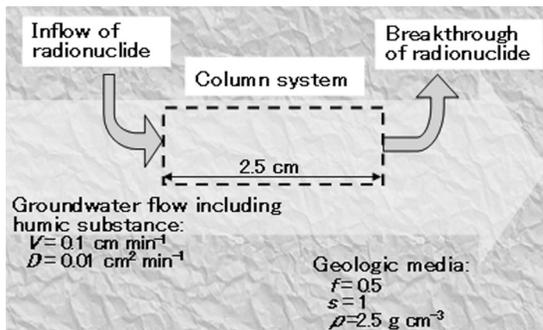


Fig.1 Schematic diagram of analytical system.

1. Water velocity  $V$  and dispersion coefficient  $D$  were set at  $0.1 \text{ cm/min}$  and  $0.01 \text{ cm}^2 \text{ min}^{-1}$ , respectively. An aqueous solution of radionuclides was continuously introduced into the column.

Based on the above assumptions, values of  $Kd_M$ ,  $Kd_{ML}$ ,  $\beta$ ,  $k_1$ ,  $k_2$  and  $C_L$  were derived as follows. The investigations of Kanno (1995) and Nagao (1995) dealt with the variation of  $\beta$  and  $C_L$  values.

### i) Instantaneous Equilibrium Transformation Model

In the case where ML did not sorb on the geologic media,  $Kd_{ML}$  was 0,  $Kd_M$  was 100, and both  $\beta$  and  $C_L$  ranged from 0 to 100. In the case where ML sorbed on the geologic media,  $Kd_{ML}$  ranged from 0 to 10,  $Kd_M$  was constant,  $\beta$  was fixed at 10, and  $C_L$  ranged from 0 to 10.

Since both the complexation and the sorption processes involved were fast compared to the mass transfer through the investigated column system, the radionuclide migration was not affected by the chemical forms of radionuclides in the inflow solution. The initial concentration of radionuclides was normalized to be 1.

### ii) Rate-Limited Transformation Model

In the case where ML did not sorb on the geologic media,  $Kd_{ML}$  was 0 and  $Kd_M$  was 100.  $C_L$  ranged from 0 to 100, and  $k_1$  and  $k_2$  ranged from 0.01 to 100 and from 0.001 to 10, respectively. In the case where ML sorbed on the geologic media,  $Kd_{ML}$  ranged from 0 to 10,  $Kd_M$  was constant,  $C_L$  ranged from 0 to 100, and  $k_1$  and  $k_2$  were fixed at 10 and 1 respectively.

In the case where the times of reactions transforming the radionuclides were not negligible in comparison with the mass transfer process, the radionuclide migration was affected by the chemical forms of radionuclides in the inflow solution. Thus, the initial concentration of radionuclides was normalized to be 1, and the proportion of cationic radionuclide M and complexed ML in the inflow solution introduced into the system was assumed to be 1 : 0.

The analytical parameters are summarized in Table 1 and Table 2. The equations for the calculation were solved with a finite-difference numerical method (Ohnuki et al., 1989). The calculation results were obtained as time dependent profiles of radionuclide concentration in pore water at the end point in the investigated column system shown in Fig. 1.

**Table 1** Values of analytical parameters in the instantaneous equilibrium transformation system.

Varied parameter	$K_{dM}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$C_L$ ( $\text{mol cm}^{-3}$ )	$\beta$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$K_{dML}$ ( $\text{cm}^3 \text{g}^{-1}$ )	Analytical result
In the case that ML does not sorb on the geologic media					
$\beta$	100	10	0	0	Fig. 2
	100	10	1	0	
	100	10	3	0	
	100	10	10	0	
	100	10	100	0	
$C_L$	100	0	10	0	Fig. 3
	100	1	10	0	
	100	3	10	0	
	100	10	10	0	
	100	100	10	0	
In the case that ML sorbs on the geologic media					
$K_{dML}$	100	10	10	0	Fig. 5
	100	10	10	1	
	100	10	10	3	
	100	10	10	10	
$C_L$	1	0	10	10	Fig. 6
	1	0.1	10	10	
	1	0.3	10	10	
	1	1	10	10	
	1	10	10	10	

**Table 2** Values of analytical parameters in the rate-limited transformation system.

Varied parameter	$K_{dM}$ ( $\text{cm}^3 \text{g}^{-1}$ )	$C_L$ ( $\text{mol cm}^{-3}$ )	$K_1$ ( $\text{cm}^3 \text{g}^{-1} \text{min}^{-1}$ )	$K_2$ ( $\text{min}^{-1}$ )	$K_{dML}$ ( $\text{cm}^3 \text{g}^{-1}$ )	Analytical result
In the case that ML does not sorb on the geologic media						
$K_1$	100	10	1	1	0	Fig. 7
	100	10	10	1	0	
	100	10	100	1	0	
$K_2$	100	10	10	1	0	Fig. 8
	100	10	10	10	0	
	100	10	10	100	0	
$C_L$	100	0	10	1	0	Fig. 9
	100	1	10	1	0	
	100	10	10	1	0	
$K_1$ and $K_2$ ( $K_1/K_2 = \text{constant}$ )	100	100	10	1	0	Fig. 10
	100	10	100	10	0	
	100	10	10	1	0	
	100	10	0.1	0.01	0	
$K_1$ and $K_2$ ( $K_1/K_2 = \text{constant}$ )	100	10	0.01	0.001	0	Fig. 10
	100	10	10	1	0	
	100	10	10	1	0.1	
	100	10	10	1	1	
$K_{dML}$	100	10	10	1	0	Fig. 11
	100	10	10	1	0.1	
	100	10	10	1	1	
	100	10	10	1	10	
$C_L$	1	0	10	1	10	Fig. 12
	1	1	10	1	10	
	1	10	10	1	10	
	1	100	10	1	10	

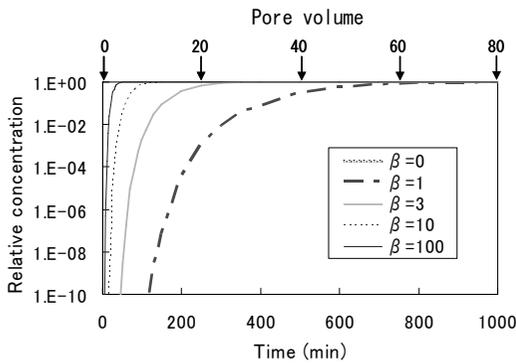
The computational program has been verified by the simulation for various radionuclide migration experiments in the field (Tanaka et al., 1993, Tanaka et al., 2003) and the laboratory scale (Tanaka et al., 2005, Tanaka et al., 2007). Particularly for the radionu-

clide migration in the presence of humic substances, the breakthrough properties in the migration system like Fig. 1 were reproduced by considering the association and the dissociation rates in the complex formation (Tanaka et al. 1995a, Tanaka et al., 2004).

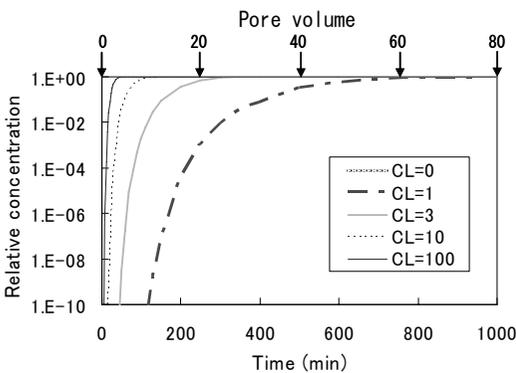
## Results and Discussion

### Instantaneous Equilibrium Transformation Model

In the instantaneous equilibrium transformation system, the breakthrough profiles of radionuclides were determined by the effective distribution coefficient, expressed by Eq. (10). **Figures 2 and 3** give the calculated breakthrough profiles for a series of equilibrium systems whose stability constant  $\beta$  varied from 0 to 100 and whose humic substance concentration  $C_L$  varied from 0 to 100, in the case where ML did not sorb on the geologic media. As shown in Fig. 2, in which  $Kd_{ML}$  is  $0 \text{ cm}^3 \text{ g}^{-1}$ , the retention time of radionuclides in the column decreased with increase in  $\beta$ , because mobile species of ML increased.



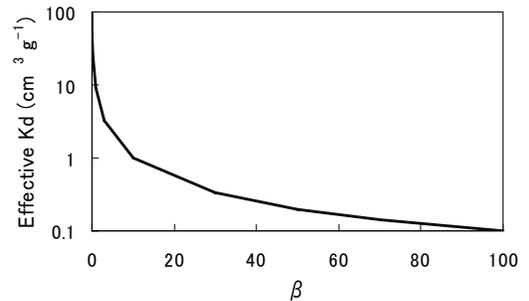
**Fig. 2** Influence of  $\beta$  on breakthrough profiles of radionuclide for the instantaneous equilibrium transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$  and  $C_L^n=10 \text{ mol cm}^{-3}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution. The curve corresponding to  $\beta=0$  is laid below  $1.E-10$  of relative concentration.



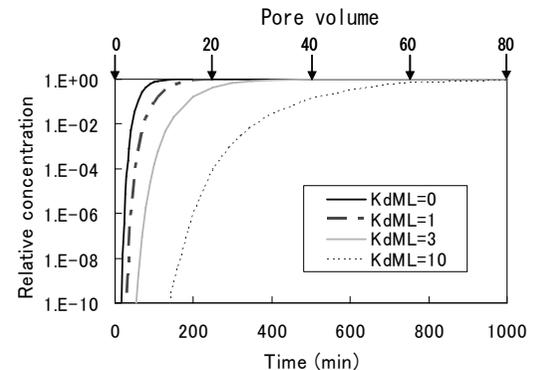
**Fig. 3** Influence of  $C_L^n$  on breakthrough profiles of radionuclide for the instantaneous equilibrium transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$  and  $\beta=10$ . Relative concentration is normalized by radionuclide concentration in the inflow solution. The curve corresponding to  $C_L^n=0$  is laid below  $1.E-10$  of relative concentration

The curve corresponding to  $\beta=0$  is entirely below  $1.E-10$  relative concentration, due to there being no mobile species of ML. The influences of  $C_L$  on the retention time were the same as those of  $\beta$ , as shown in Fig. 3, and the curve corresponding to  $C_L=0$  also is entirely below  $1.E-10$  relative concentration. The retention time of radionuclides in the equilibrium system was controlled by the effective distribution coefficient. The effective distribution coefficient is represented in **Fig. 4** as a function of  $\beta$ . Figure 4 clearly and quantitatively shows that as complexation approached zero ( $\beta=0$ ), the effective distribution coefficient approached that of the species of M with more retarded migration.

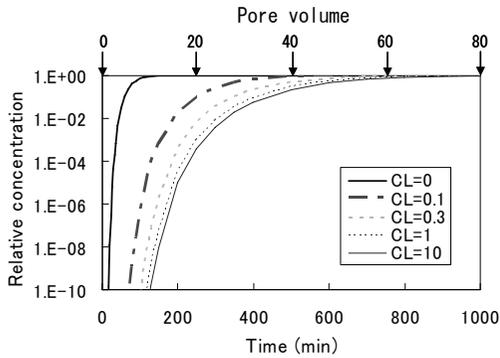
In the case where ML sorbed on the geologic media, the retention time of radionuclides in the column increased with  $Kd_{ML}$ , since the effective distribution coefficient thereby became larger, as indicated by Eq. (10). The breakthrough profiles shown in **Fig. 5** reconfirm the effect of the sorbability of ML. In the



**Fig. 4** Variation of effective distribution coefficient as function of the stability constant  $\beta$  of instantaneous equilibrium transformation system.



**Fig. 5** Influence of  $Kd_{ML}$  on breakthrough profiles of radionuclide for the instantaneous equilibrium transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $\beta=10 \text{ cm}^3 \text{ g}^{-1}$  and  $C_L^n=10 \text{ mol cm}^{-3}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.

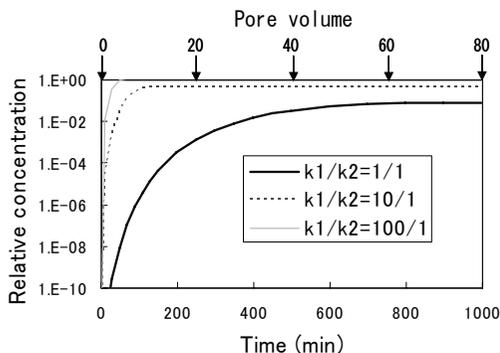


**Fig. 6** Influence of  $C_L^n$  on breakthrough profiles of radionuclide for the instantaneous equilibrium transformation system;  $Kd_M=1 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=10 \text{ cm}^3 \text{ g}^{-1}$  and  $\beta=10$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.

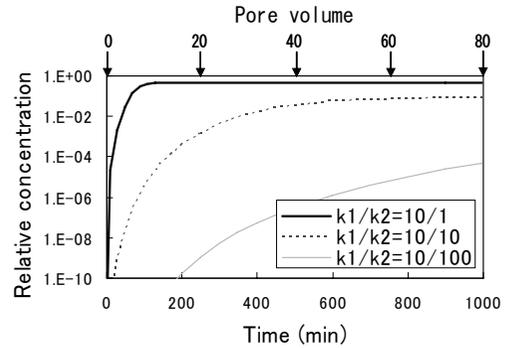
case where  $Kd_{ML} > Kd_M$ , illustrated in **Fig. 6**, the retention time of radionuclides increased with  $C_L$ , because the profile of the effective distribution coefficient where  $Kd_{ML} > Kd_M$  had a shape opposite to that in Fig. 4. These results clearly reveal that the influence of humic substances on the migratory mobility of radionuclides was dominated by the ratio between the distribution coefficients of the free cationic and of the complexed radionuclides.

#### Rate-Limited Transformation Model

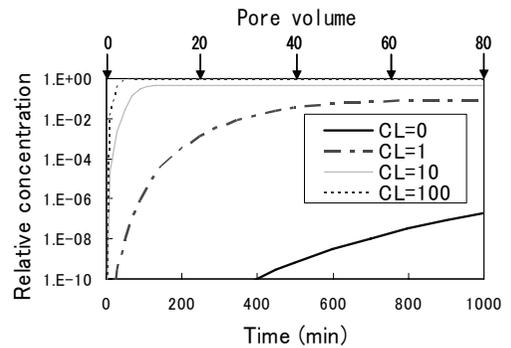
In our rate-limited transformation system, the breakthrough profiles depend on the concentration of M and ML in the non-linear reactions expressed by Eq. (12) and Eq. (13). **Figures 7 - 10** give the calculated breakthrough profiles for a series of kinetic systems, in the case where ML did not sorb on the geologic media.



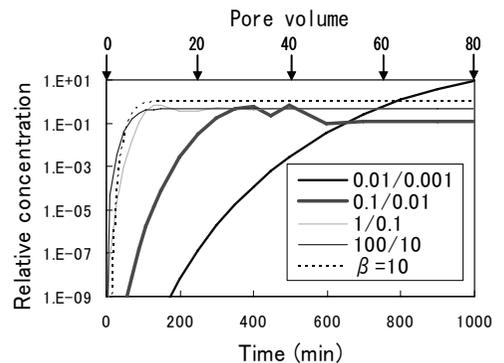
**Fig. 7** Influence of  $k_1$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$  and  $C_L^n=10 \text{ mol cm}^{-3}$ ,  $k_2=1/\text{min}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.



**Fig. 8** Influence of  $k_2$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$  and  $C_L^n=10 \text{ mol cm}^{-3}$ ,  $k_1=10 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.



**Fig. 9** Influence of  $C_L^n$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$ ,  $k_1=10 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$  and  $k_2=1 \text{ min}^{-1}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.



**Fig. 10** Influence of magnitude of  $k_1$  and  $k_2$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=0 \text{ cm}^3 \text{ g}^{-1}$  and  $C_L^n=10 \text{ mol cm}^{-3}$  and  $k_1/k_2$  ratio =10. Curve of  $\beta=10$  represents breakthrough profile in the instantaneous equilibrium transformation system. Relative concentration is normalized by radionuclide concentration in the inflow solution.

Figure 7 and Fig. 8 show the breakthrough profiles in the cases of  $k_1$  and  $k_2$  each varying from 1 to 100. The retention time of radionuclides in the column was dominated by the magnitude of  $k_2$ , and the influence of  $k_1$  was not so great. Figure 9 shows the breakthrough profiles where the organic ligand concentration  $C_L$  varied from 0 to 100,  $k_1$  was 10, and  $k_2$  was 1. The retention time of radionuclides in the column increased with  $C_L$ . Such increase in retention is similar to that seen with change in  $k_1$  in Fig. 7. The influence of  $C_L$  on the breakthrough profiles in the instantaneous equilibrium transformation system is different from these analytical results (Fig. 3). Hence, when the time of transformation between the cationic and the complexed radionuclides is not sufficiently short relative to the residence time in the system for the transformation to be considered an instantaneous reaction, the radionuclide migration behavior in porous media containing humic substances must be controlled by the kinetics of the transformation.

The breakthrough profiles of radionuclides are affected by the magnitude of the transformation rate constants  $k_1$  and  $k_2$ . Figure 10 gives the calculated breakthrough profiles where  $k_1$  varies from 0.01 to 100 with a constant  $k_1/k_2$  ratio of 10. With increase in the rate constants, the breakthrough profile reached that of the equilibrium system where  $\beta = 10$ . Parts of the curves corresponding to  $k_1 = 0.01$  and  $k_1 = 0.1$  exceed 1.0 relative concentration. This indicates that the reactions depending on M and ML concentrations are non-linear at any position in the column system. The rates of transformation between the cationic and the complexed radionuclides can be sufficiently rapid relative to the residence time in the system that it can be assumed that the migration behavior of both the free cationic radionuclide and the complexed radionuclide species is dependent on the ratio  $k_1/k_2$ , which represents the stability constant  $\beta$ .

Figure 11 and Fig. 12 give the calculated breakthrough profiles in the case where ML sorbs on the geologic media. In Fig. 11, the retention time of radionuclides through the column increased with  $Kd_{ML}$ , in the same manner as in the instantaneous equilibrium system (Fig. 5). As seen in Fig. 12, where  $Kd_{ML} > Kd_M$ , the influence of  $C_L$  on the breakthrough profiles is opposite to that in Fig. 9, as in the relationship between Fig. 3 and Fig. 6.

The above results of our analyses showed that a

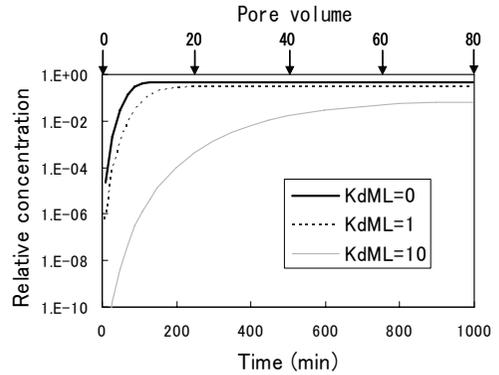


Fig. 11 Influence of  $Kd_{ML}$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=100 \text{ cm}^3 \text{ g}^{-1}$ ,  $C_L=10 \text{ mol cm}^{-3}$ ,  $k_1=10 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$  and  $k_2=1 \text{ min}^{-1}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.

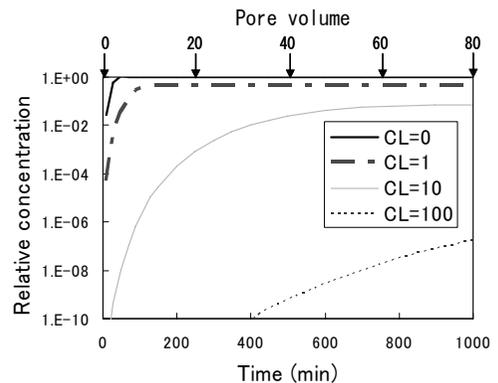


Fig. 12 Influence of  $C_L$  on breakthrough profiles of radionuclide for the rate-limited transformation system;  $Kd_M=1 \text{ cm}^3 \text{ g}^{-1}$ ,  $Kd_{ML}=10 \text{ cm}^3 \text{ g}^{-1}$ ,  $k_1=10 \text{ cm}^3 \text{ g}^{-1} \text{ min}^{-1}$  and  $k_2=1 \text{ min}^{-1}$ . Relative concentration is normalized by radionuclide concentration in the inflow solution.

transformation model based on kinetics can provide an accurate simulation of transformation and transport of radionuclides. In addition, the relative impact of radionuclide transformation on radionuclide transport is mediated by the magnitude of the rate constants  $k_1$  and  $k_2$  of the transformation. When the transformation occurs primarily where  $k_1 \ll k_2$ , the transformation from complex to cationic form should be much greater, and the retention time should reach its maximum. Larger rate constants of transformation between the free cationic and the complexed radionuclides raise migration speed between the two species. With such migration rates, the migration can be sufficiently expressed by the instantaneous equilibrium model controlled by the effective distribution coefficient.

## Conclusions

Two simplified mathematical models were used to investigate the migration behavior of radionuclides in the presence of humic substances: one describes the transport of solute undergoing linear, instantaneous equilibrium sorption and instantaneous transformation of solute species, and the other describes the transport of solute undergoing linear, instantaneous equilibrium sorption and rate-limited transformation of solute species.

The numerical simulation schematically demonstrated the influence of humic-complexation on the migration of radionuclide in geologic environment. The calculation results revealed that migratory mobility of radionuclides in the presence of humic substances is dominated by the ratio between the distribution coefficients of cationic and complexed radionuclides. In addition, the stability constant of the complex and the rate constant of the complexation significantly affected the radionuclide migration. Hence, naturally occurring humic substances, which form complexes with many cationic radionuclides, exhibit a pronounced influence on the migration behavior of radionuclides, increasing or decreasing migration speed. In a natural environment with slow groundwater velocity, on the other hand, the association and dissociation processes in the complex formation may be regarded as being in complete equilibrium. The radionuclide migration in the presence of humic substances may be quantitatively evaluated by applying the simple model based on instantaneous equilibrium transformation, except for the cases where irreversible complexes form in the geologic environment.

From the analytical results, we could specify the key parameters: the distribution coefficient, the stability constant, and the rate constants. Thereby, we may next focus our experimental studies on these important parameters and the related environment factors such as pH and temperature.

In the mathematical models presented, the transport of humic substances through porous media is regarded to be controlled by an instantaneous equilibrium sorption according to the distribution coefficient. However, the actual migration of humic substances may be controlled by more than two mechanisms, other possible mechanisms including adhesion, filtration, and straining by media matrix. This means that it is necessary to understand the mi-

gration mechanisms of humic substances themselves in porous media, in order to evaluate accurately the migration behavior of complexed radionuclides. Li et al. (2001) proposed the colloid and radionuclide migration model considering the conversion rate in mobilization/immobilization of colloid, in three-phase system of colloid, radionuclide and porous media. This model will be helpful for understanding the characteristic as the colloid of humic substances, like adhesion, filtration, and molecular size. In addition, the reactivity and mobility of humic substances, that is indisputable the interaction mechanism with the metal ion is a complex forming reaction, might be easily discussed by separating into electrolyte characteristic and colloid characteristic.

## Acknowledgment

The authors wish to express their appreciation to Dr. Shinichi Nakayama, Japan Atomic Energy Agency, for valuable discussions.

## References

- Artinger, R., Kienzler, B., Schüßler, W., Kim, J.I. (1998) Effects of humic substances on the  $^{241}\text{Am}$  migration in a sandy aquifer: column experiments with Gorleben groundwater/sediment systems. *J. Contam. Hydrol.*, 35, 261-275.
- Bidoglio, G., De Plano, A., Righetto, L. (1989) Interactions and transport of plutonium-humic acid particles in groundwater environments. In: *Scientific Basis for Nuclear Waste Management XII*, Materials Research Society, p.823-830, Pennsylvania.
- Brusseau, M.L. (1995) The effect of nonlinear sorption on transformation of contaminants during transport in porous media. *J. Contam. Hydrol.*, 17, 277-291.
- Carlsen, L., Nielsen, O.J, Bo, P. (1989) The influence of complexation on radionuclide migration: A theoretical study. *Waste Manag.*, 9, 165-169.
- Choppin, G.R. (1988) Humics and radionuclide migration. *Radiochim. Acta*, 44/45, 23-28.
- Gutierrez, M.G. Bidoglio, G. Avogadro, A., Mingarro, E., D'Alessandro, M. (1991) Experimental investigations of radionuclide transport through cored granite samples. *Radiochim. Acta*, 52/53, 213-217.
- Kanno, T. (1995) The properties of humic substances and its effect on radionuclide Migration (in Japanese). *Radioactive Waste Research*, 1, 131-162.
- Li, S.H., Jen, C.P. (2001) Migration of radionuclides in porous rock in the presence of colloids: effects of kinetic interactions. *Waste Manag.*, 21, 569-579.
- Maes, A., Debrabandere, J., Cremers, A. (1988) A modified Schubert method for the measurement of the stability of europium humic acid complexes in alkaline conditions. *Radi-*

- ochim.Acta*, 44/45, 51-57.
- McCarthy, J.F., Zachara, J.M. (1989) Subsurface transport of contaminants. *Environ.Sci.Technol.*, 23, 496-502.
- McCarthy, J.F., Czerwinski, K.R., Sanford, W.S., Jardine, P.M., Marsh, J.D. (1998) Mobilization of transuranic radionuclides from disposal trenches by natural organic matter. *J.Contam.Hydrol.*, 30, 49-77.
- Nagao, S. (1995) Characteristics of humic substances and TRU-humate complexes in groundwater (in Japanese). *Radioactive Waste Research*, 1, 231-242.
- Ohnuki, T., Takebe, S., Yamamoto, T. (1989) Development of migration prediction system (MIGSTEM) for cationic species of radionuclides through soil layers. *J.Nucl.Sci.Technol.*, 26, 795-804.
- Randall, A., Warwick, P., Lassen, P., Carlsen, L., Grindrod, P. (1994) Transport of europium and iodine through sand columns in the presence of humic acid. *Radiochim.Acta*, 66/67, 363-368.
- Robertson, D.E., Schilk, A.J., Abel, K.H., Lepel, E.A., Thomas, C.W., Pratt, S.L., Cooper, E.L., Hartwig, P., Killey, R.W.D. (1995) Chemical speciation of radionuclides migrating in groundwaters. *J. Radioanal. Nucl. Chem.*, 194, 237-252.
- Sakamoto, Y., Konishi, H., Shirahashi, K., Senoo, M., Moriyama, N. (1990) Adsorption behavior of neptunium for soil. *Radioactive Waste Manag. and Nucl.Fuel Cycle*, 15, 13-25.
- Schuessler, W., Artinger, R., Kienzler, B., Kim, J.I. (2000) Conceptual modeling of the humic colloid-borne americium(III) migration by a kinetic approach. *Environ.Sci.Technol.*, 34, 2608-2611.
- Selim, H.M., Davidson, J.M., Rao, P.S.C. (1977) Transport of reactive solutes through multilayered soils. *Soil Sci. Soc. Am. J.*, 41, 3-10.
- Stevenson, F.J. (1985) Geochemistry of soil humic substances. In: Humic Substances in Soil, Sediment, and Water. Ed. G.R. Aiken, D.M. Mcknight, B.L. Wershaw, P. MacCarthy, p.13-52, John Wiley & Sons, New York.
- Tanaka, T., Kamiyama, H., Mukai, M., Guo, Z., Li, S., Li, Z. (1993) Analysis of results obtained from field tracing test under artificial rainfall condition. Proc. of Asia Congress on Radiation Protection, Beijing, 681-684.
- Tanaka, T., Mukai, M., Senoo, M. (1995a) Influence of coexistent humic acid on adsorption and migration behavior of <sup>85</sup>Sr in a coastal sand (in Japanese). *Radioactive Waste Research*, 1, 169-176.
- Tanaka, T., Senoo, M. (1995b) Sorption of <sup>60</sup>Co, <sup>85</sup>Sr, <sup>137</sup>Cs, <sup>237</sup>Np and <sup>241</sup>Am on soil under coexistence of humic acid; effects of molecular size of humic acid. In: Scientific Basis for Nuclear Waste Management XVIII, Materials Research Society, p.1013-1020, Pennsylvania.
- Tanaka, T., Mukai, M., Li, Z., Li, S. (2003) Applicability of sorption data determined by laboratory experiment to evaluation of <sup>85</sup>Sr mobility in sub-surface field. Proc. of Transfer of Radionuclides in Biosphere -Prediction and Assessment, JAERI-Conf 2003-010, 142-149.
- Tanaka, T., Sakamoto, Y., Mukai, M., Maeda, T., Nakayama, S. (2004) Influence of humic substances on the <sup>63</sup>Ni migration through crushed rock media. *Radiochim.Acta*, 92, 725-729.
- Tanaka, T., Mukai, M., Nakayama, S. (2005) Sorption and migration of neptunium in porous sedimentary materials. Proc. of International Conference Nuclear Energy System for Future Generation and Global Sustainability (GLOBAL2005), CD-ROM GL264DF.
- Tanaka, T., Nakayama, S. (2007) Experimental and modeling studies on sorption and migration of americium in porous sedimentary materials. Proc. of 15th International Conference on Nuclear Engineering (ICONE-15), CD-ROM, ICONE-10228.