# EFFECT OF DIFFUSION AND SORPTION ON RADIOACTIVE-GAS DISTRIBUTION IN A POROUS MEDIUM

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An investigation is carried out to determine how the kinetics of sorption and of longitudinal diffusional spreading affect the concentration of a radioactive gas carried at constant velocity by a gas flow through the porous medium.

Diffusion and adsorption in the filtration of gas through a porous medium were considered in [1-3], where approximate analytical solutions were obtained for the concentration of a dynamically neutral impurity in a gas flow. The present work investigates the effect of various processes (diffusion, sorption, radioactive decay) on the concentration of a radioactive impurity at times comparable to the inverse of the kinetic-sorption coefficient.

§1. Statistical investigations of the local-velocity field for a gas in a porous medium [2] have shown that the transport of a dynamically neutral impurity is described by an equation of diffusional type. Since a radioactive impurity is adsorbed by the porous medium to some extent, there is an additional redistribution of its concentration in the gas—porous-medium system.

Taking into account diffusion, sorption, and radioactive decay, the material-balance equation for a radioactive gas is of the form [3]

$$\frac{\partial a}{\partial t} + \frac{\partial c}{\partial t} + \lambda (c + a) = \mathrm{div}\,(D_{ij}\,\mathrm{grad}\,c - \mathbf{u}\,c),$$

$$D_{ij} = (\Delta_1 - \Delta_2)|\mathbf{u}|\delta_{ij} + \Delta_2 u_i u_j / |\mathbf{u}|. \tag{1.1}$$

The simplest equation describing sorption kinetics for a radioactive gas in a porous medium is

$$\frac{\partial a}{\partial t} = \beta (c - c^*), \quad c^* = \gamma a. \tag{1.2}$$

In Eq. (1.2) it is assumed that the sorption isotherm is a Henry isotherm, which is correct for a small radioactive-gas concentration in the flow.

Note that, with given initial and boundary conditions for Eqs. (1.1) and (1.2), the initial distribution of the radioactive-gas concentration must be continuous and the boundary conditions must be consistent with the initial conditions. If the initial gas-concentration distribution is discontinuous, or if the initial and boundary conditions are inconsistent, a correct formulation of the problem must take into account the conditions at the discontinuities [2].

Consider the one-dimensional problem of the motion of a radioactive impurity carried through a porous medium by a gas flow at a constant velocity $v$. Assuming that initially there is no radioactive gas in the porous medium and in the flow, the boundary and initial conditions may be written as [2]

$$c(0,\ t) = \mu(t),\ c(\infty,\ t) = 0,\ a(x,\ 0) = 0,\ c(x,\ 0) = 0. \tag{1.3}$$

In [3], the Green function $[\mu(t) = u_0\delta(t)]$ for the system in Eqs. (1) and (2) was determined. The radioactive-gas concentration in the gas flow is written as the sum of two terms:

$$c(x,\ t) = G_1(x,\ t) + G_2(x,\ t),$$

$$G_1(x,\ t) = \frac{u_0 x}{2\sqrt{\pi D t^3}}\,\exp\left\{ -\frac{(x - vt)^2}{4Dt} - t(\lambda + \beta)\right\},$$

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$$G_2(x, t) = \frac{u_0 \beta x \sqrt{\gamma}}{\sqrt{\pi D}} \exp\{-t(\lambda + \beta\gamma)\} \int_0^t \tau^{-1}(t - \tau)^{-1/2} \times$$

$$\times \exp\left\{-\frac{(x - v\tau)^2}{4D\tau} - \tau\beta(1 - \gamma)\right\} I_1(2\beta\sqrt{\gamma\tau(t - \tau)}) \, d\tau. \tag{1.4}$$

In Eq. (1.4) the first term is the Green function for the diffusion equation in a moving medium, with a factor taking into account the decrease in the amount of radioactive gas in the flow due to decay and sorption. The second term corresponds to "discharge" of the porous medium occurring because sorption is a nonequilibrium process and vanishes at $\beta = 0$ or $\gamma = 0$. Note that without taking into account sorption and diffusion, a delta-function pulse is transported in the porous medium, without spreading, at the velocity of the carrier-gas flow. Diffusion leads to spreading of the delta-function pulse, which is transformed to a Gaussian curve, although the velocity of the pulse maximum remains the same.

Equilibrium adsorption (instantaneous establishment of adsorption equilibrium in the gas－sorbent system) leads to significant redistribution of the concentration in the flow. In this case, a single pulse again moves through the porous medium, but at a velocity less than that of the gas flow [6].

When sorption kinetics is taken into account (the length of the process is several characteristic times), the gas concentration in the flow is determined by the superposition of two pulses: The first determines the concentration of the gas that has not been adsorbed and the second the concentration of the gas desorbed into the flow. This is illustrated in Fig. 1: At small times, the flow consists mainly of unadsorbed gas (curve 1, Fig. 1); at large times, the flow is mainly of desorbed gas (curve 4, Fig. 1); at intermediate times, both unadsorbed and desorbed gas are present.

In the absence of sorption ($\gamma = \beta = 0$) and radioactive decay ($\lambda = 0$), the solution is the same as that in [4].

Accurate calculation of the integral with respect to $\tau$ in Eq. (1.4) is difficult. Analysis of the result is considerably simplified at the asymptote. For $\beta\sqrt{\gamma t} \ll 1$ and $1 + 4\beta D v^{-2}(1 - \gamma) > 0$, the integral has been calculated [5]; the second term in Eq. (1.4) then takes the form

$$G_2(x, t) = \frac{2u_0\beta^2\gamma x \sqrt{t}}{\sqrt{v^2 + 4\beta D(1 - \gamma)}} \exp\left\{\frac{xv}{2D}\left[1 - \sqrt{1 + \frac{4\beta D(1 - \gamma)}{v^2}}\right] - t(\lambda + \beta\gamma)\right\}. \tag{1.5}$$

It follows from Eq. (1.4) that, if the concentration is applied at the sorption-layer input in the form of a delta function, the radioactive-gas concentration consists, in general, of two pulses. If $\beta \gg 1$ (the case realized, as a rule, in chromatographic gas separation), $G_1(x, t)$ is negligibly small. In the limiting case as $\beta \to \infty$, $G_1(x, t) \to 0$; the adsorption is equilibrium and the gas flow contains one pulse formed as a result of impurity desorption. Without taking diffusion into account [6], under equilibrium adsorption the radioactive impurity moves in the flow at a velocity less than that of the flow. It is as if there is "instantaneous transport" of radioactive gas from the first pulse to the second by the porous medium.

When $0 < \beta D v^{-2}(1 - \gamma) \ll 1$, Eq. (1.5) leads to the value of the coordinate at which the concentration of desorbed radioactive impurity in the gas flow is a maximum:

$$x_M = v[\beta(1 - \gamma)]^{-1}[1 + \beta v^{-2}D(1 - \gamma)]. \tag{1.6}$$

It is evident from Eq. (1.6) that when $\beta\sqrt{\gamma t} \ll 1$ (the region of strongly nonequilibrium adsorption) the coordinate of the maximum is independent of time. Whereas for equilibrium adsorption ($\beta \to \infty$) (the characteristic time for the equilibrium to be established between the radioactive impurity in the flow and in the sorbing medium is much less than the characteristic time of the process as a whole) [6] $x_M = 0$, in the case when the kinetic sorption coefficient $\beta$ is finite, by contrast, $x_M \neq 0$. Note that when $D = 0$, Eq. (1.6) reduces to the expression $x_M = v[\beta(1 - \gamma)]^{-1}$, which is the same as the expression for $x_M$ obtained from the accurate solution in [6].

Differentiating the first term in Eq. (1.4) with respect to the time t leads to an expression for the time T at which the first maximum of radioactive-gas concentration reaches the coordinate $l$ in the porous medium:

$$T = lv^{-1}[1 + 4Dv^{-2}(\lambda + \beta)]^{-1/2}. \tag{1.7}$$

It is of some interest to consider the possibility of determining the relevant parameters: the diffusion coefficient and the kinetic-sorption coefficient. From Eq. (1.6), if the gas-flow velocity $v$, the coordinate $x_M$ corresponding to the concentration maximum of the desorbed radioactive gas, the kinetic-sorption coefficient $\beta$, and the coefficient $\gamma$ are known, the diffusion coefficient D may be determined in the form

$$D = x_M v - v^2 \beta^{-1}(1 - \gamma)^{-1}. \tag{1.8}$$

For a gas-flow velocity $v = 2$ cm/sec, $\beta = 0.1$ sec$^{-1}$, $\gamma = 0.1$, and $x_M = 22.52$ cm, Eq. (1.8) gives $D = 1$ cm$^2$/sec. The accuracy of this determination of the diffusion coefficient is characterized by the accuracy of the known parameters $\beta$, $\gamma$, $v$, and the measured coordinate $x_M$.

The kinetic-sorption coefficient is determined from Eq. (1.7) for known parameters $\lambda$, $D$, and $v$, and using an experimental value of the time at which the first maximum of the radioactive-gas concentration appears at the given coordinate;

$$\beta = 0.25 D^{-1}(l^2 T^2 - v^2) - \lambda. \tag{1.9}$$

The accuracy in determining $\beta$ is characterized by the accuracy of the measured time $T$ and the known parameters $D$, $l$, $v$, and $\lambda$. Note that if both $\beta$ and $D$ are unknown, they may be determined for known $T$, $l$, $x_M$, $\lambda$, $v$, and $\gamma$ by solving the system in Eqs. (1.8) and (1.9) for $\beta$ and $D$. The main difficulty in determining $\beta$ and $D$ is associated with the concentration of the radioactive impurity, which is usually small. In addition, some radionuclides are short-lived, which also complicates the determination.

§2. Solution of Eqs. (1.1) and (1.2) in analytic form for arbitrary boundary conditions leads to mathematical expressions that are difficult to analyze. Therefore in the present work a computer was used for the analysis of Eqs. (1.1) and (1.2). The calculations were made by a difference method using a four-point explicit scheme, the accuracy of which was second-order with respect to the step over the coordinate and first order with respect to the time step. In carrying out the calculations, the following dimensionless variables were introduced into Eqs. (1.1) and (1.2):

$$x' = x\lambda v^{-1}, \quad t' = t\lambda, \quad D' = Dv^{-2}\lambda, \quad \beta' = \beta\lambda^{-1}$$

(below, the primes are omitted).

It is assumed that the radioactive-gas concentration applied at the sorbing-medium input is of the form $\mu(t) = \exp\{-20(t - 0.5)^2\}$. In Fig. 1 the distribution of the radioactive-impurity concentration in the gas flow at times $t_1 = 10$, $t_2 = 20$, $t_3 = 30$, $t_4 = 40$ is shown. At $t_1$ and $t_2$ the amount of desorbed radioactive impurity in the gas flow is slight. At $t = 24.5$ the second maximum in the radioactive-gas concentration appears in the gas flow. At $t = 54$, the gas flow contains a single radioactive-gas pulse, appearing as a result of desorption.

The effect of diffusion on the radioactive-gas concentration in the flow is shown in Fig. 2. The best resolution of the two radioactive-gas pulses is obtained at $t = 35$.

As is evident from Fig. 2, the pulses of undesorbed and desorbed radioactive impurity in the gas flow coalesce into one at $D = 1.1$. Since the velocity of the desorbed-impurity maximum is $\sim \gamma(1 + \gamma)^{-1}$ [6], the coalescence of the two readioactive-impurity pulses into one occurs at lower diffusion coefficients as $\gamma$ increases.

The effect of the kinetic-sorption coefficient on the shape of the radioactive-impurity pulse in the flow is shown in Fig. 3. At time $t_1 = 10$, when $\beta = 0.1$, there is comparatively little impurity in the flow, as a result of "discharge" of the pore surface; this is in contrast with the case of the desorbed radioactive impurity at $\beta = 1$.
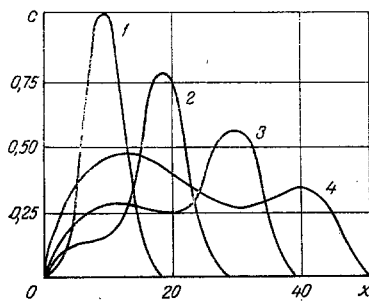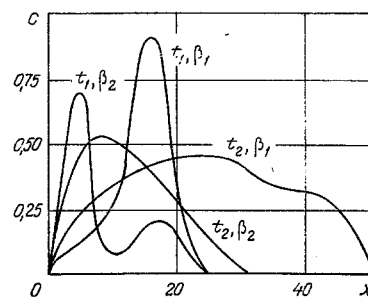


Fig. 1                                   Fig. 2

Fig. 1. Distribution of radioactive-gas concentration in porous medium: 1) $t_1 = 10$, 2) $t_2 = 20$, 3) $t_3 = 30$, 4) $t_4 = 40$; $\beta = 0.1$; $D = 0.2$; $\gamma = 0.1$.

Fig. 2. Concentration distribution for various kinetic-sorption coefficients: $t_1 = 10$, $t_2 = 40$, $\beta_1 = 0.1$, $\beta_2 = 1.0$.
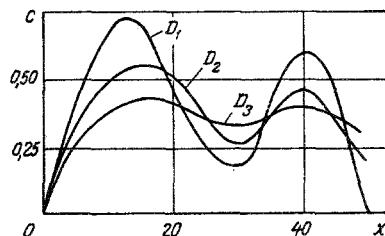
Fig. 3. Concentration distribution for various diffusion coefficients: $t=30$, $D_1=0.1$, $D_2=0.5$, $D_3=1.0$.

As a result of numerical modeling, the following relation is established between the coordinate at which the maximum of the desorbed-impurity concentration appears in the gas flow and the coefficient of longitudinal diffusional spreading: For $D=0.1$, $0.2$, $0.5$, $1.0$, and $2.0$, $x_M=22.25$, $22.30$, $22.35$, $22.52$, and $22.70$, respectively. These results are satisfactorily described by Eq. (1.6).

Note finally that the effect of radioactive decay leads to a decrease in radioactive-impurity concentration in the gas flow, and the combined effect of radioactive decay, sorption, and diffusion leads to attenuation and distortion of the initial radioactive-gas pulse and, at some values of the parameters, splitting of the pulse into two. Having measured the coordinate $x_M$ at which the maximum of the desorbed radioactive impurity appears and the time T at which the maximum of the radioactive-gas concentration reaches the coordinate $l$, and knowing the parameters $\lambda$, $\gamma$, and $\nu$, it is possible, in principle, to determine the kinetic-sorption coefficient and the longitudinal diffusion coefficient.

## NOTATION

$a(x, t)$, amount of radioactive gas adsorbed by the porous medium; $c(x, t)$, radioactive-gas concentration in the flow; $\lambda$, radioactive-decay constant; $\gamma$, coefficient inverse to the Henry coefficient; $\beta$, kinetic-sorption coefficient; D, longitudinal diffusion coefficient; $D_{ij}$, convective diffusion coefficient; $\Delta_{1,2}$, longitudinal and transverse scattering coefficients of the medium; $x_M$, coordinate at which desorbed-impurity maximum appears; $l$, coordinate of the first concentration maximum of the radioactive impurity at time T; $u$, $\nu$, gas-flow velocity; x, coordinate; t, time.

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