Journal of Engineering Physics and Thermophysics, Vol. 68, No. 4, 1995

RADIONUCLIDE ADSORPTION UPON CONVECTIVE AND DIFFUSIONAL MIGRATION IN DISPERSE MEDIA

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UDC 531.1:532.2:550.378

Equations and boundary and initial conditions of radionuclide transfer in disperse media are formulated taking into account diffusion, radioactive decay, adsorption, and convective transfer. Particular solutions of the system of equations under consideration are obtained in the case of linear Henry sorption isotherm and at constant diffusion coefficients and flow velocity. The problems are extended to the case of linear and inhomogeneous media for given sorption equations and transfer coefficients.

We consider the mathematical model of radionuclide migration in the presence of equilibrium and nonequalibrium isothermal adsorption and convective diffusion processes that are described by the diffusion equation

$$\frac{\partial c_i}{\partial t} + \mathrm{v}\cdot\mathrm{grad}\, c_i = \mathrm{div}\,(D_i\, \mathrm{grad}\, c_i) + I_m\,. \qquad (1)$$

The kinetics of the adsorption process is determined by the nonequilibrium sorption (desorption) equation

$$\frac{\partial a}{\partial t} = f\,(a\,,\ c_i)\,, \qquad (2)$$

In this case the mass source equals $I_m = \partial a/\partial t + I_{\mathrm{ext}}$. Thus, in order to study diffusion with due regard for adsorption one should solve simultaneously the diffusion equation

$$\frac{\partial c_i}{\partial t} + \mathrm{v}\cdot\mathrm{grad}\, c_i = \mathrm{div}\,(D_i\, \mathrm{grad}\, c_i) - \frac{\partial a}{\partial t} + I_{\mathrm{ext}} \qquad (3)$$

and the Eq. (2).

It is known from experiments that sorption and desorption curves do not coincide with each other, and the so-called hysteresis takes place [1]. The phenomenon of hysteresis in sorption and desorption processes leads to both processes proceeeding under nonequilibrium conditions. In the equilibrium case the right-hand side of (2) is determined by the sorption isotherm

$$\psi\,(a\,,\ c) = 0 \quad \text{or} \quad a = f_1\,(c)\,. \qquad (4)$$

Expanding, in the nonequilibrium case, the right-hand side of the equation into a Taylor series in a and c variables, we obtain

$$\frac{\partial a}{\partial t} = \sum_{i,n=0}^{\infty} B_{in}\, \overset{i}{a}\, \overset{n}{c} = B_{00} + B_{10}\, \overset{1}{a}\, \overset{0}{c} + B_{01}\, \overset{0}{a}\, \overset{1}{c} + B_{11}\, \overset{1}{a}\, \overset{1}{c} + \dots \qquad (5)$$

Retaining only linear terms in this expansion, we write the kinetic equation in the following form:

Institute for Energy Problems of the Academy of Sciences of Belarus, Academic Scientific Complex "A. V. Luikov Institute of Heat Mass Transfer, Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 68, No. 4, July-August 1995, pp. 660-677. Original article submitted February 17, 1994.

1062-0125/95/6804-0540$12.50 ©1996 Plenum Publishing Corporation

$$\frac{\partial a}{\partial t} = B_{00} + B_{10}\, a + B_{01}\, c . \tag{6}$$

The coefficients of the expansion are usually determined from approximation of experimental data. For instance, one can take the Henry isotherm

$$a = \gamma c . \tag{7}$$

as an approximating function. Therefore, relating the right-hand side of the kinetic equation with the Henry equation, we obtain

$$\frac{\partial a}{\partial t} = \beta c - \gamma a . \tag{8}$$

This very simple linear kinetic equation describes monomolecular interactions. To take into account the bimolecular interaction, one should retain quadratic terms in the expansion. In the case of polymolecular interactions, terms of higher orders should be retained in the Taylor expansion. However, for simplicity we restrict our consideration to the case of monomolecular interactions. The unknown variables a and c enter into the equation. By setting $\beta = 0$ in this equation we obtain the relaxational equation

$$\frac{\partial a}{\partial t} = -\gamma a . \tag{9}$$

Integration of this equation with the initial condition

$$t = 0 : \quad a = a_0$$

leads to

$$a = a_0 \exp(-\gamma t) . \tag{10}$$

In addition to the Henry isotherm, other dependences that approximate the equilibrium adsorption isotherm were established for various sorbents. These approximations are as follows:

the Langmuir isotherm

$$a = \frac{k_1 c}{1 + k_2 c} , \tag{11}$$

at $k_2 \to 0$ the Langmuir isotherm degenerates into the Henry isotherm;

the Haughton isotherm

$$a = k_0 + k_1 c + k_2 c^2 ; \tag{12}$$

the Brunauer, Emmet, and Teller isotherm

$$a = \frac{k_1 c}{(1 - k_2 c)(1 + k_3 c)} ; \tag{13}$$

the Freundlich isotherm

$$a = k c^n , \quad n < 1 ; \tag{14}$$

the Kisarov isotherm

$$a = \frac{k_1 c^n}{1 + k_2 c^n} . \tag{15}$$

In addition, the other forms of the kinetic equation are known:

the Hister-Wermulen equation

$$\frac{\partial a}{\partial t} = \gamma \left[(a_0 - a)\, c - \frac{1}{k_i} (c_0 - c)\, a \right] ; \tag{16}$$

the Helfferich equation

$$\frac{\partial a}{\partial t} = \gamma\, (a_0 - a) ; \tag{17}$$

the Verigin equation

$$\frac{\partial a}{\partial t} = \gamma c \tag{18}$$

etc. [1-5].

This variety of approximations of kinetic equations results from the complexity of adsorbent interaction with the sorbing substances. In what follows, we will mainly use the linear Henry isotherm (7). Sorption dynamics in the absence of diffusion and external sources was studied based on the transfer equations

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} + v \frac{\partial c}{\partial x} = 0 \tag{19}$$

and

$$\frac{\partial a}{\partial t} = \gamma\, (c - \alpha a) , \quad \alpha = 1/k_1 . \tag{20}$$

The solution of this system of equations can be obtained analytically by eliminating one of the variables a and c from the system. This problem was solved by Tikhonov et al. [6] subject to the following conditions:

$$a\,(x\,,\, 0) = 0 ; \quad c\,(x\,,\, 0) = 0 ; \quad c\,(0\,,\, t) = c_0 . \tag{21}$$

For a series of nonlinear sorption kinetic equations the system was solved numerically in a number of papers within the context of problems of ionic exchange [7], gaseous chromatography [3, 8], mixture separation [8], water recycling [9], etc. The same problems play an important role in the purification of media from radionuclides, extraction of radionuclide from food, etc.

If $D \neq 0$, one should solve the kinetic equation

$$\frac{\partial a}{\partial t} = \beta c - \gamma a \tag{22}$$

with the convective diffusion equation

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} + v \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - \lambda c + I\,(x\,,\, t) . \tag{23}$$

For the solution of the system, one should set the initial conditions

$$t = 0 : \; c = \varphi_1\,(x) , \quad a = \varphi_2\,(x) , \quad x > 0 , \tag{24}$$

along with the boundary conditions, which can be chosen in one of the following forms:

1) boundary conditions of the first kind

$$c\,|_{\mathrm{b}} = \psi_1\,(t) ; \tag{25}$$

2) boundary conditions of the second kind

$$D \frac{\partial c}{\partial x}\bigg|_{\mathrm{b}} = \psi_2\,(t) ; \tag{26}$$

3) boundary conditions of the third kind

$$\left| \alpha c + \mu D \frac{\partial c}{\partial x} \right|_{\mathrm{b}} = \psi_3 (t) ; \tag{27}$$

4) boundary conditions with the time derivative

$$\left| \alpha c + \mu D \frac{\partial c}{\partial x} + \nu \frac{\partial c}{\partial t} \right|_{\mathrm{b}} = \psi_4 (t) . \tag{28}$$

The last of the enumerated boundary conditions includes the linear combination of the sought function with first derivatives over the coordinate and time, along with all the classical-type boundary conditions of the first, second, and third kind. By setting $\mu = 0$ and $\nu = 0$ we obtain the boundary conditions of the first kind; the boundary conditions of the second and third kind are obtained by setting correspondingly $\alpha = 0$ and $\nu = 0$. Therefore, we consider the solution of the system of equations under the boundary condition (28), as well as under different generalized boundary conditions. We consider two types of generalized boundary conditions proposed presently for investigation of radionuclide transfer processes.

Radionuclide propagation in the turbulent atmosphere is described by the turbulent diffusion equation [10]

$$\frac{\partial c}{\partial t} + (\mathrm{v} \nabla c) - \omega \frac{\partial c}{\partial z} = \frac{\partial}{\partial z} \left(u_z \frac{\partial c}{\partial z} \right) + \nabla (k \nabla c) . \tag{29}$$

In the presence of deposition on the surface and secondary uplift we write the boundary condition at the surface at $z = 0$ in the form of the mass balance [10]

$$\left| u_z \frac{\partial c}{\partial z} + \omega c \right|_{z=0} = \frac{\partial c_s}{\partial t} \tag{30}$$

and of the variation of the surface concentration c_s resulting from the impurity deposition from the atmosphere $v_g c \,|_{z=0}$ and the wind pickup $\alpha_s c_s$:

$$\frac{\partial c_s}{\partial t} = v_g c - \alpha_s c_s . \tag{31}$$

In the absence of the pickup $\alpha_s = 0$ the boundary conditions transform into those proposed by A. S. Monin. The following condition is imposed at the infinity:

$$\text{when} \quad z \to \infty \qquad c_s \to 0 . \tag{32}$$

The initial conditions are as follows:

$$\begin{aligned} c (x , y , z , t = 0) &= c_0 (x , y , z) , \\ c_s (x , y , z , t = 0) &= c_{s_0} (x , y , z) . \end{aligned} \tag{33}$$

This mathematical model for radionuclide transfer in the turbulent atmosphere is considered in [11]. Different generalizations of the boundary conditions for radionuclide transfer are also possible, e.g., instead of the condition (30) we can write

$$\left| u_z \frac{\partial c}{\partial z} + \omega c \right|_{z=0} = \beta_m c_s , \tag{34}$$

$$\frac{dc_s}{dt} + \gamma \int D \frac{\partial c_s}{\partial x} dx + Q = 0 . \tag{35}$$

The latter boundary condition has the meaning of the variation in the total concentration at the surface due to diffusional processes and surface sources. If the total accretion does not take place, the condition can be expressed as follows:

$$\frac{\partial c(x)}{\partial t} + \gamma D \frac{\partial c(x)}{\partial x} = 0 . \tag{36}$$

As Eq. (28), this equation contains first derivatives with respect to time and coordinate. The equation can be rearranged to yield the different kinds of boundary conditions. For instance, by excluding the first time derivative with the use of the diffusion equation we obtain the boundary conditions in the form of

$$\alpha \frac{\partial^2 c}{\partial x^2} + \beta \frac{\partial c}{\partial x} + \delta c = 0 . \tag{37}$$

The consideration of these generalized boundary conditions dates back to the original works of A. N. Tikhonov, A. A. Samarskii, et al. It should be noted that A. N. Tikhonov proposed boundary conditions in which the order of the partial derivatives can be higher than the order of the differential equation itself [6, 12]. Upon separating variables, the separation constant will enter not only into the equation, but into the generalized boundary conditions as well. Such problems today are of both theoretical and practical interest [13].

In the case of equilibrium sorption and desorption processes we consider the linear Henry isotherm (7) in view of which the diffusion equation (1) in a porous medium with porosity m takes the form

$$m \left(\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} \right) + v \frac{\partial c}{\partial x} = D \frac{\partial}{\partial x} \frac{\partial c}{\partial x} - \lambda c - \gamma a + I_m \tag{38}$$

and is transformed to the following equation:

$$a(x) \frac{\partial c}{\partial t} + v(x) \frac{\partial c}{\partial x} = \frac{1}{x^n} \frac{\partial}{\partial x} x^n D(x) \frac{\partial c}{\partial x} - d(x)\, c + I_m , \tag{39}$$

where $n = 0$ for a plate, $n = 1$ for a cylinder, and $n = 2$ for a sphere, the coefficients $a(x)$, $v(x)$, $D(x)$, and $d(x)$ in the general case are variables determined by functions of the coordinate x, the source I_m is a function of the coordinate x and time t and the initial condition is chosen in the form (24).

We will solve the equation under the classical boundary conditions of the form (25)-(27) using the method of bounded integral transforms over the eigenfunctions ψ of the homogeneous equation

$$\mu^2 a(x)\, \psi + v(x) \frac{d\psi}{dx} = \frac{1}{x^n} \frac{d}{dx} D(x) \frac{d\psi}{dx} - d(x)\, \psi \tag{40}$$

under the homogeneous (1)-(3) and nonclassical (4) conditions of the form

$$\begin{gathered} 1)\ \psi \big|_{\mathrm{b}} = 0 ; \quad 2)\ D \frac{d\psi}{dx} \Big|_{\mathrm{b}} = 0 ; \quad 3)\ \Big| \alpha \psi + D \frac{d\psi}{dx} \Big|_{\mathrm{b}} = 0 ; \\ 4)\ \Big| (\mu^2 v + \alpha)\, \psi + D \frac{d\psi}{dx} \Big|_{\mathrm{b}} = 0 . \end{gathered} \tag{41}$$

First we consider the solution of (39) with constant coefficients $\alpha = 1$; $\nu = \nu_0$, $D = D_0$, and $\alpha = \lambda$, and with the boundary conditions (41).

As an example, we present the solution of the first boundary-value problem for (39) with the conditions (24), (25) for volume and surface radionuclide sources: $I = I_0 \exp(-kt)$, $\psi_1 = \psi_{10} \exp(-mt)$, $\psi_2 = \psi_{20} \exp(-mt)$, $\psi_2 = \psi_{20} \exp(-nt)$. The eigenfunctions of Eq. (40) are the solutions of the equation

$$\frac{d^2 X}{dx^2} - \frac{v}{D} \frac{dX}{dx} + \mu^2 X = 0 , \tag{42}$$

and take the form

$$X(x) = \exp\left(\frac{v_0 x}{2 D_0} \right) \left[A_1 \cos px + A_2 \sin px \right] , \tag{43}$$

where $p^2 = \mu^2 - v_0^2/4D_0^2$; A_1 and A_2 are the integration constants. In view of the boundary conditions of the first boundary value problem, the eigenfunctions are as follows:

$$X_n(x) = \exp\left(\frac{v_0 x}{2D_0}\right)\sin\frac{\pi n}{l}x\,, \quad n = 1\,,\ 2\,,\ \dots \tag{44}$$

and their spectrum and norm are

$$\mu^2 = \frac{v^2}{4D^2} + \left(\frac{\pi n}{l}\right)^2, \quad n = 1\,,\ 2\,,\ \dots\,; \quad \| X_n \|^2 = l/2\,. \tag{45}$$

The solution of the nonhomogeneous boundary-value problem in this case is constructed using the bounded integral transform

$$\bar{c} = \int_0^l c\exp\left(-\frac{vx}{2D}\right)\sin\frac{\pi n}{l}x\,dx \tag{46}$$

in the form of an expansion over the eigenfunctions of the problem

$$c = \sum_{n=1}^{\infty}\frac{X_n(\mu_n\,,\ x)}{\| X_n \|^2}\,\bar{c}(\mu_n\,,\ t) = \frac{2}{l}\sum_{n=1}^{\infty}\bar{c}\exp\left(-\frac{vx}{2D}\right)\sin\frac{n\pi}{l}x\,, \tag{47}$$

and $\bar{c}$ is determined from the solution of the first-order nonhomogeneous equation that involves arbitrary volume and surface radionuclide sources:

$$\frac{d\bar{c}}{dt} + \left(\lambda + D\left(\frac{\pi n}{l}\right)^2 + \frac{v^2}{4D}\right)\bar{c} = \bar{I} + \frac{D\pi n}{l}\left[\psi_0(t) - (-1)^n\exp\left(-\frac{vl}{2D}\right)\psi_l(t)\right], \tag{48}$$

$$t = 0:\ \bar{c} = \bar{c}_0 = \int_0^l \varphi(x)\exp\left(-\frac{vx}{2D}\right)\sin\frac{\pi n}{l}x\,dx\,,$$

integration of which in the general case yields

$$\bar{c} = \exp\left[-\left(\lambda + D\left(\frac{\pi n}{l}\right)^2 + \frac{v^2}{4D}\right)t\right]\left\{\int_0^t\left(\bar{I} + D\frac{\pi n}{l}\left[\psi_0(t') - (-1)^n\exp\left(-\frac{vl}{2D}\right)\psi_l(t')\right]\times\right.\right.$$

$$\left.\left.\times\exp\left[\left(\lambda + D\left(\frac{\pi n}{l}\right)^2 + \frac{v^2}{4D}\right)t'\right]\right)dt' + \bar{c}_0\right\}. \tag{49}$$

The rest seven cases of combinations of the boundary conditions of the first, second, and third kind for arbitrary initial conditions and given volume (*I*) and surface (ψ_i) radionuclide sources are considered and solved in [11]. The paper [11] is devoted to the study of convective radionuclide migration upon homogeneous linear sorption (desorption) in homogeneous and nonhomogeneous porous layers.

Let us consider the case of radionuclide diffusion and equilibrium sorption in bodies with simple geometry. These problems are solved by means of both the operational calculus and using the bounded integral transforms. Here we present as an example the solution of just one problem by means of the operational calculus combined with the methods of the residue theory at $a = 1$, $v = v_0$, $D = D_0$, $d = \lambda$, $I_m = 0$, and $\varphi = 0$ within the layer with the boundary conditions $x = 0$: $c = 0$; $x = l$: $c = c_l$.

The Laplace image of the Eq. (39) is as follows:

$$D_0\frac{d^2\bar{c}}{dx^2} - (p + \lambda)\,\bar{c} - v\frac{d\bar{c}}{dx} = 0\,. \tag{50}$$

The image solution of (50) is

$$\bar{c} = \exp\left(\frac{v(x-l)}{2D}\right) \frac{c_l \,\mathrm{sh}\,[x(v^2 + 4D(p+\lambda))^{1/2}/2D]}{p\,\mathrm{sh}\,[l(v^2 + 4D(p+\lambda))^{1/2}/2D]}, \tag{51}$$

with poles

$$p = 0 \quad \text{and} \quad p_i = -\lambda - \frac{v^2}{4D} - D\frac{n^2\pi^2}{l^2}. \tag{52}$$

Then from the residue theorem we obtain

$$c = c_l \frac{\mathrm{sh}\,[x(v^2 + 4D\lambda)^{1/2}/2D]}{\mathrm{sh}\,[l(v^2 + 4D\lambda)^{1/2}/2D]} \exp\left(\frac{v(x-l)}{2D}\right) +$$

$$+ \frac{2c_l\pi}{l^2} \exp\left(\frac{v(x-l)}{2D}\right) \sum_{n=1}^{\infty} \frac{(-1)^n n \sin(n\pi x/l)}{\lambda/D + v^2/4D^2 + n^2\pi^2/l^2} \exp\left\{-\left[\lambda \frac{v^2}{4D} + D\frac{\pi^2 n^2}{l^2}\right] t\right\}. \tag{53}$$

Let us consider the particular cases of radionuclide diffusion in the presence of volume and surface sources. In terms of these sources the diffusion equation is as follows:

$$\frac{\partial c}{\partial t} + v(x)\frac{\partial c}{\partial x} = \frac{1}{x^m}\frac{\partial}{\partial x} x^m D(x) \frac{\partial c}{\partial x} - \lambda c + I(x, t), \tag{54}$$

where the term $\partial c/\partial t$ on the left-hand side describes the local variations in concentration, and the term $v(x)(\partial c/\partial x)$ describes the convective concentration transfer with rate $v(x)$. The first term on the right-hand side describes the radionuclide diffusion in volume with the variable diffusion coefficient $D(x)$, and the second term accounts for the radioactive decay proportional to the half-life λ and the concentration c at each point of space at any time instant t; $I(x, t)$ is the volume power of external radionuclide sources.

By setting $D(x) = 0$, $v(x) = 0$, and $I(x, t) = 0$ in this equation, we obtain the following equation:

$$\frac{\partial c}{\partial t} = -\lambda c, \tag{55}$$

integration of which by separation of variables yields

$$c = c_0 \exp(-\lambda t). \tag{56}$$

This is the common radioactive decay law.

The power of radioactive isotope sources $I(x, t)$ is usually given using the expressions corresponding to the given source. If the usual source is space-uniform and possesses intensity I_0 and decays with time according to the radioactive decay law, then

$$I(x, t) = I_0 \exp(-\lambda_i t). \tag{57}$$

In the case of a point source which is placed at the point x_0 we obtain

$$I(x, t) = I_0\,\delta(x - x_0)\exp(-\lambda_i t). \tag{58}$$

We choose the initial conditions in the following form:

$$t = 0: \ c(x) = \varphi(x), \tag{59}$$

and the boundary conditions are chosen in the form of the boundary conditions of the third kind

$$\left| D(x)\frac{\partial c}{\partial x} + \beta_m(c_s - c)\right|_{\mathrm{b}} = \Phi(t). \tag{60}$$

We write the following relationship:

$$\Phi(t) = \Phi_0 \exp(-\lambda_i t), \tag{61}$$

to express the surface radionuclide density. The exponential functions can be used for $c_s(t)$:

$$c_s = c_{s_0} \exp(-\lambda_i t). \tag{62}$$

In the presence of reactions, special equations that describe the kinetics of these phenomena are used for the surface and volume sources. The $\varphi(x)$ function entering into the initial condition is usually given either as a constant, e.g., $c = c_0$, in the case of the uniform distribution of the fallen-out radionuclides, or using certain functions that approximate the initial concentration distribution over the coordinate; for instance, in the case of migration into the soil or other capillary bodies the exponential function $c(x) = c_0 \exp(-\lambda x)$, or other such functions, is frequently used.

The system of linear equations of nonequilibrium sorption can be solved by various methods, for instance, by the method of Laplace transform, by the method of integral transforms, or by numerical or approximate methods. The method of separation of variables is inapplicable to the system, as we will show. We take the kinetic and diffusion equations (22) and (23), and, by excluding a we obtain the third-order equation

$$\frac{\partial^2 c}{\partial t^2} + \beta \frac{\partial c}{\partial t} + \gamma \left(\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} - D \frac{\partial^2 c}{\partial x^2} + \lambda c - I(x, t) \right) + v \frac{\partial^2 c}{\partial x \partial t} = D \frac{\partial^3 c}{\partial x^2 \partial t} - \lambda \frac{\partial c}{\partial t} + \frac{\partial I}{\partial t}. \tag{63}$$

This equation does not permit separation of variables even at $I(x, t) = 0$.

We will seek the solution of the system of equations (22)-(23) under the initial conditions (24) and the boundary condition (28). We introduce the Laplace image of the function:

$$\bar{a} = \int_0^\infty a \exp(-pt)\, dt; \quad \bar{c} = \int_0^\infty c \exp(-pt)\, dt;$$
$$\bar{I} = \int_0^\infty I(x, t) \exp(-pt)\, dt; \quad \bar{\psi} = \int_0^\infty \psi(t) \exp(-pt)\, dt. \tag{64}$$

Applying the Laplace transform to the equation and the boundary conditions with account for the initial conditions, we obtain the system of equations

$$p\bar{a} - \varphi_2(x) = \beta\bar{c} - \gamma\bar{a},$$
$$p\bar{c} - \varphi_1(x) + p\bar{a} - \varphi_2(x) + v \frac{\partial \bar{c}}{\partial x} = D \frac{\partial^2 \bar{c}}{\partial x^2} - \lambda\bar{c} + \bar{I} \tag{65}$$

and the boundary conditions

$$\alpha c + \mu D \frac{\partial \bar{c}}{\partial x} + v p \bar{c} = \bar{\psi}.$$

Then we obtain

$$D \frac{d^2 \bar{c}}{dx^2} - v \frac{d \bar{c}}{dx} - \left(p + \frac{p\beta}{p + \gamma} + \lambda \right) \bar{c} = \varphi_1(x) - \bar{I}(x, p) + \frac{p\varphi_2(x)}{p + \gamma}. \tag{66}$$

Let us consider the homogeneous equation

$$D \frac{d^2 \bar{c}}{dx^2} - v \frac{d \bar{c}}{dx} - \left(\frac{p^2 + (\gamma + \beta + \lambda) p + \gamma\lambda}{p + \gamma} + \lambda \right) \bar{c} = 0, \tag{67}$$

the solution of which we write in the form

$$\bar{c}_{\text{hom}} = \exp\left(\frac{v}{2D}x\right)\left(c_1 \operatorname{ch}\left(\sqrt{\left(\frac{+\,4\,(p^2 + (\gamma + \beta + \lambda)\,p + \gamma\lambda)}{D\,(p + \gamma)} + \frac{v^2}{D^2}\right)}\,\frac{x}{2}\right) + \right.$$
$$\left. + \, c_2 \operatorname{sh}\left(\sqrt{\left(\frac{+\,4\,(p^2 + (\gamma + \beta + \lambda)\,p + \gamma\lambda)}{D\,(p + \gamma)} + \frac{v^2}{D^2}\right)}\,\frac{x}{2}\right)\right). \tag{68}$$

We write the particular solution of the nonhomogeneous equation (66):

$$\bar{c}_r = \frac{2}{\sqrt{\left(\frac{+\,4\,(p^2 + (\gamma + \beta + \lambda)\,p + \gamma\lambda)}{D\,(p + \gamma)} + \frac{v^2}{D^2}\right)}} \int f(t) \exp\left(-\frac{v\,(t - x)}{2D}\right) \times$$
$$\times \operatorname{sh}\left(\sqrt{\left(\frac{+\,4\,(p^2 + (\beta + \gamma + \lambda)\,p + \gamma\lambda)}{D\,(p + \gamma)} + \frac{v^2}{D^2}\right)}\,\frac{x - t}{2}\right) dt. \tag{69}$$

By using Eqs. (68) and (69), the relationship $\bar{c} = \bar{c}_r + \bar{c}_{\text{hom}}$, and the boundary condition, we find the constants c_1 and c_2:

$$x = 0: \; \alpha\bar{c} + \mu D \frac{\partial \bar{c}}{\partial x} + \nu p\bar{c} = \bar{\psi}_1\,,$$
$$x = l: \; \alpha\bar{c} - \mu D \frac{\partial \bar{c}}{\partial x} + \nu p\bar{c} = \bar{\psi}_2\,. \tag{70}$$

Let us consider the particular example when

$$I = 0\,, \quad v = 0\,, \quad \lambda = 0\,,$$
$$t = 0: \; a = 0\,, \quad c = 0\,, \tag{71}$$
$$\nu = b\,, \quad \alpha = 0\,, \quad \mu = 1\,.$$

In this case the kinetic and diffusion equations take the form

$$\frac{\partial a}{\partial t} = \beta c - \gamma a\,,$$
$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} = D \frac{\partial^2 c}{\partial x^2}\,,$$
$$t = 0: \; a = 0\,, \quad c = 0\,, \tag{72}$$
$$x = l: \; b\frac{\partial c}{\partial t} = -\,D\frac{\partial c}{\partial x}\,; \quad x = -\,l: \; b\frac{\partial c}{\partial t} = D\frac{\partial c}{\partial x}\,,$$

and we find the equations for the images:

$$p\bar{c} = -\,p\bar{a} + D\frac{d^2\bar{c}}{dx^2}\,,$$
$$p\bar{a} = \beta\bar{c} - \gamma\bar{a} \tag{73}$$

under the condition

$$-\,bc_0 - pb\bar{c} = -\,D\frac{d\bar{c}}{dx}\,, \quad x = l\,;$$
$$-\,bc_0 + pb\bar{c} = D\frac{d\bar{c}}{dx}\,, \quad x = -\,l\,. \tag{74}$$

By excluding $\bar{a}$, we obtain the following equation for $\bar{c}$:

$$\frac{d^2\bar{c}}{dx^2} + \mu^2\bar{c} = 0 \,, \quad \mu^2 = -\frac{p}{D}\,\frac{p+\gamma+\beta}{p+\gamma} \,. \tag{75}$$

The solution of this equation is as follows:

$$\bar{c} = A_1 \cos \mu x + B_1 \sin \mu x \,. \tag{76}$$

Substituting the boundary condition, we obtain

$$\bar{c} = A_1 \cos(\mu x) \,, \tag{77}$$

where

$$A_1 = \frac{bc_0}{pb\cos(\mu l) - \mu D \sin(\mu l)} \,.$$

From this image solution we find the solution of the original in the form [14]

$$c = \frac{bc_0}{b + \left(\frac{\beta}{\gamma} + 1\right) l} \sum_{n=1}^{\infty} \frac{c_0 \exp(p_n t)}{1 + \left\{1 + \frac{\beta\gamma}{(p_n+\gamma)^2}\right\} \left\{\frac{b}{2b} + \frac{p_n}{2D\mu_n^2} + \frac{\mu_n^2 bl}{2D^2\mu_n^2}\right\}} \, \frac{\cos(\mu_n x)}{\cos(\mu_n l)} \,, \tag{78}$$

where μ_n, p_n are the roots of the equations

$$\frac{bp_n}{D} = \mu_n \tan(\mu_n l) \,; \quad \mu_n^2 = -\frac{p_n}{D}\,\frac{p_n+\beta+\gamma}{p_n+\gamma} \,. \tag{79}$$

The roots p_n are determined graphically:

$$x = \mu^2 l^2 \,; \quad y = \frac{pl^2}{D} \,; \quad \xi = \frac{l^2(\beta+\gamma)}{D} \,; \quad \eta = \frac{l^2\gamma}{D} \,,$$

then

$$\frac{by}{l} = \sqrt{x}\tan\sqrt{x} \,, \quad x = \frac{-y(y+\xi)}{y+\eta} \,. \tag{80}$$

The coefficients $\sigma(x)$, $a(x)$, and $b(x)$ that enter into the diffusion equation (54) are considered to be given known quantities in the case of the phenomenological description of the mass transfer processes. They can be determined either experimentally in special laboratories, or theoretically based on more general approaches to the description of the matter, for example, on the basis of the kinetic or statistical theory and using the solution of the so-called inverse problems from the additional experimental information on heat- and mass transfer processes. For instance, the diffusion coefficient D can in the general case be presented as a complex-structured function of independent variables, coordinates, and time, and of the initially unknown thermodynamic functions of state, namely, concentration c, temperature T, pressure p, etc. The value of the diffusion coefficient depends on the intrinsic structure of the bodies and media under consideration. In the solid and gaseous states it can take different values for different substances, and is usually available from handbooks. In an analogous manner, the other coefficients can vary in both time and space, and they can also depend on certain quantities and parameters.

In order to determine the velocity v one should solve the diffusion equation simultaneously with the equations of motion, the energy equation, and other equations describing the heat- and mass transfer processes. If we restrict our attention to consideration of the sole diffusion equation and the Fick's law, then the law of velocity variations should be given, generally, as a function of coordinates and time. The same notion holds also for all the remaining functions entering into the diffusion equation (54) and the initial (24) and boundary (25)-(28) conditions. If the coefficients entering into the equation are constant within the entire region under consideration, then such a medium is referred to as homogeneous one. If the coefficients are varied as piecewise smooth functions, then the medium is nonhomogeneous. In the case where these coefficients depend also on the unknown sought functions, then such media are nonlinear. The nonlinear problems of diffusion and filtration theory are most complicated and are still poorly investigated, and various exact, approximate, asymptotic, and numerical methods are used presently in their investigations.

The above-considered operational method of separation of variables is widely used in studies of diffusion and filtration processes in homogeneous and nonhomogeneous media subject to certain constraints. In order to apply the Fourier method the equation under consideration and the boundary conditions should permit separation of variables. When the variables in a given problem are separated, the problem of investigation of the partial differential equations under the given initial and boundary conditions is reduced to the boundary-value problems for the ordinary differential equations, and consists in the determination of eigenvalues and eigenfunctions with the use of which the solution is constructed either as a series in eigenfunctions in the case of a discrete spectrum, or in the form of integrals over the eigenfunctions in the case of a continuous spectrum.

In certain nonhomogeneous media the material parameters are varied in space or in time in such a manner that the separation of variables in such equations leads to the well studied special functions. For example, if in Eq. (54) $D(x) = 1$, $\nu(x) = 1/x$, and $\lambda(x) = 0$, then this equation is the Bessel equation whose solution is well studied. Therefore, the main boundary-value problems are easily solved for such media. A series of approximations of the functional dependence of the parameters of a nonhomogeneous medium leads to other well studied types of equations. Inasmuch as all the parameters of nonhomogeneous media can be determined experimentally only with certain errors, the method of approximation of the parameters of nonhomogeneous media can be successfully used for the solution of a particular problem. In this case one uses approximating functions that can reduce the original equation with variable coefficients to an equation with structure close to that of the initial equation, but whose solutions can be obtained much more easily or are already known. Of all the possible equations, those whose solutions are most adequate to the given problem are chosen. This method is widely used for the approximate solution of linear and nonlinear ordinary and partial differential equations.

Usually, power, exponential, polynomial, and other functions are widely used for the approximation of parameters of nonhomogeneous media. However, even in the case of an arbitrary analytical dependence of the material parameter on coordinates or time, it can always be expanded into a Taylor series in powers of the argument, since any analytical function is Taylor-expandable:

$$f(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_n x^n + \ldots = \sum_{n=0}^{\infty} a_n x^n$$

or, in the multidimensional case,

$$f(x, y, z) = \sum_{i,j,k=0}^{\infty} a_{ijk} x^i y^j z^k .$$

Usually, already several first terms of the series approximate well the properties of the experimentally determined parameter of the nonhomogeneous medium, and a polynomial can be used instead of the series.

Differential equations for nonhomogeneous media with polynomial approximations include variable coefficients in polynomial form; certain of the equations are already studied, and others lead to new special functions.

In the case of the polynomial approximation, Eq. (67) takes the form

$$p_0(x) \frac{d^2 X}{dx^2} + p_1(x) \frac{dX}{dx} + p_2(x) X = 0 , \tag{81}$$

where the coefficients $p_0(x)$, $p_1(x)$, and $p_2(x)$ are polynomials of the form

$$p_0(x) = a_0 + a_1 x + a_2 x^2 + \ldots + a_k x^k ,$$

$$p_1(x) = b_0 + b_1 x + b_2 x^2 + \ldots + b_n x^n , \tag{82}$$

$$p_2(x) = c_0 + c_1 x + c_2 x^2 + \dots + c_m x^m .$$

These equations arise when a nonhomogeneous media with polynomial approximations of parameters are studied, as well as when separating variables in multiple orthogonal coordinate systems, when the polynomial $p_2(x)$ depends on a separation constant that can be related to c_0.

In studies of linear equations of the general form with variable coefficients, the so-called singular points of the differential equation play an important role; they are such values x_0 of the argument of the differential equation of the form (81) in which the functions $p_0(x)$, $p_1(x)$, and $p_2(x)$ possess characteristic singularities. If these functions take finite values in the point $x \to x_0$, then the point x_0 is called usual; otherwise, it is singular. The point $x = x_0$ in which $p_1(x)/p_0(x)$ and $p_2(x)/p_0(x)$ are divergent but $(x - x_0)p_1/p_0$ and $(x - x_0)^2 p_2/p_0$ remain finite, is called a regular singular point. The point $x = x_0$ is called an irregular point or a significant singularity if $p_1(x)/p_0(x)$ and $p_2(x)/p_0(x)$ diverge faster than $1/(x - x_0)$ and $1/(x - x_0)^2$ at $x \to x_0$, respectively; in this case x_0 is assumed to take finite values.

If $x \to x_0 \to \infty$, then using the substitution

$$x = 1/z \tag{83}$$

Eq. (81) can be put in the following form:

$$p_0\left(\frac{1}{z}\right) z^4 \frac{d^2X}{dz^2} + \left[2z^3 - z^2 p_1\left(\frac{1}{z}\right)\right] \frac{dX}{dz} + p_2\left(\frac{1}{z}\right) X = 0 . \tag{84}$$

If all the coefficients $[2z^3 - z^2 p(1/z)]/p_0(1/z)z^4$ and $p_2(1/z)/p_0(1/z)z^4$ are finite at the point $z = 0$, then the point $z = 0$ is called an ordinary point. If the coefficients diverge, but not faster than $1/z$ and $1/z^2$, respectively, then the point $(z = 0,\ x \to \infty)$ is called a regular point, otherwise it is an irregular singular point.

For equations with regular singular points Fuchs proved an important theorem and gave methods of solution; therefore, these equations were named after him. To ensure that the linear differential equation

$$y'' + p_1(x)\, y' + p_2(x)\, y = 0 \tag{85}$$

possesses a fundamental system of solutions $y_1(x)$ and $y_2(x)$ that can be presented in the vicinity of $x = x_0$ in the form

$$y_1(x) = (x - x_0)^{r_1} \varphi_1(x)\,; \quad y_2(x) = (x - x_0)^{r_2} \varphi_2(x) \tag{86}$$

or

$$y_2 = y_1(x) \left[A \ln (x - x_0) + \psi(x)\right],$$

where $\varphi_1(x)$, $\varphi_2(x)$, and $\psi(x)$ are single-valued analytical functions that possess not more than one pole at the point x_0, it is necessary and sufficient that $p_1(x)$ and $p_2(x)$ possess poles of not more than first and second orders, respectively, i.e.,

$$p_1(x) = \frac{A(x)}{x}\,; \quad p_2(x) = \frac{B(x)}{x}\,, \tag{87}$$

where

$$A(x) = \sum_{n=0}^{k} a_n x^n\,; \quad B(x) = \sum_{n=0}^{\infty} b_n x^n . \tag{88}$$

Then the equation takes the following form:

$$x^2 y'' + xA(x)\, y' + B(x)\, y = 0 . \tag{89}$$

Let the functions in the form of the generalized power series

$$y = x^r \sum_{n=0}^{\infty} c_n x^n . \tag{90}$$

satisfy this equation. Here r and c_n are not yet defined. Accounting for the relationships

$$xy' = x^r \sum_{n=0}^{\infty} (r + n)\, c_n x^n ,$$

$$x^2 y'' = x^r \sum_{n=0}^{\infty} (r + n)\,(r + n - 1)\, c_n x^n , \tag{91}$$

we obtain after substituting (90) and (91) into (89):

$$\sum_{n=0}^{\infty} (r + n)\,(r + n - 1)\, c_n x^n + \sum_{n=0}^{\infty} (r + n)\, c_n x^n \sum_{n=0}^{\infty} a_n x^n + \sum_{n=0}^{\infty} c_n x^n \sum_{n=0}^{\infty} b_n x^n = 0 \tag{92}$$

or, equating coefficients with similar powers of x:

$$\sum_{n=0}^{\infty} \left\{ (r + n)\,(r + n - 1)\, c_n + \sum_{m=0}^{n} [\, (r + m)\, a_{n-m} + b_{n-m}\,]\, c_m \right\} x^n = 0 . \tag{93}$$

The series (93) will satisfy the equation if

$$(r + n)\,(r + n - 1)\, c_n + \sum_{m=0}^{\infty} [\, (r + m)\, a_{n-m} + b_{n-m}\,]\, c_m = 0 , \tag{94}$$

i.e., the recurrence relationship

$$[\, (r + n)\,(r + n - 1)\,(r + n)\, a_0 + b_0\,] c_n = \sum_{m=0}^{n-1} [\, (r + m)\, a_{n-m} + b_{n-m}\,]\, c_m . \tag{95}$$

is satisfied.

We write several first expressions by equating to zero coefficients with powers of x:

$$\begin{array}{l|l} x^r & [\, (r - 1)\, r + a_0 r + b_0\,]\, c_0 = 0 , \\ x^{r+1} & [\, (r + 1)\, r + a_0\, (r + 1) + b_0\,]\, c_1 + a_1 r c_0 + b_1 c_0 = 0 , \\ x^{r+2} & [\, (r + 2)\,(r + 1) + a_0\,(r + 2) + b_0\,]\, c_2 + a_1\,(r + 1)\, c_1 + a_2 r c_0 + b_1 c_1 + b_2 c_0 = 0 . \end{array} \tag{96}$$

Since $c_0 \neq 0$, then, in order to determine r of the generalized series we obtain the so-called characteristic equation

$$r\,(r - 1) + a_0 r + b_0 = 0 . \tag{97}$$

Its roots are

$$r_{1,2} = -\frac{a_0 - 1}{2} \pm \sqrt{\left(\left(\frac{a_0 - 1}{2} \right)^2 - b_0 \right)} , \tag{98}$$

it should be noted that they are equal at $((a_0 - 1)/2)^2 = b_0$, different at $(a_0 - 1)^2/4 > b_0$, and imaginary at $(a_0 - 1)^2/4 < b_0$. We assume that $\mathrm{Re}(r_1) \geq \mathrm{Re}(r_2)$. Then the series

$$y_1\,(x) = x^{r_1} \sum_{n=0}^{\infty} c_n x^n , \tag{99}$$

corresponds to the root r_1 of the determining equation, and the coefficients c_n are determined from the recurrence relationship (95).

Two cases should be considered separately for the other root r_2:

1) $S = r_1 - r_2$ is an integer positive number or zero.

2) $S = r_1 - r_2$ is noninteger.

The latter case is nonsingular and gives the second linearly independent solution in the form

$$y_2(x) = x^r \sum_{n=0}^{\infty} g_n x^n . \tag{100}$$

However, the former case is singular. In order to find the second independent solution we will use the formula

$$y_2(x) = c_2 y_1 \ln x + x^{r_2} \sum_{n=0}^{\infty} \gamma_n x^n , \tag{101}$$

where the coefficients γ_n are determined after equating to zero multipliers with similar powers of x^n in the terms that do not contain ln x as a multiplier.

The general solution of the Eq. (85) is represented by the sum of two linearly independent solutions y_1 and y_2, i.e.,

$$y = c_1 y_1 (x, \alpha) + c_2 y_2 (x, \alpha) . \tag{102}$$

The functions $y_1(x, \alpha)$ and $y_2(x, \alpha)$ are also called fundamental solutions, and with their help solutions of homogeneous and nonhomogeneous boundary-value problems can be constructed. To do this, we consider the unified record of the boundary conditions in the form of the so-called generalized fifth boundary-value problem [15]:

$$\begin{aligned} &\left(\alpha_1 u + \beta_1 \frac{\partial u}{\partial x}\right)\Big|_{x=0} + \left(\alpha_2 u + \beta_2 \frac{\partial u}{\partial x}\right)\Big|_{x=a} = 0 , \\ &\left(\alpha_3 u + \beta_3 \frac{\partial u}{\partial x}\right)\Big|_{x=0} + \left(\alpha_4 u + \beta_4 \frac{\partial u}{\partial x}\right)\Big|_{x=a} = 0 , \end{aligned} \tag{103}$$

where α_i and β_i are coefficients the choice of which can transform the boundary conditions (103) into the boundary conditions of the first to the fourth kind.

Upon separation of variables the boundary-value problem for the function y is transformed into the following form:

$$\begin{aligned} &\alpha_1 y(0) + \alpha_2 y(a) + \beta_1 y'(0) + \beta_2 y'(a) = 0 , \\ &\alpha_3 y(0) + \alpha_4 y(a) + \beta_3 y'(0) + \beta_4 y'(a) = 0 . \end{aligned} \tag{104}$$

In order to determine the constants c_1 and c_2 and the separation constant α we will use (102) and (104):

$$\begin{aligned} &|\alpha_1 c_1 y_1 + \alpha_1 c_2 y_2 + \alpha_2 c_1 y_1' + y_2' \alpha_2 c_2 + \\ &+ \beta_1 c_1 y_1 + \beta_1 c_2 y_2 + \beta_2 c_1 y_1' + \beta_2 c_2 y_2' |_{x=0} = 0 , \\ &|\alpha_3 c_1 y_1 + \alpha_3 c_2 y_2 + \alpha_4 c_2 y_2' + \alpha_4 c_1 y_1' + \\ &+ \beta_3 c_1 y_1 + \beta_3 c_2 y_2 + \beta_4 c_1 y_1' + \beta_4 c_2 y_2' |_{x=a} = 0 . \end{aligned} \tag{105}$$

The system of homogeneous equations has a solution if its determinant equals zero:

$$\begin{vmatrix} (\alpha_1 y_1 + \alpha_2 y_1' + \beta_1 y_1 + \beta_2 y_1') & (\alpha_1 y_2 + \alpha_2 y_2' + \beta_1 y_2 + \beta_2 y_2') \\ (\alpha_3 y_1 + \alpha_4 y_1' + \beta_3 y_1 + \beta_4 y_1') & (\alpha_3 y_2 + \alpha_4 y_2' + \beta_3 y_2 + \beta_4 y_2') \end{vmatrix} = 0 . \tag{106}$$

From a consideration of the determinant, a transcendental equation with respect to the unknown parameter α is obtained, and, consequently, we find the eigenfunctions $y_1(x)$ and $y_2(x)$ with the use of which boundary-value problems of various kinds are solved.

If the parameters of the medium vary periodically in space, than instead of polynomial approximations of the coefficients, the Fourier series

$$f(x) = \sum a_n \cos \mu_n x + \sum b_n \sin \mu_n x,$$

should be used, and then the solution of (54) is reduced to investigation of equations with periodic or quasiperiodic coefficients, the theory of which is well developed [16]. In the case of nonlinear dependences the solution can be obtained in exceptional cases [13]. Therefore numerical, approximate, asymptotic, variational, and other methods play an important role here.

NOTATION

I_m, mass source of the ith component being adsorbed in the solid dispersed phase; c_i, concentration of the diffusing substance; v, velocity; t, time; a, concentration of the radionuclide being adsorbed; f, a certain function dependent on the interaction law of the adsorbent with the sorbing substance; γ, the Henry constant; k, k_0, k_1, k_2, k_3, and n, certain constants; c_0, radionuclide concentration at $x = 0$; φ_1 and φ_2, given functions of the coordinate x; c, impurity concentration in the atmosphere; ω, gravitational impurity sedimentation rate; v, vector of the gravitational wind velocity; u_z, k, vertical and horizontal diffusion coefficients; α, β, δ, certain coefficients; c_0, radioactive isotope concentration at $t = 0$; λ, half-life; $\delta(x)$, Dirac's δ-function; β_m, mass transfer coefficient; c_s, surface radionuclide concentration; $\Phi(t)$, surface density of external radionuclide sources; $p(x)$, coefficients. Subscripts: ext, external source; b, boundary.

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