

# Numerical modeling of radionuclide migration in porous media with nonequilibrium sorption

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**Abstract**—When radionuclides migrate in porous media with water serving as carrier, the mechanism of sorption and desorption is not negligible. Nonequilibrium conditions exist in sorption and desorption. In this paper, a numerical model of radionuclide migration with nonequilibrium sorption was developed. The algorithm of numerical discretizing and direct substituting was adopted in coupling of the convective-dispersive equation and the nonequilibrium sorption isotherm in this model, and this makes it easier to solve the model numerically. A quantitative analysis is made for the first time that the influence of nonequilibrium sorption, represented by the rate coefficient which shows how quickly the nonequilibrium condition in sorption and desorption reaches equilibrium on the migration of radionuclide, and results show that it affects the migration perceptibly. Finally the model was verified by using the observed data of radionuclide migration test conducted in the field, and which clarified its availability.

**Keywords:** radionuclide migration; sorption and desorption; nonequilibrium sorption; rate coefficient.

## 1 Introduction

The mathematical model of radionuclide migration is a model of solute transport. As a special kind of solutes, radionuclides are more easily sorbed by porous media when they migrate with water serving as carrier. Thus sorption and desorption is one of the most important mechanisms in radionuclide migration and they occur under nonequilibrium conditions. Nevertheless in current mathematical models of radionuclide migration it is generally assumed that sorption and desorption reach equilibrium immediately, that is, the solution phase concentration and solid phase concentration of radionuclide reach their corresponding equilibrium concentration instantaneously. The mathematical model of this kind is nominated as mathematical model of radionuclide migration with equilibrium sorption, in which the nonequilibrium conditions in sorption and desorption are not taken into account. The mathe-

mathematical model of radionuclide migration in which the nonequilibrium conditions in sorption and desorption are taken into account is termed as mathematical model of radionuclide migration with nonequilibrium sorption. A few research has been devoted to on this kind of model. So far mathematical models developed for solute transport with nonequilibrium sorption usually prescribe solute transport only under conditions of indoor tests, steady flow, and homogeneous media. On the basis of studies by former researchers, a two-dimensional finite element model for radionuclide migration with nonequilibrium sorption in saturated and/or unsaturated zone is established. And this model is more comprehensive and more applicable according to the mechanisms taken into account. The first-order nonequilibrium sorption isotherm was assumed in this model and the algorithm of numerical discretizing and direct substituting was adopted in coupling of the convective-dispersive equation and the nonequilibrium sorption isotherm, which makes it easier to solve the model numerically. Hence this model is applicable to the complicated condition of transient flow domain. A quantitative analysis is made for the first time that the influence of nonequilibrium sorption, represented by the rate coefficient which shows how quickly the nonequilibrium conditions in sorption and desorption reach equilibrium on the migration of radionuclides by adjusting the rate coefficient. The field test of radionuclide migration was conducted in order to verify the feasibility of this model and to eliminate the size effect of indoor tests, and results show that this model can delineate the migration of radionuclide better. Therefore studies on this problem can provide a theoretical basis and methodology for the disposal of low/middle level radioactive waste, solid waste disposal and environmental assessments of groundwater pollution by fertilizers or pesticides etc.

## 2 Finite element model for radionuclide migration with nonequilibrium sorption

The theoretical basis of mathematical model of radionuclide migration is the convective-dispersive theory and the derivation of governing equation is based on mass conservation law. As to radionuclide migration with sorption and desorption, while the liquid phase serves as carrier, the convection, diffusion and hydrodynamic dispersion are the main mechanisms governing migration. The solution phase concentration of radionuclide varies because of the convection, diffusion and hydrodynamic dispersion, and thus it affects the distribution of solid phase concentration of radionuclide. The solid phase concentration and solution phase concentration of radionuclide are inter-related and restricted, and this results in the retardation of radionuclide migration in porous media. Assuming that the density of liquid phase is constant, the convective-dispersive equation for radionuclide migration included mechanisms of convection, dispersion, and sorption can thus be written as follows :

$$\frac{\partial}{\partial t}(\theta c + \rho s) = -\nabla \cdot [c\vec{V} - \theta\vec{D} \cdot \nabla c] - \lambda(\theta c + \rho s) - (\theta c + \rho s)\alpha' \frac{\partial h}{\partial x} + M, \quad (1)$$

where  $c$  is the solution phase concentration [M/L<sup>3</sup>];  $s$  is the solid phase concentration;  $\theta$  is

water content;  $\rho$  is the medium bulk density  $[M/L^3]$ ;  $\vec{V}$  is the flow velocity  $[L/T]$ ;  $\vec{D}$  is the dispersion tensor  $[L^2/T]$ ;  $\alpha'$  is the modified compressibility of the medium;  $h$  is the water head or metric potential  $[L]$ ;  $\lambda$  is the radioactive decay factor;  $M$  is source or sink flux  $[M/(T \cdot L^3)]$ .

In Equation (1),  $\theta$ ,  $h$  and  $\vec{V}$  can be determined from the water flow model. Independent variables include  $x$ ,  $z$  and  $t$  (two-dimensional flow in vertical section is assumed) and variables to be solved are  $c$  and  $s$ . Thus an additional equation should be added in order to solve Equation (1). In former mathematical model for radionuclide migration with equilibrium sorption the assumption was made that  $c$  is linear with  $s$ , which is independent on time. Hence the nonequilibrium conditions in sorption and desorption were neglected accordingly. If the nonequilibrium conditions in sorption and desorption are considered, the nonequilibrium sorption isotherm should be adopted, that is,

$$\frac{\partial c}{\partial t} = \alpha(K_d c - s), \quad (2)$$

where  $K_d$  is the equilibrium distribution coefficient  $[L^3/M]$ ; which is the ratio of solid phase concentration to solution phase concentration when sorption and desorption reach equilibrium;  $\alpha$  is the equilibrium rate coefficient  $[T^{-1}]$ , which represents how quickly sorption and desorption reach equilibrium. These two coefficients rely both on the property of radionuclide and on the characteristics of the media.

Equation (2) shows that the sorption rate is proportional to the difference of the dissolved concentration and the sorbed concentration. When  $c > s/K_d$ , the sorption rate is greater than the desorption rate; when  $c < s/K_d$ , the sorption rate is less than the desorption rate; when sorption and desorption reach equilibrium,  $\partial c/\partial t$  ought to be zero, Equation (2) can then be written as

$$s = K_d c. \quad (3)$$

Obviously, equilibrium sorption is just a special case of nonequilibrium sorption.

Equations (1) and (2) are two basic equations of the two-dimensional mathematical model for radionuclide migration with nonequilibrium sorption in saturated and/or unsaturated zone. The initial and boundary conditions are

$$\begin{cases} c|_{t=0} = c_0 \\ s|_{t=0} = s_0, \end{cases} \quad (4)$$

$$\begin{cases} c|_{B_1} = c_1 \\ \vec{n} \cdot (\vec{V}c - \theta \vec{D} \cdot \nabla c)|_{B_2} = q_2 \\ (\alpha c + \frac{\partial c}{\partial t})|_{B_3} = q_3, \end{cases} \quad (5)$$

where  $c_0$  is the initial dissolved concentration;  $s_0$  is the initial sorbed concentration;  $c_1$  is the dissolved concentration on boundary  $B_1$ ;  $q_2$  is the mass flux on boundary  $B_2$ ;  $q_3$  is a known function on boundary  $B_3$ ;  $\alpha$  is a constant which is greater than or equal to zero;  $\vec{n}$  is an unit normal vector.

Based on Galerkin finite element method,  $c$  and  $s$  are discretized, and substituted into E-

quation (1), then

$$\begin{aligned}
 & \left[ \int_{\Omega} \theta W_i N_j d\Omega \right] \frac{dc}{dt} \Big|_j + \left[ \int_{\Omega} \rho W_i N_j d\Omega \right] \frac{ds}{dt} \Big|_j \\
 & + \left[ \int_{\Omega} ((\nabla W_i) \cdot \vec{D} (\nabla N_j) - (\nabla W_i \cdot \nabla N_j) + W_i (\frac{\partial \theta}{\partial x} + \alpha' \theta \frac{\partial h}{\partial x} + \lambda \theta) N_j) d\Omega \right] c_j \\
 & + \left[ \int_{\Omega} W_i (\alpha' \rho \frac{\partial h}{\partial x} + \lambda \rho) N_j d\Omega \right] s_j + \int_{\Omega} -W_i M d\Omega + \int_{\Omega} W_i [(-\theta \vec{D} \cdot \nabla c + \vec{V} c) \cdot \vec{n}] dB = 0,
 \end{aligned} \tag{6}$$

$i = 1, 2, \dots, n$

where  $\Omega$  is the flow domain;  $W$  is the weighing function;  $N$  is the basis function.

Equation (6) can be written in matrix form as

$$[M] \left\{ \frac{dc}{dt} \right\} + [M'] \left\{ \frac{ds}{dt} \right\} + [S] \{c\} + [S'] \{s\} + \{D\} + \{Q\} = \{0\}, \tag{7}$$

where  $[M]$  and  $[M']$  are coefficient matrices related to the water content and the density of the medium;  $\{c\}$  and  $\{s\}$  are the unknown vectors;  $[S]$  and  $[S']$  are coefficient matrices related to the convection and dispersion;  $\{D\}$  and  $\{Q\}$  are load vectors related to the source and the boundary conditions.

Equation (7) is a first-order differential equation including  $dc/dt$  and  $ds/dt$ . Finite difference methods are used in the approximation of the time derivative. Thus Equation (7) can be written as

$$[C] \{c\} + [C'] \{s\} = \{R\} - [Q], \tag{8}$$

where the formulation of  $[C]$ ,  $[C']$ ,  $\{c\}$ ,  $\{s\}$  and  $\{R\}$  varies in form due to the finite difference method adopted in. For example when the backward difference method is adopted in the approximation of the time derivative,  $dc/dt$  and  $ds/dt$ ,  $[C]$ ,  $[C']$ ,  $\{c\}$ ,  $\{s\}$  and  $\{R\}$  can be expressed as

$$\begin{cases}
 [C] = [M]/\Delta t + [S] \\
 [C'] = [M']/\Delta t + [S'] \\
 \{c\} = \{c\}_{t+\Delta t} \\
 \{s\} = \{s\}_{t+\Delta t} \\
 \{R\} = [M] \{c\}_t / \Delta t + [M'] \{s\}_t / \Delta t - \{D\}.
 \end{cases} \tag{9}$$

Equation (8) is a coupled equation in which the number of unknown variables is greater than the number of equations. Thus the nonequilibrium sorption isotherm, that is Equation (2), must be coupled in it in order to solve these equations. Similarly, variables  $c$  and  $s$  in Equation (2) are discretized, then Equation (2) can be expressed as

$$\{S\} = \frac{\alpha K_d \omega_1 \Delta t}{\omega + \alpha \omega_1 \Delta t} \{c\} + \frac{\alpha K_d \omega_2 \Delta t}{\omega + \alpha \omega_1 \Delta t} \{c\} + \frac{\omega - \alpha \omega_2 \Delta t}{\omega + \alpha \omega_1 \Delta t} \{S\}_t, \tag{10}$$

where  $\omega$ ,  $\omega_1$  and  $\omega_2$  are the difference factors depending on the finite difference method adopted in the approximation of the time derivative. When the central difference method is used,  $\omega$  is set to 1,  $\omega_1$  and  $\omega_2$  are both set to 1/2; when the backward difference method is adopted,  $\omega$  and  $\omega_1$  are set to 1,  $\omega_2$  to 0; when the mid- difference method is applied,  $\omega$  is set to 2,  $\omega_1$  to 1, and  $\omega_2$  to 0.

Substituting Equation (10) into Equation (8), then we obtain an equation containing only the unknown vector  $\{c\}$ , that is

only the unknown vector  $\{c\}$ , that is

$$[A]\{c\} = \{y\}, \quad (11)$$

where  $[A]$  and  $\{y\}$  represent the following

$$\begin{cases} [A] = [C] + \frac{\alpha K_d \omega_1}{\omega + \alpha \omega_1 \Delta t} [C'] \\ \{y\} = \{R\} - \{Q\} - \frac{\alpha K_d \omega_2 \Delta t}{\omega + \alpha \omega_1 \Delta t} [C'] \{c\}_t - \frac{\omega - \alpha \omega_2 \Delta t}{\omega + \alpha \omega_1 \Delta t} [C'] \{S\}_t. \end{cases} \quad (12)$$

After all, the numerical solution for radionuclide migration with nonequilibrium sorption can be obtained from Equation (11) and Equation(10).

### 3 Theoretical analysis of the influence of nonequilibrium sorption on radionuclide migration

The influence of nonequilibrium sorption on radionuclide migration is represented in terms of the rate coefficient. In order to analyze the influence of nonequilibrium sorption on radionuclide migration, an ideal example is taken and theoretical analysis is made. Supposing that a soil column is 200 cm long, and at one end of the soil column water with some kind of solute was percolated through percolation and lasting one day, then pure water was allowed to infiltrate. The other end of the soil column serves as the outlet. Boundary conditions can be generalized as one end being total flux boundary and the other end being flow out (dispersion of zero) boundary. Parameters assumed in this example are:  $V=2$  cm/d,  $K_d=1$ ,  $\alpha_L=5$  cm,  $\theta=0.4$ .

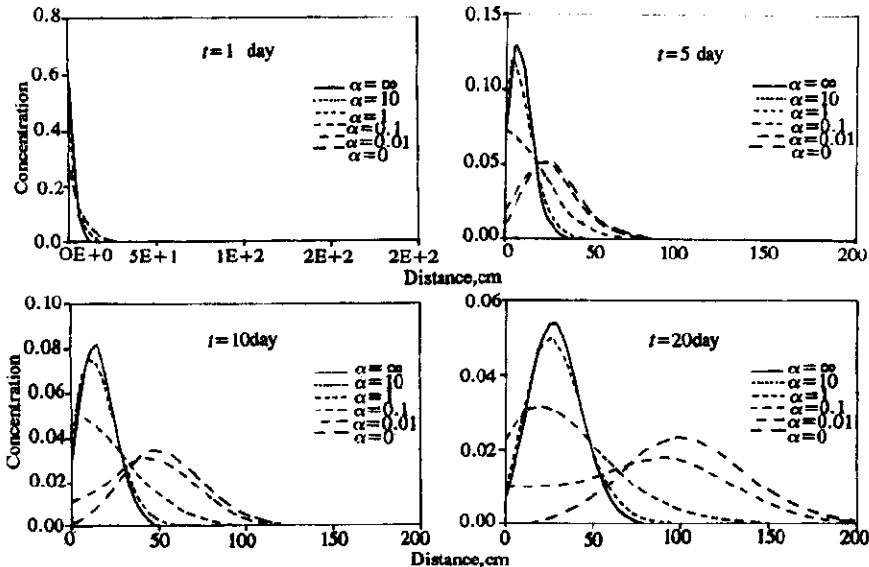


Fig. 1 Influence of nonequilibrium sorption on radionuclide migration

Numerical calculations are made theoretically corresponding to different rate coefficient. So comparison of numerical solutions for different rate coefficients can be made to each

other and to equilibrium solution, as shown in Fig. 1. Results show that when  $\alpha$  is very large ( $\infty$ ) nonequilibrium solution is equivalent to equilibrium solution; when  $\alpha \geq 1$  the nonequilibrium condition in sorption affects radionuclide migration slightly; when  $\alpha = 0.1$ , the nonequilibrium condition in sorption affects radionuclide migration dramatically, as shown in Fig. 1. After 10 days migration the peak concentration for nonequilibrium solution is only half the peak concentration for equilibrium solution. With the decrease of  $\alpha$ , radionuclide migration with nonequilibrium sorption exceeds that with equilibrium sorption more and more. When  $\alpha \geq 0.1$ , the peak concentration of radionuclide decreases with the decrease of  $\alpha$  and the concentration curve for nonequilibrium solution is less symmetric compared to the concentration curve for equilibrium solution. While  $\alpha < 0.1$ , the peak for nonequilibrium solutions precedes even more with the decrease of  $\alpha$ , but it has a tendency of increasing. When  $\alpha = 0.01$ , the migrating distance represented by peak concentration of radionuclide is almost the same as the migration distance for solute transport without sorption.

#### 4 Numerical modeling of radionuclide migration in the field test

A radionuclide migration test in the field was conducted so that the numerical model can be verified by the observed test data and compared with the results with equilibrium sorption.

The field test for radionuclide migration was conducted in a testing hall somewhere in Shanxi Province. There were two pits, pit D and pit E located in the testing hall. The area of either pit D or pit E was 200cm  $\times$  200cm. Pit D was 30cm deep and pit E was 100cm deep. At the bottom of each pit a soil layer containing the radionuclide  $^{85}\text{Sr}$  with thickness of 0.7 cm was put and above this soil layer, ordinary soil was backfilled up to the ground-level. Artificial sprinkling was made on the ground and the sprinkling intensity was 1.5 cm/d. The sprinkling began on July 21, 1989. It lasted until July 20, 1991. Samples of soil core were taken periodically to monitor the migration of the radionuclide.

According to the symmetry of the test and the analysis of the observed data of the migration test, the migration of radionuclide in the field test may be generalized as an one-dimensional problem. The migration of radionuclide  $^{85}\text{Sr}$  was simulated by using this numerical model for radionuclide migration with nonequilibrium sorption. The depth simulated for either pit D or pit E was 200 cm. The upper boundary (on the ground) was considered the total flux of zero boundary and the lower boundary was considered flow out boundary (dispersion flux of zero) approximately. The radioactive soil layer was prescribed by initial concentrations. The flow domain was taken as transient.

Simulation results for radionuclide ( $^{85}\text{Sr}$ ) migration are shown in Table 1 and Fig. 2. From Table 1 and Fig. 2 it is shown that the simulated parameters varied somehow, which represented the heterogeneity of the medium. Comparison of numerical solution for radionuclide migration with nonequilibrium sorption to numerical solution for radionuclide migration with equilibrium sorption also given in Table 1 and Fig. 2. As seen in the table and the figure, the concentration curves simulated by numerical model for radionuclide migration with

nonequilibrium sorption has the characteristics of asymmetry to some extent and they fit in with the observed data better. This shows that this numerical model simulates the migration of radionuclide better. Moreover, the simulated parameter of the rate coefficient for the migration of radionuclide  $^{85}\text{Sr}$  varies between 0.3990—0.5898 and it affects radionuclide migration obviously but not significantly, this coincides with the analysis of the influence of nonequilibrium sorption on radionuclide migration.

Table 1 Simulated parameters for radionuclide migration

Sample No.	Distribution coefficient $K_d, \text{cm}^3\text{g}^{-1}$	Dispersivity $\alpha, \text{cm}$	Rate coefficient $\alpha, \text{d}^{-1}$	Average error	Maximum error	Remark
SCD-7	49.168	0.14057	0.45028	5.401	9.406	Noneq. sorp.
			$\infty$	7.190	10.657	Eq. sorp.
SCD-8	61.194	0.22368	0.58983	28.896	54.593	Noneq. sorp.
			$\infty$	29.560	64.505	Eq. sorp.
SCE-2	28.603	0.22763	0.53248	21.493	53.791	Noneq. sorp.
			$\infty$	27.797	56.897	Eq. sorp.
SCE-7	52.060	0.34558	0.39900	20.526	41.074	Noneq. sorp.
			$\infty$	27.843	60.859	Eq. sorp.

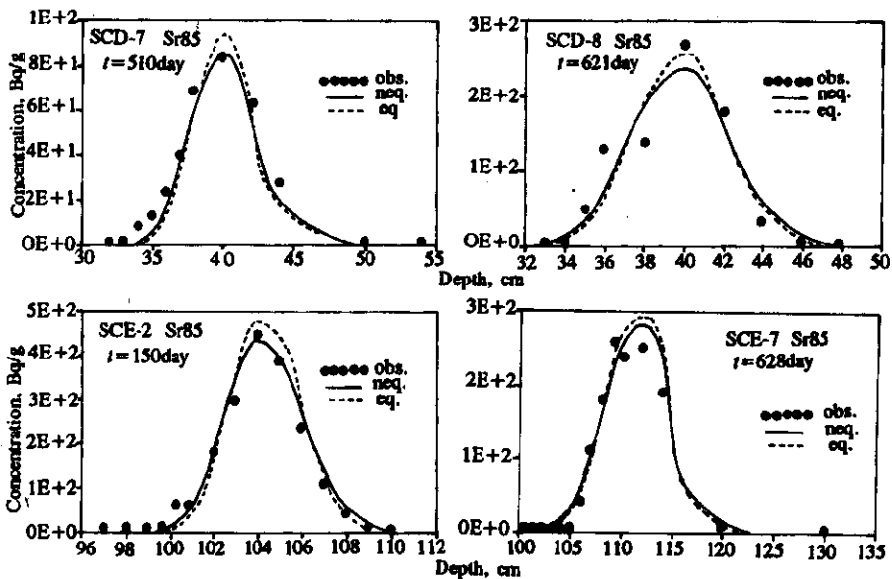


Fig. 2 Simulation of radionuclide migration in the field test

obs. , observed concentration neq. , nonequilibrium solution  
eq. , equilibrium solution

## 5 Summary

The numerical model of radionuclide migration with nonequilibrium sorption developed

in this paper is more comprehensive and more useful due to the mechanism of nonequilibrium sorption included in. Thus makes it easier to solve this model numerically that the algorithm of numeric discretizing and direct substituting is adopted in the coupling of the convective-dispersive equation and the nonequilibrium sorption isotherm. The influence of nonequilibrium sorption on radionuclide migration varies with the rate coefficient which shows how quickly nonequilibrium conditions in sorption and desorption reach equilibrium, and it can be either slight or dramatic. Results of the simulation of radionuclide migration in the field test show that this model can describe radionuclide migration better.

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