The modelling of transportation process in porous media: transportation through channels

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Abstract. The paper is devoted to the study of solute transport through the channels. Since the fluid velocity in the present system is very heterogeneous, the transfer of solute particles has nontrivial properties. Particles of solute hold near the walls, which leads to the time lag of a large number of particles from the main mass flow. As a result, the transport process may become anomalous. Such flows are possible in a porous medium, where the anomalous transport is frequently observed and confirmed by numerous experiments. Usually, such transport is associated with sticking of particles on the pore walls. In the present paper, we had shown that the slow flow in a viscous boundary layer itself can be a reason for the anomalous transport.

1. Introduction

The transport process in a fluid flow is usually described by the Advection-Diffusion equations (ADE), see [1]. Advective transportation is caused by the flow itself. Diffusion is a random transport process, which arises due to thermal fluctuations. These two processes can be separated from each other in the presence of macroscopic flow. However, if the flow has a complex structure (for example, when considering turbulence flow [2] or flow through a porous medium [3]), then the average characteristics are used for the flow description. In this case, all additional transport processes arising due to the flow microstructure are also referred to as diffusion, i.e. turbulent diffusion [4] or effective diffusivity [5] for transport through a porous medium. In papers [6, 7], based on various assumptions about the microstructure of the flow, the contribution of the flow to the diffusion process is estimated. From these papers, one key condition about the flow structure can be distinguished: the flow velocity distributions should be such that for a transfer of particles in this flow the first moment (the ensemble is averaged over time) and the second moment (the ensemble is averaged over the space) exist and have finite values. For specific systems, this condition is not always true, and as a result, the various deviations from the standard diffusion law are observed.

Transport processes through porous massif are a part of many technological processes (filtration plants, soil irrigation, liquid waste disposal, etc.). The liquid flow that saturates a porous medium, has a rather complicated structure since it flows around many obstacles. An exact accounting of the entire flow structure for any massive object is impossible, because the averaging approach is usually performed. The presence of a complex flux leads to some corrections in the model of diffusive transport. Most often for transport in porous media, these corrections are limited to estimating the additional contribution to the diffusion coefficient [8,9].
While the equation of diffusion does not change. However, the essential deviation of results from those predicted by the classical model has been repeatedly found in experiments [10–12]. In most experiments, the dependence of concentration on time far from the inlet or the breakthrough curve is measured. The form of these curves for classical ADE should be symmetrical. However, the experimental data shows the asymmetrical form of the breakthrough curve [10]. The concentration increases faster than decreases and this difference is usually explained by immobilization of solute to a solid matrix on media.

The immobilization is often modelled using the MIM (mobile/immobile media) approach [13]. The simplest model is the linear sorption model or standard MIM model [13, 14]. The linear model predicts asymmetrical breakthrough curve where the increasing and decreasing of concentration can be fitted by exponential laws with different coefficients. However, the results of experimental studies [15, 16] have shown that the concentration decline is governed by the power law. The explanation of this power law dependence is presented in [17]. It is assumed that a solute in porous media immobilizes within random time intervals and the transport is anomalous. The physical meaning of this model is still not entirely clear and even disputed by many researchers. The explanation of power distribution based on fundamental interactions is still required. The present paper is devoted to filling this gap and for this reason, the impact of flow structure to the transportation process is investigated.

As it is shown in pioneer work [18], in complex periodical flow with chaotic areas the anomalous transport is observed. Later the anomalous transport was found for real turbulent flows [19] and for complex laminar flow: for an infinite periodical system of vortices [20] or for flow through the infinite periodical lattice of solid cylinders [21]. The main reason of abnormality of transport is viscosity because the motion near the solid wall is very slow and for vortices, the motion away from the center is also very slow. This slow motion produces a very long time for transportation of some particles, as a result, the total average time tends to infinity. In the present paper this effect is demonstrated for a simpler situation: flow in the channel. The breakthrough curve with power-law tail is obtained.

2. The properties of transportation process

The transport process can be described as “random jumps” of an ensemble of particles. We assume that every particle jumps to the random distance in a random direction with probability density \( p(x, y, z) \) and particle spends random time with probability density \( w(t) \) for this jump. Following the paper [22], we use the Laplace–Fourier transformation for \( p(x, y, z) \) and \( w(t) \). Let

\[
\mathcal{L}[F](s) = \int_0^\infty F(t) \exp\{-st\} \, dt
\]

and

\[
\hat{F}(k_x, k_y, k_z) = \iiint F(x, y, z) \exp\{-i(k_x x + k_y y + k_z z)\} \, dk_x dk_y dk_z
\]

be the Laplace transform and the Fourier transform of \( F(x, y, z) \) varying in space. Into the frameworks of this approach the Laplace–Fourier transform of particle concentration function can be written in form [23]

\[
\mathcal{L}[\hat{C}](k_x, k_y, k_z, s) = \hat{\rho}(k_x, k_y, k_z) \frac{1 - \mathcal{L}[w](s)}{s [1 - \mathcal{L}[w](s)\hat{\rho}(k_x, k_y, k_z)]},
\]

(1)

where \( \hat{\rho}(k_x, k_y, k_z) \) is the Fourier transformation of initial distribution of particles. In the isotropic case the distribution of particle jumps is the normal distribution which has the Fourier transformation \( \hat{\rho}(k_x, k_y, k_z, s) = \exp\{-M/2(k_x^2 + k_y^2 + k_z^2)\} \), where \( M \) is the second order central moment for the particle jumps distributions (the value of \( M \) is the same for all combinations of coordinates because of an isotropy). The last expression is the result of the central limit theorem and it is accurate only when moment \( M \) exists and finite. For the distribution \( w(t) \) the analogue limit theorem gives exponential distribution and the Laplace transformation in the form of \( \mathcal{L}[w](s) = \exp(-Ts) \), where \( T \) is the mean time of particle spends
into each jump. This relation is also justified for the finite $T$. As a result, if $M$ and $T$ exist and finite then in the macroscopic limit (when $x, y, z, t \to \infty$ or $k_x, k_y, k_z, s \to 0$) the equation (1) take the form

$$s\mathcal{L}[\hat{C}] (k_x, k_y, k_z, s) - \rho (k_x, k_y, k_z) = -M/2T \left( k_x^2 + k_y^2 + k_z^2 \right) \mathcal{L}[\hat{C}] (k_x, k_y, k_z, s),$$  \hfill (2)

or in $(x, y, z, t)$ space

$$\frac{\partial C (x, y, z, t)}{\partial t} = \frac{M}{2T} \Delta C (x, y, z, t),$$  \hfill (3)

where $D = M/2T$ is diffusivity. The existence of fluid flow is taking into account by the including of additional term $V \cdot \nabla C$ to the right part of equation (3) where $V$ is the flow velocity, as result one can obtain the standard ADE equation

$$\frac{\partial C (x, y, z, t)}{\partial t} + V \cdot \nabla C (x, y, z, t) = \frac{M}{2T} \Delta C (x, y, z, t).$$  \hfill (4)

In the opposite case when $T \to \infty$, the limit distribution can be obtained by Levy generalized limit theorem [24]: $\mathcal{L}[w](s) = \exp (-\tau s^\beta)$ where $0 < \beta < 1$. It means that equation (1) in the macroscopic limit becomes

$$s^{\beta} \mathcal{L}[\hat{C}] (k_x, k_y, k_z, s) - s^{\beta-1} \hat{\rho} (k_x, k_y, k_z) = -M/2\tau \left( k_x^2 + k_y^2 + k_z^2 \right) \mathcal{L}[\hat{C}] (k_x, k_y, k_z, s),$$  \hfill (5)

or in $(x, y, z, t)$ space

$$\frac{\partial^\beta C (x, y, z, t)}{\partial^\beta t} = \frac{M}{2\tau} \Delta C (x, y, z, t),$$  \hfill (6)

where $\frac{\partial^\beta C(x,y,z,t)}{\partial^\beta t} = \frac{1}{\Gamma(1-\beta)} \int_0^t \frac{1}{\tau^{1-\beta}} C (x, y, z, t') dt'$ is the fractional derivative of Caputo type [22]. From physical point of view it means that particle movement is very slow. Some particles trapped by external forces or their macroscopic velocity significantly decreases.

### 3. Transport through porous media

The experimental investigation of dissolution of localized concentration peak into the porous media shows that the breakthrough curves have the asymmetrical form [10] (see figure 1). Usually, the reason of such behaviour is explained by the immobilisation of particles by the solid matrix of media. The immobilisation is consider in the frameworks of MIM (mobile/immobile media) approach [13] where the solute is separated into two phases. The first is a mobile phase, which is composed of moving particles with volumic concentration $C$. The motion of such solute is described by the standard ADE. The second phase is called immobile and contains particles with volumic concentration $Q$ which steak to the solid matrix. This phase of solute does not move and its dynamics is described by the solute flux exchange between phases. The general equations within the MIM approach of solute concentration evolution can be written as

$$\frac{\partial}{\partial t} (C + Q) = \nabla \cdot (D \nabla C - \mathbf{V} C),$$

$$\frac{\partial}{\partial t} Q = R (C, Q),$$  \hfill (7)

where $D$ is the effective solute diffusivity, $\mathbf{V}$ is the vector of the filtration flow velocity. The first equation of (7) is ADE with the additional term $(\partial_t Q)$ describing the solute influx to the immobile phase. The second equation (7) is the kinetic equation. It reflects the dependence of the solute influx on the solute concentrations in both phases or it can be interpreted as kinetics.
of phase transition. The function $R(C, Q)$ is the kinetic function, which is defined by the specific type of the MIM model.

The most simple model of this type is linear MIM with $R(C, Q) = aC - bQ$ where $a$ and $b$ are the coefficients of linear adsorption and desorption consequently. The linear model allows to obtain asymmetric breakthrough curve for one dimensional transport (along $x$ axis) with asymptotic concentration increasing as $1/\sqrt{Dt} \exp\left(-\frac{(x-Vt)^2}{4Dt}\right)$ and asymptotic decline of concentration as $\sqrt{\frac{a+b}{bDt}} \exp\left(-\frac{(a+b)(x-Vt)^2}{4bDt}\right)$ (see figure 1, central panel). This result was approved early by experimental data [10]. However, later experimental investigations are recognised that decreasing of concentration should be described by power law [15,16], nowadays many studies of transport in various porous media confirm that fact. It is known that the subdiffusive equation (6) has a solution with power-law asymptotic. Due to that fact, in the paper [17] the fractional variant of MIM model was suggested in the form

$$
\frac{\partial}{\partial t}(C + Q) = \nabla \cdot (DC - VC),
$$

where $0 < \beta < 1$ is the exponent of the Levy stable law and $\lambda$ is the mobility parameter. Equation (8) describes the breakthrough curve with the same as ADE early-time asymptote (increasing) and power-law late time (decreasing) asymptote in form $C \sim \frac{1}{\lambda^\beta} \exp \frac{Vx}{\lambda D}$ [25] (see figure 1, right panel). The solutions of MIM model have a good agreement with experimental data, but it means that the immobilized particles should spend very long time without motion. Attempts to model the immobilization process as a random walk process in channel with sticking particles to the walls, cannot give the specific distribution of waiting times ($w(t)$). The particle can stick to the wall only if it is at the distance about size of particle (see [26]). The random walks process is a standard homogeneous random process with finite moments. The probability of particle attaching and detaching obeys to the normal distribution and as a result, we have exponential asymptotic to the breakthrough curves. In this approach the influence of flow structure to the transportation process is not investigated. The next section is devoted to the demonstration that the consideration of velocity distribution on microscale can provide the power-law asymptotes with exponent $\beta < 1$.

![Figure 1](image-url)

**Figure 1.** The characteristic breakthrough curves for dissolution of concentration peak. Left panel – standard ADE equation (4). Central panel – linear MIM equation (7) for $a = 1, b = 1$. Right panel – MIM equation (8) for $\beta = 0.75, \lambda = 1$. The decline of concentration is indicated in each panel.
4. Transport through the channel

For simplicity we consider the transport of solute through the channel along \( x \) direction with plate walls. The velocity \( V(y) \) is given. We assume that the width of the channel is \( L = 1 \). Initial distribution of solute is homogeneous in the rectangular \( x \in [0, d] \) and \( y \in [0, 1] \). The boundary conditions on the channel walls are \( V(0) = V(1) = 0 \) (see figure 2). The problem of such transport is governed by

\[
\frac{\partial C(x, y, t)}{\partial t} + V \frac{\partial C(x, y, t)}{\partial x} = 0, \tag{9}
\]

where \( \theta(x) \) is Heaviside function. The initial conditions for a small value of \( d \) model the initial concentration peak. The solution of problem \((9)\) is \( C(x, y, t) = \theta(x - V(y)t) - \theta(x - V(y)t - d) \).

To compare with the experiments one needs to obtain average concentration near \( x = X \):

\[ \overline{C}(X, t) = \int_{X}^{X+d} dx \int_{0}^{1} C(x, y, t) dy. \]

The calculation of integral \( \overline{C}(X, t) \) is the same problem as calculation of shaded areas square in figure 2.

The equation \( X/t = V(y) \) for late time asymptotes \((t \to \infty)\) has only two roots localized near the walls \( y_1 = g_1(X/t) \) and \( y_2 = g_2(X/t) \). For each root we have one polygon (see figure 2). The sum of squares bounded by that polygons gives the asymptote of average concentration.

For small \( d \) we can estimate the average concentration as

\[ \overline{C}(X, t) = S_1 + S_2 \approx 2d^2 \left( \frac{\partial g_1(X/t)}{\partial X} - \frac{\partial g_2(X/t)}{\partial X} \right), \tag{10} \]

where \( S_1 \) and \( S_2 \) the squares of polygons near bottom and top walls consequently. For estimation of functions \( g_1 \) and \( g_2 \) we assume that near the wall (into the viscous boundary layer) the velocity profile can be approximated by the power law \( V \sim y^{q_1} \) near bottom wall and \( V \sim (1-y)^{q_2} \) near top wall. For the Poiseille flow \( q_1 = q_2 = 1 \) but in the porous media the form of profile is very complex. The flow through a grid of channels and solid clogs deforms the velocity profile, as well if the wall has the finite curvature, then \( q \) becomes more than 1 (for example, for sphere \( q = 2 \)). In the case of power law profile near the wall the solutions are \( q_1 = (X/t)^{1/q_1} \) and \( q_2 = 1 - (X/t)^{1/q_2} \). As a result, the average concentration long time asymptotics can be estimated as

\[ \overline{C}(X, t) \approx 2d^2 \left( X^{1/q_1} t^{-1/q_1} + X^{1/q_2} t^{-1/q_2} \right) \sim t^{-\frac{1}{q}}, \quad q = \max \{q_1, q_2\}. \tag{11} \]

The real porous media has an ensemble of channels for each of them we have the analogue of random jumps. We assume that distance \( X \) in the channel is the “length of jump” and \( \overline{C}(X, t) \) is the distribution of waiting time. In this case for any value of exponent \( q \geq 1 \) the first moment on time will be infinite and, thus, the resulted transport becomes subdiffusive.

5. Direct numerical calculation

In order to approve the estimation \((11)\) we provide the direct numerical calculations of problem \((9)\). For this we use implicit finite differences scheme with homogeneous grid. The problem was solved in rectangular channel with ratio (length to width) \( 20 \times 1 \). The profile of velocity sets by the function \( V = f(y) \). The boundary conditions on the side walls is given by \( C = 0 \). We solve the problem up to the time \( T = 20/f^* \), where \( f^* \) is the maximal value of function \( f(y) \). The breakthrough curve as the dependence of \( \overline{C}(X, t) = \int_{0}^{X} dx \int_{0}^{1} C(x, y, t) dy \) on time for \( X = 1 \) is presented in figure 3. As it can be seen from figure 3 the estimation \((11)\) is confirmed.
Figure 2. The example of concentration field evolution from initial peak \( (t = 0) \) to late time \( (t \gg 1) \). The initial concentration distributes homogeneously into the rectangular \( x \in [0, d] \) and \( y \in [0, 1] \) (left panel). The average concentration near \( x = X \) can be calculated as square of red shaded polygons (right panel).

Figure 3. The dependencies of \( C(X, t) \) on time for two profiles of velocity in the point \( X = 1 \). The dependencies are presented in linear scale (left panel) and in log-log scale (right panel). Curves 1 correspond to \( V(y) = y(1-y) \) (see the profile 1). Curves 2 correspond to \( V(y) = y(1-y) \) (see the profile 2). The power law asymptotes are indicated by red lines.

6. Conclusion
The possible mechanism of the anomalous transport through porous media is described. Usually, the anomalous transport is registered by the power-law late time asymptote for the breakthrough curve. The reason of anomalous transport is the slow motion near the solid walls of pores. The power of such asymptote is defined by the profile of flow in the boundary layer near the wall. The estimation of this law is obtained. Many aspects of this problem should be investigated additionally. The important feature is the influence of dispersion of channel width and velocity profile for the transport. Another factor is the influence of molecular diffusion and sorption of particles on the walls of channel. The accounting of these properties is the subject of future investigations.
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