

**COLLOID-FACILITATED MIGRATION OF RADIONUCLIDES IN POROUS ROCK:
NONEQUILIBRIUM SORPTION EFFECTS**

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ABSTRACT

The colloid-facilitated radionuclide migration with radioactive decay in porous media is investigated in this paper. The sorption processes for radionuclides with the solid matrix and colloids are treated as nonequilibrium in the present model. Radionuclides are distributed among in the liquid phase, the solid matrix, and mobile and immobile colloids. The transport mechanisms for radionuclides are considered as advection, dispersion, radioactive decay and adsorption-desorption interaction with the solid matrix or colloids. The coupled colloid and radionuclide transport equations are solved simultaneously under different interaction models. An analytical solution can be obtained under the simplified linear equilibrium interaction mechanism. The adsorption processes for radionuclides with colloids and the porous rock can be assumed nonequilibrium and modeled by the linear kinetic adsorption. The numerical method can be used to solve the coupled colloid and radionuclide transport equations under nonequilibrium sorption assumption. It can be examined that colloids in the liquid phase act as mobile vehicles to enhance the migration of radionuclides, however, the solid matrix and immobile colloids play a role of retardation effect. The reaction rates of the adsorption processes for radionuclides with the solid matrix and colloids affect the transport characteristics of radionuclides. The fast reaction rate for radionuclides with colloids leads a higher concentration of radionuclides adsorbed on colloids in dispersed phase and enlarges the acceleration effect caused by colloids. However, the fast reaction rate for radionuclides with solid matrix enlarges the retardation effect caused by the solid matrix. The adsorption parameters for radionuclides with colloids as well as the solid matrix strongly affect the radionuclide migration in porous media.

INTRODUCTION

The study of radionuclide migration through the subsurface is an important issue in the safety assessment of nuclear waste repositories. It has been recognized that the adsorption process to the solid matrix could limit the mobility of radionuclides in the groundwater system. However, investigations suggest that colloids dispersed in the groundwater provide an additional phase for radionuclides (1) and enhance the transport of radionuclides (2,3). Colloids, in the classic

definition, mean particles or macromolecules smaller than 1 μm in diameter, but longer than 1 nm (4). These particles are typically smaller than intergranular pores and fractures in rock and can travel long distance with the groundwater. Since the sizes of colloids are very small, the colloids suspended in the groundwater have large surface area ($\sim 10^3 \text{ m}^2/\text{g}$) (5) and huge adsorption capability for radionuclides. Thus, the migration of radionuclides is controlled not only by the adsorption on the solid matrix, but also the transport characteristics of colloids. Failure to account for the colloid transport can lead to serious underestimates of the distance that radionuclides can migrate. Therefore, it is necessary to study the transport behavior of radionuclides in the presence of colloids.

The colloids may occur naturally in the groundwater system. Natural colloids, which are ubiquitous in all groundwater system, are composed of inorganic and organic molecular constituents or microorganisms. The colloids may also be produced from leaching of the waste form, corrosion of canister, and degradation of engineering backfill or buffer materials (6,7). These colloids are chemically surface active and readily adsorb many radionuclides. Much effort has been focus on elucidating the transport characteristics of radioactive colloids through laboratory and field studies (8-11). Colloid formation and physical models for transport which concerns only radioactive colloids in porous media have been proposed in the literature (12,13). The coupled transport equations for both colloids and radionuclides can be solved simultaneously by using several models (14). Theoretical studies for modeling the radionuclide transport that incorporates colloid phase have been proposed in literature (15-17). Most investigation assumed a local equilibrium for contaminant transport in dealing with the adsorption interactions among each species (contaminant, colloids and the solid matrix). Under the simplified linear equilibrium interaction mechanism, analytical solutions can be obtained. Experimental evidence has cast doubt on the validity of this assumption (18,19). The effect of nonequilibrium adsorption model on the colloid-facilitated contaminant transport in fractured rock (20) and porous media (21,22) has also been investigated in the previous studies. However, the colloid-facilitated migration of radionuclides including radioactive decay mechanism in porous media has not been modeled in literature. In this paper, the coupled colloid and radionuclide transport with radioactive decay in porous media is solved numerically under the assumption of the nonequilibrium adsorption interactions for radionuclides with the solid matrix and colloids. The reaction rates of the adsorption processes for radionuclides with the solid matrix and colloids are also investigated and compared in the present work.

PHYSICAL MODELING

For the coupled colloid and radionuclide transport in porous media, the following assumptions are considered to establish the governing equations:

1. The porosity of porous media is constant and all of the pore spaces are filled with water.
2. Groundwater flows very slow and is treated as laminar flow in porous media. The velocities of colloids and groundwater are uniform and constant.
3. The mechanism of dispersion for colloids and radionuclides satisfy the Fick's law.
4. The one-dimensional transport for both colloids and radionuclides is considered.

While the mechanisms of advection, dispersion and adsorption-desorption with the solid matrix are taken into consideration, the mass conservation of the suspended colloids can be written as following:

$$\theta \frac{\partial C}{\partial t} + \theta V_c \frac{\partial C}{\partial x} - \theta D_c \frac{\partial^2 C}{\partial x^2} = -P^C \quad (1)$$

Where C ([M/L³]; mass-of-colloids-in-liquid-phase/volume-of-pore-water) is the concentration of colloids in dispersed phase, x [L] is the spatial coordinate for the flow direction, t [T] is time, θ is the porosity of porous media and V_c [L/T], D_c [L²/T] are the average velocity and the dispersion coefficient for colloids, respectively. P^C [M/L³/T] is the production term for adsorption-desorption with the solid matrix and can be formulated based on different interaction mechanism. The mass balance equation for colloids attached on the solid matrix (σ_c [M/L³]; mass-of-colloids-sorbed-on-the-solid-matrix/volume-of-pore-water) can be expressed as:

$$\theta \frac{\partial \sigma_c}{\partial t} = P^C \quad (2)$$

Similar, the mass conservation equations for radionuclides in the porous media can be formulated as:

$$\theta \frac{\partial N}{\partial t} + \theta V \frac{\partial N}{\partial x} - \theta D \frac{\partial^2 N}{\partial x^2} + \theta \lambda N = -P^N - P^m - P^{im} \quad (3)$$

$$\theta \frac{\partial \sigma_N}{\partial t} + \theta \lambda \sigma_N = P^N \quad (4)$$

$$\theta \frac{\partial N_m}{\partial t} + \theta V_c \frac{\partial N_m}{\partial x} - \theta D_c \frac{\partial^2 N_m}{\partial x^2} + \theta \lambda N_m = P^m - P^{NC} \quad (5)$$

$$\theta \frac{\partial \sigma_{im}}{\partial t} + \theta \lambda \sigma_{im} = P^{im} + P^{NC} \quad (6)$$

Where N ($[M/L^3]$; mass-of-radionuclides-in-the-liquid-phase/volume-of-pore-water) is the radionuclide concentration in liquid phase, σ_N ($[M/L^3]$; mass-of-radionuclides-sorbed-on-the-solid-matrix/volume-of-pore-water) is the concentration of radionuclides sorbed onto the solid matrix. N_m and σ_{im} ($[M/L^3]$; mass-of-radionuclides-bound-to-colloids/volume-of-pore-water) are the concentrations of radionuclides sorbed to mobile and immobile colloids, respectively. λ $[1/T]$ is the radioactive decay constant for the radionuclides. V and D are the average velocity of groundwater and dispersion coefficient for radionuclides in porous media, respectively. The transport characteristics of the radionuclides bound to colloids are determined by those of colloids, such as the velocity and the dispersion coefficient. The production terms in these transport equations for radionuclides are employed for radionuclides to describe the adsorption-desorption interaction with colloids and the solid matrix. The production term, P^N , is employed for the interaction of radionuclides with the solid matrix. The production terms for radionuclide adsorption to mobile and immobile colloids are expressed as P^m and P^{im} , respectively. Furthermore, P^{NC} is a production term accounting for mobilization or immobilization of radionuclides bound to colloids due to interaction of colloids with the solid matrix. The total concentration of radionuclides in mobile phases can be given as:

$$N_T = N + N_m \quad (7)$$

Since the colloids may occur in the natural groundwater system for a very long time, it is reasonable to assume that the colloid concentration is independent of time and space, that is, a constant value of C_0 (17). Thus, the mass conservation equations of Eqs. (1)-(2) can be vanished. The colloid concentrations for both mobile and immobile colloids are independent of time and space. It can be considered that the interaction process of colloids and the solid matrix achieve equilibrium due to that the natural colloids have existed in the aquifer system for a long time. The concentration of colloids attached on the solid matrix can be expressed in term of the concentration of colloids in dispersed phase by linear adsorption isotherm (23,24).

$$\sigma_c = Kd^c C_0 \quad (8)$$

where Kd^c is the distribution coefficient for colloids on the solid matrix. The transport equations for radionuclides shown in Eqs. (3)-(6) can be solved using further assumptions for adsorption-desorption processes.

EQUILIBRIUM MODEL FOR RADIONUCLIDE ADSORPTION

When radionuclides are adsorbed on the solid matrix or the mobile/immobile colloids, the adsorption-desorption process can be characterized by isotherms that describe the equilibrium relationship between free and sorbed species concentrations at a given temperature. This equilibrium assumption is reasonable when the reaction rate is fast. Since the equilibrium has been achieved, the concentrations of free and sorbed radionuclides can be related by adsorption isotherms. The production terms in the governing equations can be vanished by adding the transport equations for radionuclides. For the concentrations of free radionuclides in aqueous phase adsorbed on the solid matrix, the relation of the concentration between radionuclides in liquid phase and adsorbed on the solid matrix using linear adsorption isotherm can be expressed as:

$$\sigma_N = Kd^N \cdot N \quad (9)$$

where Kd^N is the distribution coefficient for radionuclides on the solid matrix. Under the linear equilibrium assumption, the concentrations of radionuclides on mobile and immobile colloids can be formulated as (22):

$$N_m = Kd^m C_0 N \quad (10)$$

$$\sigma_{im} = Kd^{im} \cdot \sigma_C \cdot N = Kd^{im} Kd^C C_0 N \quad (11)$$

where Kd^m and Kd^{im} are the distribution coefficients for radionuclides on mobile and immobile colloids, respectively. Combining Eqs. (3)-(6) and (8)-(11), the governing equation for radionuclide transport in porous media can be expressed as:

$$\begin{aligned} & (1 + Kd^N + Kd^m C_0 + Kd^C Kd^{im} C_0) \theta \frac{\partial N}{\partial t} + (V + V_c Kd^m C_0) \theta \frac{\partial N}{\partial x} \\ & - (D + D_c Kd^m C_0) \theta \frac{\partial^2 N}{\partial x^2} + \lambda \theta (1 + Kd^N + Kd^m C_0 + Kd^C Kd^{im} C_0) N = 0 \end{aligned} \quad (12)$$

The governing equation can be further reduced by defining the effective retardation factor and dispersion coefficient (22). The equation is reduced to the traditional advection-dispersion transport equation with the radioactive decay term.

$$\frac{\partial N}{\partial t} + \frac{V}{R^*} \frac{\partial N}{\partial x} - \frac{D^*}{R^*} \frac{\partial^2 N}{\partial x^2} + \lambda N = 0 \quad (13)$$

where R^* and D^* are the effective retardation factor and dispersion coefficient, respectively. The modified parameters are given as:

$$R^* = \frac{1 + Kd^N + (Kd^m + Kd^C Kd^{im})C_0}{1 + \frac{V_c}{V} \cdot Kd^m C_0} \quad (14)$$

$$D^* = \frac{1 + \frac{D_c}{D} \cdot Kd^m C_0}{1 + \frac{V_c}{V} \cdot Kd^m C_0} D \quad (15)$$

This equation can be solved analytically with suitable initial and boundary conditions. In this work, an infinite porous media is considered and the following initial and boundary conditions are assumed:

$$N(x, t = 0) = 0 \quad (16)$$

$$N(x = 0, t) = N_0 \quad (17)$$

$$N(x = \infty, t) = 0 \quad (18)$$

The analytical solution can be obtained as following:

$$N(x, t) = N_0 \exp\left(\frac{Vx}{2D^*}\right) \frac{2}{\sqrt{\pi}} \int_{\frac{\eta}{2\sqrt{t}}}^{\infty} \exp\left(-\xi^2 - \frac{\eta^2 \beta}{4\xi^2}\right) d\xi$$

$$\eta = \sqrt{\frac{R^*}{D^*}} x, \quad \beta = \frac{V^2}{4R^* D^*} + \lambda \quad (19)$$

where η and β are integral parameters. The total mobile concentration of radionuclides can be obtained as:

$$\begin{aligned} N_T &= N + N_m \\ &= (1 + Kd^m C_0) N \\ &= (1 + Kd^m C_0) N_0 \exp\left(\frac{Vx}{2D^*}\right) \frac{2}{\sqrt{\pi}} \int_{\frac{\eta}{2\sqrt{t}}}^{\infty} \exp\left(-\xi^2 - \frac{\eta^2 \beta}{4\xi^2}\right) d\xi \\ &= N_{T0} \exp\left(\frac{Vx}{2D^*}\right) \frac{2}{\sqrt{\pi}} \int_{\frac{\eta}{2\sqrt{t}}}^{\infty} \exp\left(-\xi^2 - \frac{\eta^2 \beta}{4\xi^2}\right) d\xi \end{aligned} \quad (20)$$

where $N_{T0} = (1 + Kd^m C_0) N_0$, that is the total mobile concentration at $x = 0$.

NONEQUILIBRIUM MODEL FOR RADIONUCLIDE ADSORPTION

When the processes of radionuclides adsorbed on the solid matrix or colloids are not in the equilibrium state, radionuclides deposit on the solid matrix or colloids and may be remobilized in the groundwater system. The processes can be represented by a first order kinetic approach. Thus, the production terms in the transport equations for radionuclides can be described by linear kinetic adsorption interaction. In order to study the kinetic adsorption processes for radionuclides with the solid matrix and colloids, two cases are categorized in the present paper. In Case 1, the reaction rate of the adsorption processes for radionuclides with the solid matrix is considered that it is fast enough (compare with the process for colloids) to achieve the equilibrium state. This assumption is made to simplify the problem and focus on the adsorption mechanism of colloids only. Relatively, the adsorption process for radionuclides with colloids (both mobile and immobile colloids) is modeled by the linear kinetic adsorption interaction. In Case 2, both the adsorption processes for radionuclides with the solid matrix and colloids are modeled by the linear kinetic interaction. The transport equations for radionuclides can be solved under these assumptions for adsorption-desorption interactions in the two cases.

Case 1: Linear kinetic adsorption interactions for radionuclides with colloids

Since the adsorption process for radionuclides with the solid matrix is treated as equilibrium, the concentrations of radionuclides in liquid phase and adsorbed on the solid matrix can be related by linear isotherm.

$$\sigma_N = Kd^N \cdot N \quad (21)$$

where Kd^N is the distribution coefficient for radionuclides on the solid matrix. The adsorption-desorption processes for radionuclides with colloids (both mobile and immobile colloids) are treated as linear kinetic interaction and the production terms in the transport equations for radionuclides can be written as following:

$$P^m = \theta(k_f^m C_0 N - k_b^m N_m) \quad (22)$$

where k_f^m and k_b^m are the forward and backward reaction rate for the reaction of radionuclides adsorbed on the mobile colloids, respectively. Similarly, the rest of production terms can be given as:

$$\begin{aligned} P^{im} &= \theta(k_f^{im} \sigma_c N - k_b^{im} \sigma^{im}) \\ &= \theta(k_f^{im} K d^C C_0 N - k_b^{im} \sigma^{im}) \end{aligned} \quad (23)$$

$$P^{NC} = \theta(k_f^{NC} N_m - k_b^{NC} \sigma^{im}) \quad (24)$$

where k_f^{NC} and k_b^{NC} are the forward and backward reaction rate for the reaction of mobilization or immobilization of radionuclides bound to colloids due to the interaction of colloids with the solid matrix, respectively. It should be noticed that although the concentrations of colloids in dispersed phase and attached on the solid matrix have achieved equilibrium, the concentrations of radionuclides bound to mobile and immobile colloids do not reach the equilibrium state due to the reversible equilibrium state of colloids. The distributions of radionuclides bound to mobile and immobile colloids are not uniform, hence, the production term, which describes the interaction process of radionuclides on mobile and immobile colloids, should be reserved in the governing equation. Applying Eqs. (21)-(24), the transport equations of radionuclides can be reduced as the following:

$$\begin{aligned} (1 + K d^N) \frac{\partial N}{\partial t} + V \frac{\partial N}{\partial x} - D \frac{\partial^2 N}{\partial x^2} + \lambda(1 + K d^N) N = \\ - (k_f^m N - k_b^m N_m) - (k_f^{im} N - k_b^{im} \sigma^N) \end{aligned} \quad (25)$$

$$\begin{aligned} \frac{\partial N_m}{\partial t} + V_c \frac{\partial N_m}{\partial x} - D_c \frac{\partial^2 N_m}{\partial x^2} + \lambda N_m = \\ (k_f^m N - k_b^m N_m) - (k_f^{NC} N_m - k_b^{NC} \sigma^{im}) \end{aligned} \quad (26)$$

$$\frac{\partial \sigma^{im}}{\partial t} + \lambda \sigma^{im} = (k_f^{im} N - k_b^{im} \sigma^{im}) + (k_f^{NC} N_m - k_b^{NC} \sigma^{im}) \quad (27)$$

where $k_f^m = k_f^m C_0$ and $k_f^{im} = k_f^{im} K d^C C_0$.

In Eqs. (25)-(27), the three unknown concentrations, N , N_m and σ^{im} , can be solved numerically with the following initial and boundary conditions:
Initial conditions

$$N(x, t = 0) = 0 \quad (28a)$$

$$N_m(x, t = 0) = 0 \quad (28b)$$

$$\sigma^{im}(x, t = 0) = 0 \quad (28c)$$

Boundary conditions

$$N(x = 0, t) = N_0 \quad (29a)$$

$$N(x = \infty, t) = 0 \quad (29b)$$

$$N_m(x = 0, t) = 0 \quad (29c)$$

$$N_m(x = \infty, t) = 0 \quad (29d)$$

$$\sigma^{im}(x = 0, t) = 0 \quad (29e)$$

$$\sigma^{im}(x = \infty, t) = 0 \quad (29f)$$

The governing equations together with the initial and boundary conditions may be solved by a fully implicit finite difference method which employs a two-point backward difference approximation in time (Euler implicit scheme), a central difference approximation for second derivative in spatial coordinate and upwind difference approximation for first derivative in spatial coordinate (25).

Case 2: Linear kinetic adsorption interactions for radionuclides with colloids and the solid matrix

Further, it can be also take into consideration that the adsorption process for radionuclides with the solid matrix is a linear kinetic interaction. The concentration of radionuclides adsorbed on the solid matrix can be expressed as:

$$P^N = \theta(k_f^N N - k_b^N \sigma^N) \quad (30)$$

Therefore, the transport equations for radionuclides can be written as follows under the linear kinetic adsorption model:

$$\begin{aligned} \frac{\partial N}{\partial t} + V \frac{\partial N}{\partial x} - D \frac{\partial^2 N}{\partial x^2} + \lambda N = & -(k_f^N N - k_b^N \sigma^N) \\ & - (k_f^m N - k_b^m N_m) - (k_f^{im} N - k_b^{im} \sigma^{im}) \end{aligned} \quad (31)$$

$$\frac{\partial \sigma^N}{\partial t} + \lambda \sigma^N = k_f^N N - k_b^N \sigma^N \quad (32)$$

$$\frac{\partial N_m}{\partial t} + V_c \frac{\partial N_m}{\partial x} - D_c \frac{\partial^2 N_m}{\partial x^2} + \lambda N_m = (k_f^m N - k_b^m N_m) - (k_f^{NC} N_m - k_b^{NC} \sigma^{im}) \quad (33)$$

$$\frac{\partial \sigma^{im}}{\partial t} + \lambda \sigma^{im} = (k_f^{im} N - k_b^{im} \sigma^{im}) + (k_f^{NC} N_m - k_b^{NC} \sigma^{im}) \quad (34)$$

Here, four governing equations are obtained and the concentration of radionuclides adsorbed on the solid matrix, σ^N , should be solved in the same time. Hence, additional initial and boundary conditions are needed.

Initial condition for σ^N :

$$\sigma^N(x, t = 0) = 0 \quad (35)$$

Boundary conditions for σ^N :

$$\sigma^N(x = 0, t) = 0 \quad (36a)$$

$$\sigma^N(x = \infty, t) = 0 \quad (36b)$$

Similarly, Eqs. (31)-(34) can be also solved numerically using the same numerical scheme, which mentioned in case 1.

ANALYTICAL SOLUTION FOR NONEQUILIBRIUM ADSORPTION MODEL: RADIONUCLIDES TRANSPORT IN POROUS MEDIA IN THE ABSENCE OF COLLOIDS

It is difficult to obtain analytical solutions for Case 1 or Case 2. When colloids in the groundwater system do not take into consideration, the radionuclide transport equation can be solved analytically under linear kinetic adsorption model. Only Eqs. (3) and (4) need to be solved and the production terms, P^m and P^{im} , in Eq. (3) are zero due to the absence of colloids. The production term, P^N , for the interaction of radionuclides with the solid matrix can be formulated by Eq. (30) under linear kinetic adsorption model. The governing equations are given as:

$$\frac{\partial N}{\partial t} + V \frac{\partial N}{\partial x} - D \frac{\partial^2 N}{\partial x^2} + \lambda N = -(k_f^N N - k_b^N \sigma^N) \quad (37)$$

$$\frac{\partial \sigma^N}{\partial t} + \lambda \sigma^N = k_f^N N - k_b^N \sigma^N \quad (38)$$

Using Laplace and inverse Laplace transform, the transport equations for radionuclides can be solved with initial and boundary conditions (Eqs. (28a), (29a), (29b), (35) and (36)). The analytical solution for radionuclide transport in porous media under linear kinetic adsorption model in the absent of colloids can be expressed as (26):

$$N(x,t) = N_0 \frac{2}{\pi} \int_{\frac{\eta}{2\sqrt{t}}}^{\infty} \exp\left[\frac{Vx}{2D} - \xi^2 - \frac{\eta^2}{4\xi^2}(\beta_1 - \beta_3)\right] \cdot \left\{F_1(t) + \beta_3 \int_{\frac{\eta^2}{4\xi^2}}^{\eta^2} F_1(\tau) d\tau\right\} d\xi$$

$$F_1(t) = \exp(-\beta_3 t) I_0 \left[\frac{\eta}{\xi} \sqrt{\beta_2 \left(t - \frac{\eta^2}{4\xi^2}\right)} \right] h\left(t - \frac{\eta^2}{4\xi^2}\right)$$

$$\eta = \frac{x}{\sqrt{D}}, \quad \beta_1 = \lambda + \frac{V^2}{4D} + k_f^N, \quad \beta_2 = k_f^N k_b^N, \quad \beta_3 = \lambda + k_b^N \quad (39)$$

where I_0 is modified Bessel function of zero order and h is the Heaviside step function. This analytical solution is used to verify and comparison the numerical solutions for Case 1 and Case 2.

NUMERICAL ILLUSTRATIONS

To illustrate the numerical solutions for Case 1 and Case 2, the parameters listed in Table 1 are used. According to the literature about the field experiments of natural colloids in groundwater systems (27), the typical concentration of natural colloids can be estimated as 0.1 kg/m^3 . Two sets of adsorption interaction parameters for radionuclides with colloids are used under the assumption in Case 1. The adsorption interaction parameters in Case 1b are one order of magnitude larger than those in Case 1a, but the ratios of forward to backward reaction rates remain constant values. Thus, it is indicated that the reaction rates for radionuclides with colloids in Case 1b are faster than those in Case 1a. The normalized concentrations for total mobile radionuclides at 1, 5, 10, and 50 years are plotted in Fig. 1. The normalized radionuclide concentrations with/without colloids and that under the linear equilibrium assumption (LEA) are also shown in this figure for comparison. The reaction rate of the adsorption process for radionuclides with colloids is treated as infinite under the linear equilibrium assumption. Under the linear equilibrium assumption, the concentrations of radionuclides sorbed on colloids (mobile and immobile colloids) achieve the equilibrium state on the instant, therefore, the radionuclide concentration is higher than that in Case 1a and 1b due to

the acceleration effect by mobile colloids. The colloids in dispersed phase act as mobile vehicle to enhance the migration of radionuclides in porous media. The amount of radionuclides bound to mobile colloids affects the acceleration effect. At 1 year, the normalized concentration of radionuclides for Case 1a is similar to that for LEA (without colloids). The acceleration effect caused by colloids in Case 1a is not apparent due to slow reaction rates of the adsorption process for radionuclides with colloids. It can be clearly observed that the normalized concentration profile for radionuclides in Case 1b at 1 year exhibits tailing near $x = 1\text{m}$. A fraction of radionuclides sorbed on mobile colloids, thus, these radionuclides have less probability of being sorbed by immobile phase and can transport further than other radionuclides. The exhibition of tailing in the concentration profile for Case 1b becomes weaker as time increases. The fraction of radionuclides on mobile colloids increases with time, therefore, the shape of the concentration profile becomes more smoothly (without tailing). The exhibition of tailing can also be found in Case 1a. However, it takes more time to get a smooth concentration profile in Case 1a because of its slow reaction rates. As time increases, the normalized concentration and the migration distance of radionuclides for Case 1a and 1b are larger than those for LEA (without colloids). This is because that the amount of radionuclides adsorbed on colloids increases as time increases, therefore, the acceleration effect also increases with time.

The total mobile radionuclides consist of radionuclides in liquid phase and bound to mobile colloids. The normalized concentrations of radionuclides in liquid phase (N) and adsorbed on mobile colloids (N_m) for Case 1a and 1b when time equals to 10 years are shown in Fig. 2. The normalized concentration of radionuclides in liquid phase is unity at the source ($x = 0$) and then decreases to zero as the distance away from the source. The normalized concentration of radionuclides adsorbed on mobile colloids is zero at the source and increases as the distance from the source increases. At the position of x equals to one, the normalized concentrations of radionuclides adsorbed on mobile colloids reach the maximum value and then decrease to zero. It can be observed in Fig. 2 that total mobile radionuclides are contributed mainly from radionuclides in liquid phase in Case 1b for $x > 0.5\text{m}$. The fraction of radionuclides sorbed on mobile colloids in Case 1a is relatively less than that in Case 1b due to the slow reaction rate of the adsorption process in Case 1a. When the reaction rate of adsorption interaction is fast (Case 1b), the concentration of radionuclides adsorbed on mobile colloids increases significantly. In Fig. 2, it is indicated that the faster reaction rate of the adsorption process causes that the concentration of radionuclides bound to mobile colloids increases faster.

In Case 2, both the adsorption-desorption interactions for radionuclides with the solid matrix and colloids are modeled by linear kinetic adsorption. Three sets of adsorption interaction

parameters for radionuclides with the solid matrix and colloids are used for Case 2. In Case 2a, typical interaction parameters are used for a standard case. The forward and backward reaction rates of adsorption processes for radionuclides with colloids in Case 2b are one order magnitude faster than those in Case 2a and the ratios of forward to backward reaction rates remain constant values. The interaction parameters for radionuclides with the solid matrix do not change in Case 2b. In contrast, the interaction parameters for radionuclides with colloids in Case 2c are the same with those in Case 2a but the forward and backward reaction rates of the adsorption process for radionuclides with the solid matrix is set as one order magnitude faster than that in Case 2a with the same ratio. The normalized concentration profiles of total mobile radionuclides at different time for Case 2 are plotted in Fig. 3. The concentrations for Case 2a and 2b are almost coincident at one year and the difference between the two concentrations increases at 5 years. The reaction rate for radionuclides with colloids in Case 2b is faster than that in Case 2a. As time increases, the concentration of radionuclides bound to colloids increases more rapidly due to the faster reaction rate. Thus, the effect that colloids enhance the migration of radionuclides causes a higher concentration of total mobile radionuclides. It is also observed that both the concentrations for Case 2a and 2b at one year are lower than that for the case in which colloids do not take into consideration. This is because that colloids in the groundwater system may be mobile or immobile. Mobile colloids enhance the migration of radionuclides but immobile colloids retard the transport of radionuclides. In the early time, the acceleration effect caused by mobile colloids do not show up under the kinetic adsorption model. As time goes by, the colloid-facilitated effect becomes dominating. Thus, the radionuclide concentration for Case 2b is higher than that for the case without colloids when time is larger than 5 years. But the radionuclide concentration for Case 2a is a little higher than that for the case without colloids at time equals to 50 years due to slow reaction rate. The reaction rate of the adsorption process for radionuclides with the solid matrix is fast in Case 2c. At 1 year, the fast reaction rate of the adsorption process for radionuclides with the solid matrix increases the concentration of radionuclides adsorbed on the solid matrix and decreases the concentration of radionuclides in liquid phase. The concentration of radionuclides for Case 2c is much lower than that for the case without colloids because of the fast reaction rate of the adsorption process for radionuclides with the solid matrix, which acts as immobile carrier and retards the migration of radionuclides. As time increases, the concentration for Case 2c is close to that for Case 2a. This indicates that the kinetic interaction parameters for radionuclides with the solid matrix do not strongly affect the transport characteristics of radionuclide migration for longer time.

The normalized concentrations of radionuclides in liquid phase and adsorbed on mobile colloids in Case 2 when time equals to 10 years are plotted in Fig. 4. For Case 2a and 2b, it can be

observed clearly that the fastest reaction rate in Case 2b of the adsorption process for radionuclides with colloids causes a higher concentration of radionuclides on mobile colloids. It is also shown in this figure that total mobile radionuclide concentration is mainly contributed by radionuclides bound to mobile colloids in Case 2b for $x > 0.5\text{m}$. The concentration of radionuclides in liquid phase at the distance away from the source is quite low, thus, the retardation effect caused by immobile colloids become weaker due to low concentration of free radionuclides in liquid phase. The numerical solutions indicate that the reaction rate for radionuclides with colloids strongly affect the transport behavior of radionuclides in porous media. It can be clearly shown that total mobile radionuclides mainly consist by radionuclides in liquid phase for Case 2a and 2c only at $x < 1\text{m}$. The results indicate that the influence of changing interaction parameters for radionuclides with the solid matrix is much weaker than that of changing interaction parameters for radionuclides with colloids. Mobile colloids enhance the transport properties of radionuclides in porous media and the interaction characteristics of the adsorption mechanism between colloids and radionuclides strongly influence the radionuclide migration.

CONCLUSIONS

The migration of radionuclides in porous media in the presence of colloids is modeled in this work. In the present model, the interactions for radionuclides with the solid matrix as well as the colloids can be treated as kinetic processes. The colloids may be mobile or immobile and mobile colloids facilitate the transport of radionuclides in the groundwater system. Immobile colloids and the solid matrix retard the radionuclide migration. Under the kinetic adsorption model, the reaction rates of the interaction processes for radionuclides with mobile and immobile carriers affect the transport characteristics of radionuclides. The different reaction rates for the interaction processes with colloids and the solid matrix are investigated in the present work.

Using numerical illustration, the findings in the present paper can be summarized as following:

1. When the adsorption process for radionuclides with the solid matrix is treated as equilibrium state but the adsorption process for radionuclides with colloids is modeled by kinetic adsorption (Case 1) or both interactions for radionuclides with the solid matrix and colloids is modeled by kinetic adsorption (Case 2), the fast reaction rate for radionuclides with colloids increases the concentration of radionuclides adsorbed on colloids. The higher concentration of radionuclides adsorbed on colloids enhance the transport of radionuclides.
2. Colloids in the groundwater system play both the roles of mobile and immobile carriers. The reaction rate of the interaction for radionuclides with colloids may influence the acceleration and retardation effect on the migration of radionuclides.

3. However, the solid matrix acts as an immobile carrier. The fast reaction rate of the adsorption process for radionuclides decreases the concentration of total mobile radionuclides and enlarges the retardation effect caused by the solid matrix.

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REFERENCES

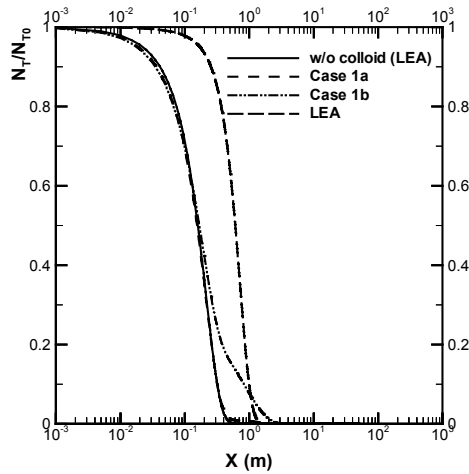
1. McCarthy, J. F. and Zachara, J. M., Subsurface transport of contaminants, *Environ. Sci. Technol.*, **23**(5): 496 (1989).
2. Nelson, D. M. and Orlandini, K. A., Source effects on actinide movement in groundwater, *ANL 86-15*, Argonne National Laboratory (1986).
3. Kersting, A. B., Efurud, D. W., Finnegan, D. L., Rokop, D. J., Smith, D. K. and Thompson, J. L., Migration of plutonium in ground water at the Nevada Test Site, *Nature*, **397**: 56 (1999).
4. Chung, J. Y. and Lee, K. J., Formation and transport of radioactive colloids in porous media, *Waste Manag.*, **13**(8): 599 (1993).
5. Ramsay, J. D. F., The role of colloids in the release of nuclides from nuclear waste, *Radiochim. Acta*, **44/45**: 165 (1988).
6. Avogadro, A. and DeMarsily, G., The role of colloids in nuclear waste disposal, *Mat. Res. Soc. Symp. Proc.*, **26**: 495 (1984).
7. Bates, J. K., Bradley, J. P., Teetsov, A., Bradley, C. R. and Buchholtz ten Brick, M., Colloid formation during waste form reaction: implication for nuclear waste disposal, *Science*, **256**: 649 (1992).
8. Kim, I., Buckau, G., Rommel, H. and Sohnus, B., The migration behaviour of transuranium elements in Gorleben aquifer systems: colloid generation and retention process, *Mater. Res. Soc. Symp. Proc.*, **127**: 849 (1989).
9. Gutierrez, M. G., Bidoglio, G., Avogadro, A., Mingarro, E. and D'Alessandro, M., Experimental investigations of radionuclide transport through cored granite samples, *Radiochim. Acta*, **52/53**: 213 (1991).
10. Nagasaki, S., Tanaka, S. and Suzuki, A., Influence of Fe(III) colloids on Np(V) migration through quartz-packed columns, *J. Nucl. Sci. Technol.*, **31**(2): 143 (1994).
11. Tanaka, S. and Nagasaki, S., Impact of colloid generation on actinide migration in high-level radioactive waste disposal: overview and laboratory analysis, *Nucl. Technol.*, **118**(1): 58 (1997).

12. Saltelli, A., Avogadro A. and Bidoglio, G., Americium filtration in glauconitic sand columns, *Nucl. Technol.*, **67**: 245 (1984).
13. Travis, B. J. and Nuttall, H. E., Analysis of colloid transport, *Mater. Res. Soc. Symp. Proc.*, **50**: 737 (1985).
14. Mills, W. M., Liu, S. and Fong, F. K., Literature review and model (COMET) for colloid/metal transport in porous media, *Groundwater*, **29**: 199 (1991).
15. Hwang, Y., Chambre, P. L., Lee, W. W.-L. and Pigford., T. H., Analytical studies of colloid transport in fractured porous media, *Mater. Res. Soc. Symp. Proc.*, **176**:599 (1990).
16. Grindrod, P., The impact of colloids on the migration and dispersal of radionuclides within fractured rock, *J. Contam. Hydrol.*, **13**: 167 (1993).
17. Baek, I. and Pitt, Jr, W. W., Colloid-facilitated radionuclide transport in fracture porous rock, *Waste Manag.*, **16**(4): 313 (1996).
18. Cacheris, W. P. and Choppin, G. R., Dissociation kinetics of thorium-humate complex, *Radiochim. Acta*, **42**: 185 (1987).
19. Choppin, G. R., The role of natural organics in radionuclide migration in natural aquifer systems, *Radiochim. Acta*, **58/59**: 113 (1992).
20. Ibaraki, M. and Sudicky, E. A., Colloid-facilitated contaminant transport in discretely fractured porous media - 1. numerical formulation and sensitivity analysis, *Water Resour. Res.*, **31**(12): 2945 (1995).
21. Corapcioglu, M. Y. and Jiang, S., Colloid-facilitated groundwater contaminant transport, *Water Resour. Res.*, **29**(7): 2215 (1993).
22. van de Weerd, H., Leijnse, A. and van Riemsdijk, W. H., Transport of reactive colloids and contaminants in groundwater: effect of nonlinear kinetic interactions, *J. Contam. Hydrol.*, **32**: 313 (1998).
23. Fetter, C. W., *Contaminant Hydrogeology*, Macmillan Publishing Co., New York (1993).
24. Bedient, B. P., Rifai, H. S. and Newell, C. J., *Groundwater Contamination Transport and Remediation*, 1st Ed., PTR Prentice-Hall, New Jersey (1994).
25. Wang, H. F. and Anderson, M. P. *Introduction to groundwater modeling: finite difference and finite element methods*, W. H. Greeman, New York (1982).
26. Lee, C. H., *Studies of nonequilibrium sorption effects on nuclide transport in fractured rock*, Ph. D. Thesis, National Tsing Hua University, Taiwan (1993).
27. Lieser, K. H., Ament, A., Hill, R., Singh, R. N., Stingl, U. and Thybusch, B., Colloids in groundwater and their influence on migration of tracer elements and radionuclides, *Radiochimica Acta*, **49**: 83 (1990).

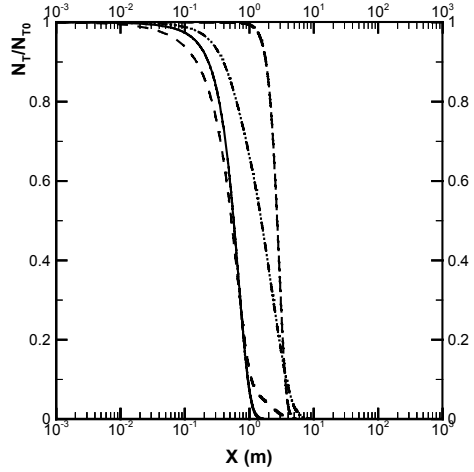
Table 1 Parameters for radionuclide and colloids

Transport parameters:		
	$V = 10 \text{ m/yr}$	$V_c = 10 \text{ m/yr}$
	$D = 1 \text{ m}^2/\text{yr}$	$D_c = 1 \text{ m}^2/\text{yr}$
	$Kd^N = 100$	$Kd^C = 10$
	$\lambda = 3.240 \times 10^{-7} \text{ yr}^{-1}$ (for ^{237}Np)	$C_0 = 0.1 \text{ kg/m}^3$
Interaction parameters:		
Case 1a	$k_f^m = 10.$	$k_b^m = 0.1$
	$k_f^{im} = 10.$	$k_b^{im} = 0.1$
	$k_f^{NC} = 1.0$	$k_b^{NC} = 0.1$
Case 1b	$k_f^m = 100.$	$k_b^m = 1.0$
	$k_f^{im} = 100.$	$k_b^{im} = 1.0$
	$k_f^{NC} = 10.$	$k_b^{NC} = 1.0$
Case 2a	$k_f^m = 10.$	$k_b^m = 0.1$
	$k_f^{im} = 10.$	$k_b^{im} = 0.1$
	$k_f^{NC} = 1.0$	$k_b^{NC} = 0.1$
	$k_f^N = 10.$	$k_b^N = 0.1$
Case 2b	$k_f^m = 100.$	$k_b^m = 1.0$
	$k_f^{im} = 100.$	$k_b^{im} = 1.0$
	$k_f^{NC} = 10.$	$k_b^{NC} = 1.0$
	$k_f^N = 10.$	$k_b^N = 0.1$
Case 2c	$k_f^m = 10.$	$k_b^m = 0.1$
	$k_f^{im} = 10.$	$k_b^{im} = 0.1$
	$k_f^{NC} = 1.0$	$k_b^{NC} = 0.1$
	$k_f^N = 100.$	$k_b^N = 1.0$

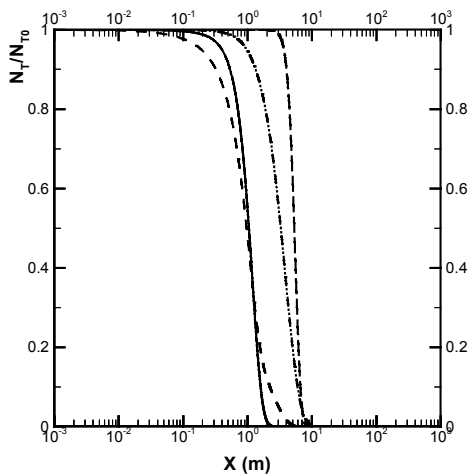
1 Year



5 Years



10 Years



50 Years

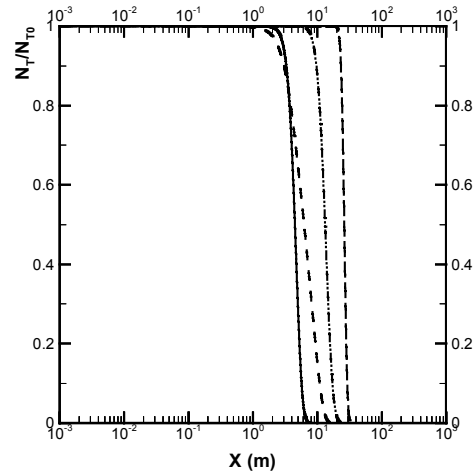


Figure 1 Normalized total mobile concentration profiles for radionuclides at different time (1, 5, 10 and 50 years) under different adsorption model in Case 1.

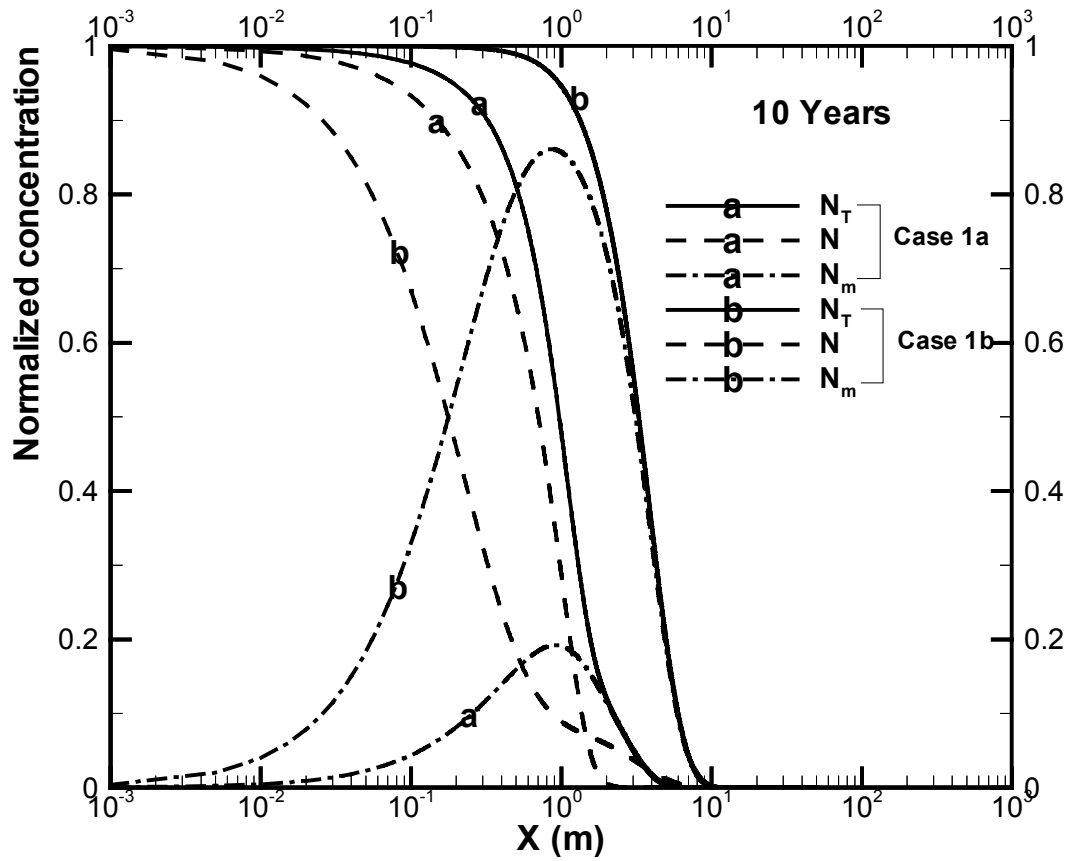


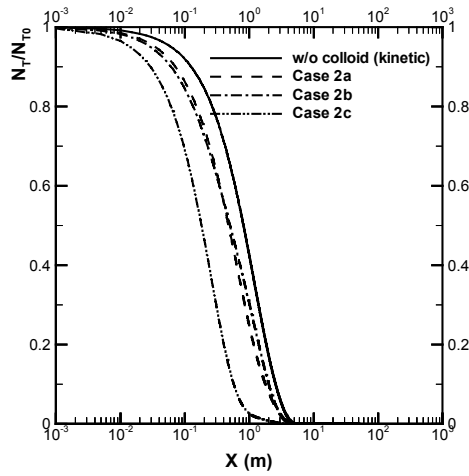
Figure 2 Normalized concentration profiles for radionuclides distributed in different phases at 10 years in Case 1.

N : radionuclides in liquid phase

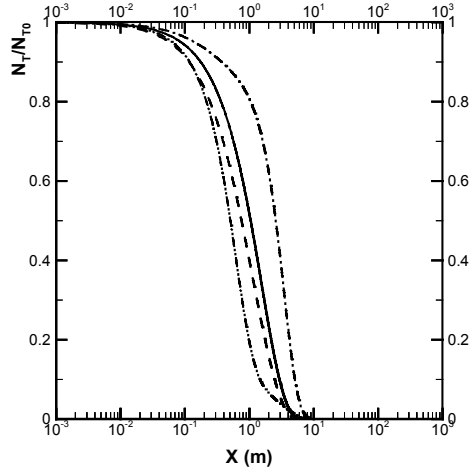
N_m : radionuclides adsorbed on mobile colloids

N_T : total mobile radionuclides ($N_T = N + N_m$)

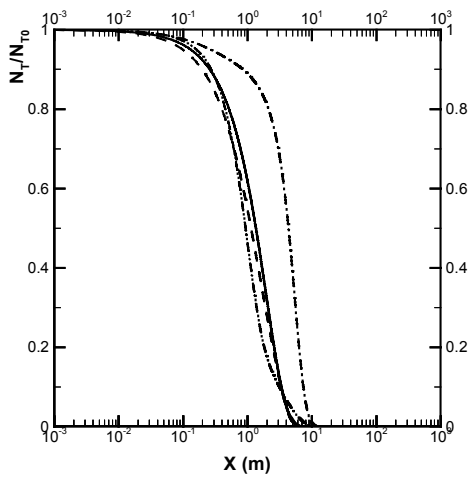
1 Year



5 Years



10 Years



50 Years

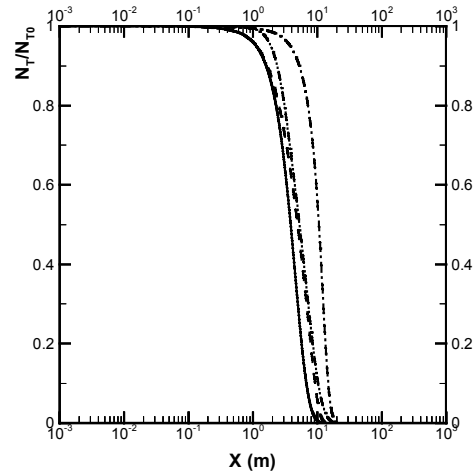


Figure 3 Normalized total mobile concentration profiles for radionuclides at different time (1, 5, 10 and 50 years) under different adsorption model in Case 2.

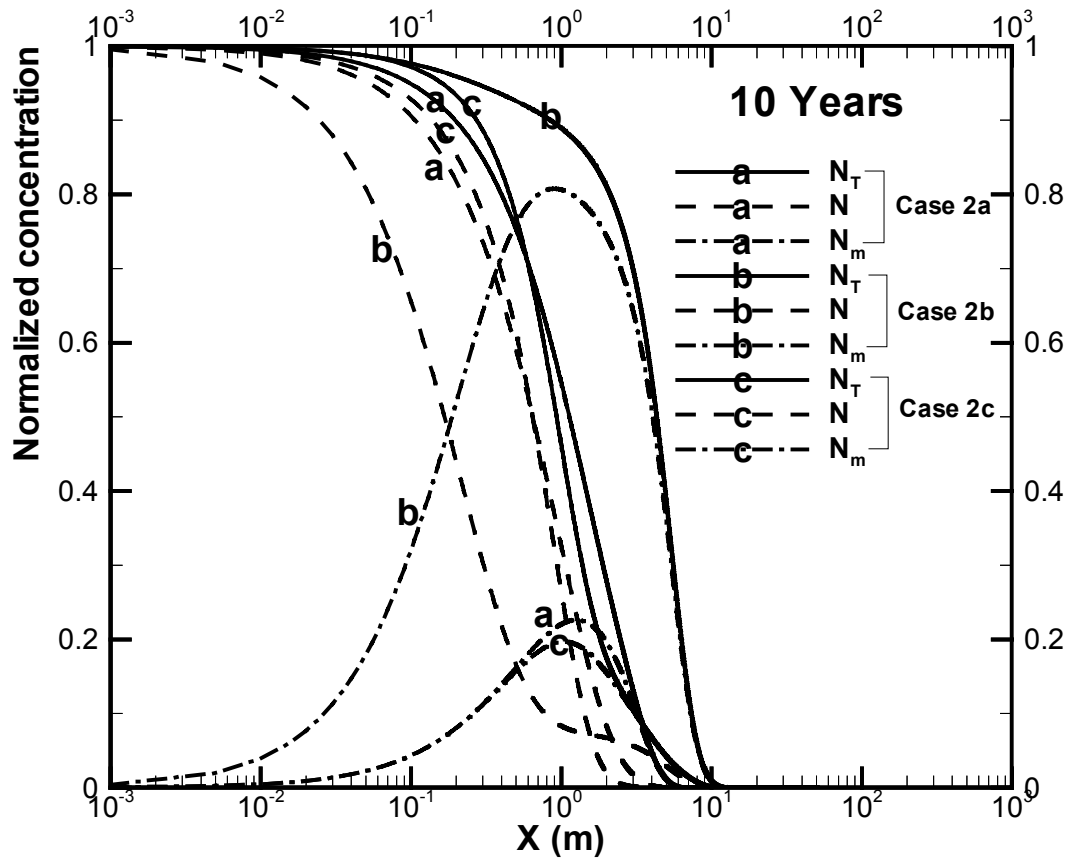


Figure 4 Normalized concentration profiles for radionuclides distributed in different phases at 10 years in Case 2.

N : radionuclides in liquid phase

N_m : radionuclides adsorbed on mobile colloids

N_T : total mobile radionuclides ($N_T = N + N_m$)