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GREEN'S-FUNCTION METHOD FOR SOLVING PROBLEMS OF NONEQUILIBRIUM ADSORPTION AND CONVECTIVE DIFFUSION OF IMPURITY IN A MEDIUM

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The Green's function method is used to solve problems of impurity transfer by a carrier-gas flow in a semiinfinite medium, taking account of convective diffusion, nonequilibrium adsorption, and radioactive decay.

In describing the propagation of adsorbed impurity in a porous medium under the action of a carrier gas, as a rule, account is taken of longitudinal diffusion and mass transfer from a gas flow to the adsorbent granule. The convective-diffusion coefficient depends on the velocity of carrier-gas motion and the characteristic dimension of the porous medium $D = D_0 + \Delta v$ [1]. Hence it follows that, for a homogeneous porous medium and a constant gas-flow velocity, the convective diffusion coefficient is a constant and does not depend on the coordinates and the time. The characteristic length of the porous layer, beginning with which convective diffusion significantly influence the impurity characteristics, is determined from the estimate $l \geqslant \sqrt{Dt_0}$, although in reality the impurity "front" may be distorted on account of diffusional blurring at relatively small distances.

Impurity adsorption is divided into three stages [2]: external mass transfer, the act of adsorption, and internal diffusion in adsorbent grains. The second stage usually occurs considerably more rapidly than the other two.

External mass transfer occurs by molecular diffusion to the surface and mixing of impurity in the flow and is characterized by a kinetic adsorption coefficient β, which is related to the flow velocity and grain size by the dimensionless equation [2] $Nu = A\,Re^n Pr^m$. For a homogeneous porous medium and at constant gas-flow velocity, the kinetic adsorption coefficient will also be constant.

The adsorption kinetics must be taken into account when $t \sim \beta^{-1}$, i.e., when the characteristic time of the process is comparable with the inverse of the kinetic coefficient.

If the characteristic grain size of the porous medium satisfies the condition $d \ll \sqrt{D_0 t_0}$, the propagation of adsorbed impurity in the porous medium when $d^2 D_0^{-1} \ll t_0 \lesssim l^2 D^{-1}$ is described by the following system of equations

$$u_t + a_t + vu_x + \lambda(u + a) = Du_{xx}, \tag{1}$$

$$a_t = \beta(u - u^*) - \lambda a, \quad u^* = \gamma a. \tag{2}$$

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In Eqs. (1) and (2), it is taken into account that the impurity being transferred is adsorbed according to a linear Henry's law, which is valid with a small impurity concentration in the gas flow. In addition, it is assumed that the impurity undergoes radioactive decay. The system in Eqs. (1) and (2) is used in describing nonsteady heat transfer by liquid in a motionless granular mass [3]. Its approximate solution by reduction to an evolutionary equation was outlined in [4].

In [5], it was shown that the boundary condition need only be specified for the function u(x, t). The initial and boundary conditions for Eqs. (1) and (2) take the form

$$u(x,\ 0) = \psi_1(x), \quad a(x,\ 0) = \psi_2(x), \quad u(0,\ t) = \varphi(t). \tag{3}$$

Matching of the initial and boundary conditions was also considered in [6]. The problem of impurity propagation by a gas flow was considered in [1-9]. In [6], the influence of nonequilibrium adsorption and convective diffusion with constant boundary conditions and zero initial conditions — u(0, t) = 1, u(x, 0) = a(x, 0) = 0 — was investigated. In [7], Eqs. (1) and (2) were solved for the case when the impurity concentration reaches the input to the mass in the form of a delta function with respect to the time.

In the present work, the solution of Eqs. (1) and (2) with initial and boundary conditions of the general type in Eq. (3) is obtained in quadratures.

To determine the impurity concentration u(x, t), which is a solution of Eqs. (1) and (2) with the conditions in Eq. (3), use is made of the Green's-function method, which is well known for equations of hyperbolic and parabolic type [10, 11], i.e., the solution of the system is sought in the form of integrals of the initial and boundary problems

$$u(x,\ t) = \int_0^t \Phi(x;\ t-\tau)\,\varphi(\tau)\,d\tau + \sum_{i=1}^{2} \int_0^\infty G_i(x-\xi;\ t)\,\psi_i(\xi)\,d\xi. \tag{4}$$

Here the functions G_i(x, ξ; t) (i = 1, 2) are components of the Green's tensor [11] corresponding to the function u(x, t) of the boundary problem in Eqs. (1)-(3) for a rectilinear halfline. Essentially, the function G_i(x, ξ; t) for fixed i coincides with the solution of Eqs. (1) and (2) u(x, t) with specially chosen initial and boundary conditions

$$u(x,\ 0) = \delta(x-\xi), \quad a(x,\ 0) = 0, \quad u(0,\ t) = 0, \quad i = 1, \tag{5}$$

$$u(x,\ 0) = 0, \quad a(x,\ 0) = \delta(x-\xi), \quad u(0,\ t) = 0, \quad i = 2. \tag{6}$$

It may be shown that the function Φ(x, t) is obtained from G_1(x, ξ; t) by the following transition to the limit

$$\Phi(x,\ t) = D \lim_{\xi \to 0} \frac{\partial}{\partial \xi} G_1(x,\ \xi;\ t). \tag{7}$$

The function Φ(x, t) is often called the response function of the medium. Its analytical form was obtained in [7].

With known Φ(x, t), G_i(x, ξ; t) (i = 1, 2), the solution for Eqs. (1) and (2) with conditions of the arbitrary type in Eq. (3) is reduced to calculating the single integrals in Eq. (4). This calculation may be performed with approximate analytical or numerical methods using standard integral-calculation programs.

First, an auxiliary problem is solved. The component of the Green's-tensor component H_1(x, ξ; t) corresponding to the solution of the Cauchy problem of Eqs. (1) and (2) under the following conditions is determined

$$u(x,\ 0) = \delta(x-\xi), \quad a(x,\ 0) = 0, \quad -\infty < x < \infty, \quad t \geqslant 0. \tag{8}$$

Applying a Laplacian transformation with respect to the time and a Fourier transformation with respect to the coordinate to Eqs. (1) and (2) and the condition in Eq. (8), the function

$$U(\omega,\ p) = (2\pi)^{-1/2} \int_0^\infty dt \int_{-\infty}^{\infty} dx u(x,\ t) \exp\{-pt - i\omega x\}$$

is found in the form

$$U(\omega,\ p) = +(2\pi)^{-1/2}\ i\,(\nu^2 + 4Dq\,(p))^{-1/2}\ [(\omega + i\omega_1)^{-1} - (\omega + i\omega_2)^{-1}]\ \exp\{-i\omega\xi\}. \tag{9}$$

Here

$$\omega_{1,2} = (2D)^{-1}\ [\nu \pm (\nu^2 + 4Dq\,(p))^{1/2}];\quad q\,(p) = (p + \lambda)\ [1 + \beta\,(p + \lambda + \beta\gamma)^{-1}].$$

Using back-transformation and the generalized Efros tensor [12] to find the function corresponding to the transform in Eq. (9), the component of the Green's tensor $H_1(x, \xi; t)$ of Eqs. (1) and (2) with the conditions in Eq. (8) is obtained

$$H_1(x,\ \xi;\ t) = (4\pi Dt)^{-1/2} \exp\{-\lambda t\}\ [S(x,\ \xi;\ t) + \beta\,(\gamma t)^{1/2} \int_0^t A_1(t,\ \tau)\ S(x,\ \xi;\ \tau)\ d\tau], \tag{10}$$

$$S(x,\ \xi;\ t) = \exp\{-(x - \xi - \nu t)^2\ (4Dt)^{-1} - \beta t\},\quad A_1(t,\ \tau) =$$

$$= (t - \tau)^{-1/2}\ I_1[2\beta\ \sqrt{\gamma\tau\,(t - \tau)}\ ]\ \exp\{-\beta\gamma\,(t - \tau)\}.$$

Here $I_1(z)$ is a Bessel function of the first kind with an imaginary argument.

Since $u(x, t) = H_1(x, \xi; t)$ with the conditions in Eq. (8) and $u(x, t) = \exp\{-2\xi\nu(2D)^{-1}\} - H_1(x, -\xi; t)$ is also a solution of Eqs. (1) and (2) with the initial conditions

$$u(x,\ 0) = \exp\{-2\xi\nu\,(2D)^{-1}\}\ \delta\,(x + \xi),\quad a\,(x,\ 0) = 0,\quad -\infty < x < \infty,$$

$$t \geqslant 0,$$

it follows that

$$G_1(x,\ \xi;\ t) = H_1(x,\ \xi;\ t) - \exp\{-2\xi\nu\,(2D)^{-1}\}\ H_1(x,\ -\xi;\ t). \tag{11}$$

The function $G_1(x, \xi; t)$ satisfies Eqs. (1) and (2) with the initial and boundary conditions in Eq. (5).

The function $\Phi(x, t)$ is found from the expression for the transition to the limit in Eq. (7); it may expediently be written as the sum of two terms

$$\Phi\,(x,\ t) = x\,(4\pi Dt^3)^{-1/2} \exp\{-\lambda t\}\ [\Phi_1(x,\ t) + \Phi_2(x,\ t)],$$

$$\Phi_1(x,\ t) = \exp\{-\beta t - (x - \nu t)^2\ (4Dt)^{-1}\}, \tag{12}$$

$$\Phi_2(x,\ t) = \beta\gamma^{1/2}\ t^{3/2} \int_0^t d\tau\tau^{-1}\,(t - \tau)^{-1/2}\ I_1[2\beta\ \sqrt{\gamma\tau\,(t - \tau)}\ ]\ \exp\{-\beta\gamma\,(t - \tau)\}\ \Phi_1(x,\ \tau).$$

Analogously to $G_1(x, \xi; t)$, the Green's-tensor component $G_2(x, \xi; t)$ of Eqs. (1) and (2) on a rectilinear halfline under the condition in Eq. (6) is determined

$$G_2(x,\ \xi;\ t) = H_2(x,\ \xi;\ t) - \exp\{-2\xi\,(2D)^{-1}\ \nu\}\ H_2(x,\ -\xi;\ t)), \tag{13}$$

where

$$H_2(x,\ \xi;\ t) = (4D\pi)^{-1/2}\ \beta\gamma \exp\{-\lambda t\} \int_0^t A_2(t,\ \tau)\ S(x,\ \xi;\ \tau)\ d\tau;$$

$$A_2(t,\ \tau) = \tau^{-1/2}\ I_0[2\beta\ \sqrt{\gamma\tau\,(t - \tau)}\ ]\ \exp\{-\beta\gamma\,(t - \tau\}.$$

Using Eqs. (4) and (11)-(13), the solution of Eqs. (1) and (2) with the arbitrary initial and boundary conditions in Eq. (3) may be found.

Suppose that the impurity-concentration distribution in the flow and porous medium initially is a rectangular pulse

$$u(0,\ t)=0,\quad u(x,\ 0)=\gamma c\,[\Theta(x)-\Theta(l-x)],\quad a(x,\ 0)=c\,[\Theta(x)-\Theta(l-x)]. \tag{14}$$

The significance of Eq. (14) is that in some volume of the porous medium there is equilibrium between the impurity in the flow and in the adsorbent according to Henry's law, and when t > 0 carrier-gas motion at constant velocity ν begins.

Using the Green's-tensor components in Eqs. (11) and (13), the solution of Eqs. (1) and (2) with the condition in Eq. (14) is obtained from Eq. (4)

$$u(x,\ t)=c\gamma(4\pi Dt)^{-1/2}\,[Q_l(x,\ t)\exp\{-(\beta+\lambda)\,t\}+\beta t^{1/2}\exp\{-(\lambda-\beta\gamma)\,t\}] \tag{15}$$

$$\times\sum_{j=1}^{2}\gamma^{\frac{2-j}{2}}\int_0^t[\tau^{1-j}(t-\tau)^{j-2}]^{1/2}\,I_{2-j}\,[2\beta\sqrt{\gamma\tau(t-\tau)}\,]\,Q_l(x,\ \tau)\ \exp\{-(1-\gamma)\,\beta\tau\}\,d\tau,$$

where

$$Q_l(x,\ t)=\frac{1}{2}\,(4\pi Dt)^{1/2}\{\operatorname{erf}[(x-\nu t)\,(4Dt)^{-1/2}]- \tag{16}$$

$$-\operatorname{erf}[(x-l-\nu t)\,(4Dt)^{-1/2}]-\exp\{\nu xD^{-1}\}\,[\operatorname{erf}[x+l+\nu t)\,(4Dt)^{-1/2}]-\operatorname{erf}[(x+\nu t)\,(4Dt)^{-1/2}]]\}.$$

Here erf(z) is the probability integral.

As $l\to\infty$, which corresponds to the case of a uniform initial concentration distribution — u(x, 0), a(x, 0) — it is found that

$$u(0,\ t)=0,\quad a(x,\ 0)=c,\quad u(x,\ 0)=\gamma c,\quad x\geqslant 0. \tag{17}$$

Then Eq. (16) is written in the form

$$\lim_{l\to\infty}Q_l(x,\ t)=\frac{1}{2}\ (4\pi Dt)^{1/2}\{1+\operatorname{erf}[(x-\nu t)\,(4Dt)^{-1/2}]-\exp\{\nu xD^{-1}\}\operatorname{erfc}[(x+\nu t)\,(4Dt)^{-1/2}]\}.$$

Here erfc(z) = 1 − erf(z).

Consider the limiting cases of equilibrium ($\beta\to\infty$) and strongly nonequilibrium adsorption ($\beta\gamma^{1,2}t\ll 1$).

If the characteristic time for the establishment of equilibrium between the radioactive impurity in the flow and in the adsorbent is much less than the characteristic time of the process, adsorption occurs "instantaneously." As $\beta\to\infty$, Eq. (2) transforms to the equation $u=\gamma a$. As $\beta\to\infty$, the solution in Eq. (15) takes the form

$$u(x,\ t)=c\,(4\pi Dt)^{-1/2}\,\gamma^{1/2}\,(1+\gamma)^{1/2}\,Q_l(x,\ \gamma(1+\gamma)^{-1}\,t)\exp\{-\lambda t\}. \tag{18}$$

For (17) the solution of (18) has the form

$$u(x,\ t)=\frac{1}{2}\ c\gamma\exp\{-\lambda t\}\,\{1+\operatorname{erf}[(x-\nu t_1)\,(4Dt_1)^{-1/2}] \tag{19}$$

$$-\exp\{\nu xD^{-1}\}\operatorname{erfc}[(x+\nu t_1)\,(4Dt_1)^{-1/2}]\},$$

where $t_1=\gamma(1+\gamma)^{-1}$.

At fixed i, the solution in Eq. (19) increases monotonically with x($u_x>0$) from $\lim_{x\to 0}u(x,\ t)=0$ to $\lim_{x\to\infty}u(x,\ t)=c\gamma\exp\{-\lambda t\}$. The coordinate $x\approx\nu t$ when $\nu t\gg(4Dt)^{1/2}$ is a point of

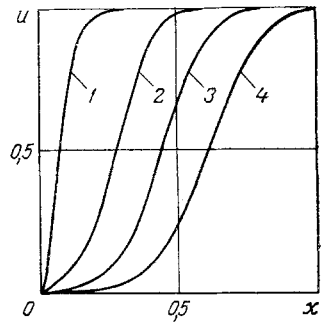

Fig. 1. Impurity concentration in gas-carrier flow u(x, t) for t = 10, 40, 70, and 90 sec (curves 1-4, respectively) when ν = 2 cm/sec, D = $4 \cdot 10^{-4}$ m/sec, λ = $2.78 \cdot 10^{-5}$ sec^{-1}, γ = 0.5, c = $1/\gamma$.

inflection of the function u(x, t). The solution in Eq. (19) at different moments of time is shown in Fig. 1.

For strongly nonequilibrium adsorption ($\beta\gamma^{1/2}t \ll 1$), asymptoic expansion of the Bessel function at small values of the argument is used. The solution u(x, t) takes the form

$$u(x,\ t) = c(4\pi Dt)^{-1/2}\,[Q_l(x,\ t)\exp\{-(\beta+\lambda)\,t\} + \beta\gamma t^{1/2}\int\limits_0^t d\tau\tau^{-1/2}\,(\beta\tau+1)\,Q_l(x,\ \tau)\exp\{-(1-\gamma)\,\beta\tau\}]. \quad (20)$$

The integrand in Eq. (20) is continuous; therefore according to the theorem of the mean

$$u(x,\ t) = c(4\pi Dt)^{-1/2}\,[Q_l(x,\ t)\exp\{-(\beta+\lambda)\,t\} + \beta\gamma t^{3/2}\,t_1(\beta t_1+1)\,Q_l(x,\ t_1)\exp\{-(1-\gamma)\,\beta t_1\}], \quad (21)$$

where $t_1 \in (0, t)$. The solution in Eq. (21) is the sum of two terms; the first corresponds to the solution of the diffusion equation in a moving medium; the second is due to desorption of impurity from the medium. As $l \to \infty$ when $\nu t \gg (4Dt)^{1/2}$, each of the terms in Eq. (21) is of qualitatively the same form as a function of x as in the case of equilibrium adosrption, i.e., in Eq. (18).

When $\beta \gg t_0^{-1}$ (the case of weakly nonequilibrium adsorption), the asymptotic solution of Eqs. (1) and (2) constructed using the Green's-function method coincides with the solution obtained by the method proposed in [4].

NOTATION

D_0, molecular-diffusion coefficient; Δ, constant of dimensionality length characterizing the geometry of the porous layer; t_0, characteristic sorption time; u*, concentration of sorbed material at equilibrium; A, n, m, constants; Nu, Re, Pr, Nusselt, Reynolds, and Prandtl numbers; u(x, t), concentration of radioactive impurity in gas flow; a(x, t), amount of adsorbed impurity per unit volume of porous medium; β, kinematic mass-transfer coefficient; ν, carrier-gas velocity; λ, radioactive decay constant; γ, inverse of Henry coefficient; D, longitudinal diffusion coefficient; c, l, parameters in initial conditions; $\Theta(x)$, Heaviside function; $H_i(x, \xi; t)$, $G_i(x, \xi; t)$, Green's tensor components on a straight line and a rectilinear halfline.

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