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We obtain and study an analytical solution for the one-dimensional problem of the filtration of a solution in cracked-porous media with allowance for the dependence of the saturation concentration on the composition of the solution.

Mathematical simulation of mass transfer during filtration of solutions in crackedporous media is of interest in relation to the contamination of subterranean water and the determination of the structure of zones where ground waters with different compositions mix. At a constant saturation concentration the salient features of such mass transfer are described by the known solutions of the problem of the migration of radioactive pollution in cracked rocks [1, 2]. In actual fact, the saturation concentration is variable as a rule and depends on the composition of the subterranean water. Below we give a generalization of the solutions [1, 2] to this case.

1. Formulation of the Problem. When mathematical models of mass transfer in crackedporous media are being substantiated it is usually assumed that the permeability of the porous matrix (blocks) is several orders of magnitude lower than that of the cracks. This gives rise to ideas concerning the existence of two main transfer mechanisms, convective in cracks and molecular-diffusion in blocks [3, 4].

Let us consider how a cracked-porous medium filled with a solution with equilibrium concentration c_* , reacts when a solution with a different composition penetrates into the cracks. We assume that the flow is uniform and the filtration flow rate v is constant. The incoming solution contains a passive impurity which affects the solubility of the substance of the porous matrix.

The mass transfer in the cracks is described by

$$\frac{\partial}{\partial x}\left(mD\frac{\partial c}{\partial x}\right) + q - v\frac{\partial c}{\partial x} - \frac{\partial}{\partial t}(mc) = 0, \ x > 0, \ t > 0;$$
(1)

$$c(x, 0) = c_*, x > 0; c(0, t) = c_1, c(\infty, t) < \infty, t > 0.$$
⁽²⁾

Here

$$q = q_1 + q_2; \tag{3}$$

$$c_{0}(\mathfrak{d}) = \mathbf{v}\mathfrak{d} + c_{*}; \tag{4}$$

 ϑ is the concentration of the passive impurity [6]; ν is a constant; and D(v) - const is the effective diffusion coefficient. The quantity q_2 is determined from the solution of ancillary problem of mass transfer in a typical block [4]:

 $q_1 = \gamma (c_0 - c) [5];$

$$\frac{\partial}{\partial y} \left(\tilde{m} \tilde{D} \frac{\partial \tilde{c}}{\partial y} \right) + \tilde{\gamma} \left(c_0 - \tilde{c} \right) - \frac{\partial}{\partial t} \left(\tilde{m} \tilde{c} \right) = 0,$$
(5)

$$c(y, 0) = c_*, \quad c(0, t) = c(x, t),$$
 (6)

whereupon we have

$$q_{2}(x, t) = m\sigma \tilde{D} \frac{\partial \tilde{c}}{\partial y}(0, t),$$
(7)

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where $\sigma = 2\tilde{m}/H$ is the specific area of "windows" from blocks in cracks [1]; *H* is the crack opening; and a tilde denotes a block parameter. The distribution of the passive impurity is also described by Eqs. (1)-(7) when $c = \vartheta$, $\gamma = \nu = c_* = 0$ and $\vartheta(0, t) = \vartheta_0$ in Eq. (2). The solution of the problem for this case is known [4]. The problem considered in [1, 2] is obtained when $\vartheta = 0$, $c_* = 0$.

The mathematical model of mass transfer in the form (1)-(7) reflects the main features of the formation and structure of the mixing zones during the return flow of subterranean waters from massive rock of one composition into a massif with a different composition and also during the migration of pollutants from the compact zone of the massif. We note that the boundary condition in (6) corresponds to the case of a block of unbounded volume (half-space). For times $t \ll L^2/\tilde{D}$ (L is the characteristic linear size of the block) Eqs. (5) and (6) reflect the process of mass transfer in a block of any configuration [3].

<u>2. Fundamental Relations.</u> It is convenient to use the Laplace transform when constructing the solution of the problem (1)-(7). According to [4], the distribution of the passive impurity for cracks in the space of transforms is described by

$$\vartheta(\xi, s) = \frac{\vartheta_0}{s} \exp\left\{\xi\left[\frac{-\mathrm{Pe}}{4} - \sqrt{-\frac{\mathrm{Pe}^2}{4} + \frac{\tilde{D}}{D}}(s + \sqrt{\tilde{s})}\right]\right\}.$$

where s is parameter of the Laplace transform, $\xi = \sigma x$, and Pe = $v/(mD\sigma)$ is the Péclet number. The problem of the impurity distribution in the block is a standard heat conduction problem for a semibounded region [7]. Its solution gives for $\vartheta(y, t)$ the expression

$$\tilde{\Theta}(y, t) = \frac{y}{2\sqrt{\pi\tilde{D}}} \int_{0}^{t} \frac{\vartheta(x, \tau)}{(t-\tau)^{3/2}} \exp\left[-\frac{y^{2}}{4\tilde{D}(t-\tau)}\right] d\tau.$$
(8)

Going over to dimensionless time $\lambda = t \tilde{D} \sigma^2$ and applying the Laplace transformation to the right side of (8), we obtain

$$\vartheta(\eta, s) = \vartheta(\xi, s) \exp(-\eta(\sqrt{s}),$$

where $\eta = \sigma y$.

When the impurity distribution is known the value of the flow q_2 from the blocks is found from the solution of the problem (4)-(6), which the substitution $u = (\tilde{c}-c_*)\exp(\beta t)$ and $\beta = \tilde{\gamma}/\tilde{m}$ reduces to the familiar problem of heat conduction with distribution heat sources [8]:

$$\frac{\partial u}{\partial t} - \beta v \vartheta \exp(\beta t) := \tilde{D} \frac{\partial^2 u}{\partial y^2},$$
$$u(y, 0) = 0, \quad u(0, t) = (c - c_*) \exp(\beta t).$$

Using its solution [8, p. 215], we obtain for q_2 the expression

$$q_{2} = \frac{\sigma m \sqrt{\tilde{D}}}{\sqrt{\pi}} \left\{ -\exp\left(-\beta t\right) \frac{\partial}{\partial t} \int_{0}^{t} \frac{c - c_{*}}{\sqrt{t - \tau}} \exp\left(\beta\tau\right) d\tau + \frac{\beta v}{2\tilde{D}} \exp\left(-\beta t\right) \int_{0}^{\infty} \int_{0}^{t} \frac{y \exp\left(\beta\tau\right)}{(t - \tau)^{3/2}} \exp\left[-\frac{y^{2}}{4\tilde{D}\left(t - \tau\right)}\right] \tilde{\vartheta}\left(y, \tau\right) d\tau dy \right\}$$
(9)

Now for the concentration in the cracks we have in the transforms the equation

$$\begin{aligned} \frac{d^2\omega}{d\xi^2} - \operatorname{Pe} \frac{d\omega}{d\xi} &- \left[\frac{\tilde{D}}{D}\left(s + \sqrt{s + \beta_1}\right) + \gamma_0 \operatorname{Pe}\right] \omega\left(\xi, s\right) + \\ &+ K_1 \operatorname{Pe} \left[1 + \frac{\beta m}{\beta_1 \gamma}\left(\sqrt{s + \beta_1} - \sqrt{s}\right)\right] \frac{\vartheta\left(\xi, s\right)}{\vartheta_0} = 0, \end{aligned}$$
where $\omega = (c - c_*)/(c_1 - c_*), \ \beta_1 = \beta/(\tilde{D}\sigma^2), \ K_1 = \nu\gamma\vartheta_0/(c_1 - c_*), \ \gamma_0 = \gamma/(\upsilon\sigma)$

With the initial-boundary conditions corresponding to (2), its solution is

$$w(\xi, s) = \frac{1}{s} \left(1 - \frac{K_1}{\gamma_0} \right) \exp\left\{ \xi \left[\frac{\operatorname{Pe}}{2} - \frac{V - \frac{\overline{Pe^2}}{4} + \gamma_0 \operatorname{Pe} + \frac{\overline{D}}{D} \left(s + \sqrt{s + \beta_1} \right)} \right] \right\} + \frac{K_1}{s\gamma_0} \exp\left\{ \xi \left[\frac{\operatorname{Pe}}{2} - \sqrt{\frac{\operatorname{Pe^2}}{4} + \frac{\overline{D}}{D} \left(s + \sqrt{s} \right)} \right] \right\}.$$
(10)

To reproduce the original of (10) it is sufficient to know the original of

$$\frac{1}{s} \exp \left(-\sqrt{As + B\sqrt{s + \beta} + C}\right).$$

The latter was found in [1]. Omitting the final result because it is so cumbersome, we confine the discussion here to the asymptotic behavior of the solution for long times. Small values of s correspond to them in the transforms [9]. Disregarding quantities of the order of s or higher in (10), we obtain

$$w(\xi, s) = \frac{1}{s} \left(1 - \frac{K_1}{\gamma_0} \right) \exp \left[\xi \left(\frac{Pe}{2} - \frac{1}{2} - \frac{V}{\gamma_0} \right) + \frac{K_1}{s\gamma_0} \exp \left(-\frac{m\tilde{D}\sigma\xi V\bar{s}}{v} \right) \right] + \frac{K_1}{s\gamma_0} \exp \left(-\frac{m\tilde{D}\sigma\xi V\bar{s}}{v} \right).$$

Or in the originals

$$\omega(x, t) = \frac{c - c_*}{c_1 - c_*} = \left(1 - \frac{K_1}{\gamma_0}\right) \exp\left[\sigma x \left(\frac{Pe}{2} - \frac{1}{2}\right) - \sqrt{\frac{Pe^2}{4} + \gamma_0 Pe + \frac{\tilde{D}}{D} \sqrt{\tilde{\beta}_1}}\right] + \frac{K_1}{\gamma_0} \operatorname{erfc}\left(\frac{m\sigma x \tilde{D}}{2v \sqrt{\tilde{D}t}}\right)$$

At $t = \infty$ this suggests a description of the structure of the stationary mixing zone:

$$c(x, \infty) = c_* + v\vartheta_0 + (c_1 - c_* - v\vartheta_0) \times \exp\left[\sigma x \left(\frac{\mathrm{Pe}}{2} - \sqrt{\frac{\mathrm{Pe}^2}{4} + \gamma_0 \mathrm{Pe} + \frac{\tilde{D}}{D} \sqrt{\tilde{\beta}_1}}\right)\right]. \tag{11}$$

The results can be generalized to the case of a block of finite size. As in [2], for this purpose we consider a system of parallel cracks separated by a layer (blocks) of thickness L. The initial-boundary conditions (6) for the concentration in the block are replaced by

$$\tilde{c}(y, 0) = c_*, \quad \tilde{c}(0, t) = \tilde{c}(L, t) = c(x, t), \quad 0 \leq y \leq L.$$
 (6')

Further discussions are carried out in a similar manner for the case of a block of unbounded size. As a result the transform of the solution is obtained in the form

$$\omega\left(\xi, s\right) = \frac{1}{s} \left(1 - \frac{K_{1}}{\gamma_{0}}\right) \exp\left\{\xi\left[\frac{Pe}{2} - \frac{V}{4} + \gamma_{0}Pe + \frac{\tilde{D}}{D}\left(s + V\overline{s + \beta_{1}} \operatorname{th} \frac{V\overline{s + \beta_{1}}}{2\varkappa}\right)\right]\right\} + \frac{K_{1}}{s\gamma_{0}} \exp\left\{\xi\left[\frac{Pe}{2} - \sqrt{\frac{Pe^{2}}{4} + \frac{\tilde{D}}{D}\left(s + V\overline{s}\operatorname{th} \frac{V\overline{s}}{2\varkappa}\right)}\right]\right\},$$
(12)

where $\varkappa = (L\sigma)^{-1}$.

To reproduce the original of (12) it is sufficient to know the original of

$$\frac{1}{s}\exp\left(-\sqrt{As+B\sqrt{s+\beta}\,\mathrm{th}\frac{\sqrt{s+\beta}}{2\varkappa}+C}\right).$$

The latter was found in [2]. The structure of the stationary mixing zone is described by

$$w(x, \infty) = \frac{c(x, \infty) - c_*}{c_1 - c_*} = \left(1 - \frac{K_1}{\gamma_0}\right) \exp\left[\sigma x \left(\frac{\operatorname{Pe}}{2} - \sqrt{\frac{\operatorname{Pe}^2}{4} + \gamma_0 \operatorname{Pe} + \frac{\widetilde{D}\sqrt{\widetilde{\beta}_1}}{D}} \operatorname{th}\frac{\sqrt{\widetilde{\beta}_1}}{2\varkappa}}\right)\right].$$
(13)

<u>3. Discussion.</u> 1. The existence of a mixing zone in the above problem at $t \to \infty$ is due only to the source of concentration from the interaction of the solution with the rock. In actual fact, in the absence of sources $(\gamma = \tilde{\gamma} = 0)$ Eq. (11), which describes the structure of this zone, degenerates into the equality w = 1 or $c = c_1$. The mass transfer in the blocks is affected only on the effective length ℓ of the mixing zone, which is determined from the exponent in (11). In the general case

$$I = \left[\sqrt{\frac{v^2}{4m^2D^2} + \frac{\gamma}{mD}} + \frac{2\tilde{m}}{HD} \sqrt{\beta\tilde{D}} - \frac{v}{2mD} \right]^{-1}$$

For impermeable blocks $(\tilde{m} = 0)$

$$l_0 = \left[\sqrt{\frac{v^2}{4m^2D^2} + \frac{\gamma}{mD}} - \frac{v}{2mD}\right]^{-1}.$$

We note that $\ell_0 > \ell$.

2. Under real conditions, as a rule, $\varkappa = H/(2\tilde{m}L) \ll 1$. The solution of the problem for a system of cracks (12) goes over as $\varkappa \to 0$ into the solution (10) for a block of infinite size. Study of the case $\varkappa \sim 1$ thus is not of major importance in itself.

3. The scheme adopted for solving the initial problem is fairly universal and admits generalization. Thus ϑ can be construed as the concentration of a radioactive impurity. Its distribution in blocks and cracks was found in [1, 2]. The radiolysis products shift the heterogeneous equilibrium [10] and change the saturation concentration. If this change is described by Eq. (4), the solution is obtained in much the same way as (10). The structure of the corresponding stationary mixing zone is characterized by

$$\times \left\{ 1 - \frac{K_{1}\beta_{1} \left[1 - \frac{\delta_{1}}{\beta_{1}} + \frac{\beta m}{\beta_{1}\gamma} \left(V\overline{\beta_{1}} - V\overline{\delta_{1}}\right) \right]}{\gamma_{0} \left(\beta_{1} - \delta_{1}\right) \left[1 - \frac{\delta_{0}}{\gamma_{0}} + \frac{\beta m}{\beta_{1}\gamma} \left(V\overline{\beta_{1}} - V\overline{\delta_{1}}\right) \right]} \times \right. \\ \times \exp \left[\sigma x \left(\frac{Pe}{2} - \sqrt{\frac{Pe^{2}}{4} + \gamma_{0} Pe + \frac{\overline{D}V\overline{\beta_{1}}}{D}} \right) \right] \right\} + \left. + \frac{\left(c_{1} - c_{*}\right) K_{1}\beta_{1} \left[1 - \frac{\delta_{1}}{\beta_{1}} - \frac{\beta m}{\beta_{1}\gamma} \left(V\overline{\beta_{1}} - V\overline{\delta_{1}}\right) \right]}{\gamma_{0} \left(\beta_{1} - \delta_{1}\right) \left[1 - \frac{\delta_{0}}{\gamma_{0}} + \frac{\beta m}{\beta_{1}\gamma} \left(V\overline{\beta_{1}} - V\overline{\delta_{1}}\right) \right]}{\gamma_{0} \left(\gamma_{1} - \delta_{1}\right) \left[1 - \frac{\delta_{0}}{\gamma_{0}} + \frac{\beta m}{\beta_{1}\gamma} \left(V\overline{\beta_{1}} - V\overline{\delta_{1}}\right) \right]} \right] \right\} \\ \times \exp \left[\sigma x \left(\frac{Pe}{2} - \sqrt{\frac{Pe^{2}}{4} - \delta_{0} Pe + \frac{\overline{D}V\overline{\delta_{1}}}{D}} \right) \right],$$
(14)

where $\delta = \ln 2/t_{1/2}$, $t_{1/2}$ is the half-life, $\delta_0 = m\delta/(v\sigma)$, and $\delta_1 = \delta/(\tilde{D}\sigma^2)$. At $\delta = 0$ Eq. (14) goes over into Eq. (11). Radioactive decay leads to the depletion of the impurity at infinity and, therefore, $c(x, \infty)$ tends to c_* , as $x \to \infty$.

NOTATION

x, y, coordinates; t, τ , time; c, concentration of the dissolving substance in the liquid; ϑ , concentration of the passive impurity; c_* , equilibrium concentration of the

solution at $\vartheta = 0$; v, filtration flow rate; D, effective diffusion coefficient; q_1 , flux of dissolved substance from the crack walls; q_2 , flux of dissolved substance from the blocks; γ , dissolution rate constant; m, crack volume; H, crack opening; σ , specific area of "windows" from blocks into cracks; L, thickness of the porous block; s, Laplace transform parameter; $\xi = \sigma x$ and $\eta = \sigma y$, dimensionless length; Pe = $v/(mD\sigma)$, Péclet number; $\lambda = t\tilde{D}\sigma^2$, dimensionless time (the tilde denotes the respective parameters of the block); $\beta = \tilde{\gamma}/\tilde{m}$, reduced rate constant of dissolution in the block; $w = (c - c_*)/(c_1 - c_*)$, dimensionless concentration; $\beta_1 = \beta/(\tilde{D}\sigma^2)$, dimensionless rate constant of dissolution in the block; ν , $K_1 = \nu\gamma_0\vartheta_0/(c_1 - c_*)$, constant; $\varkappa = (L\sigma)^{-1}$, dimensionless scale parameter; $\delta = \ln 2/t_{1/2}$, rate constant of radio-active decay; and $t_{1/2}$, half-life.

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