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Application of Fractional Differential Equations for Modeling the Anomalous Diffusion of Contaminant from Fracture into Porous Rock Matrix with Bordering Alteration Zone

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Abstract Solute diffusion from a fracture into a porous rock with an altered zone bordering the fracture is modeled by a system of two diffusion equations (one for the altered zone and another for the intact porous matrix) with different coefficients of effective diffusivity. Since experimental studies of diffusion into rock samples with altered zones indicate that mathematical models of diffusion based on Fick's law do not adequately describe the concentration field in a sample, fractional order diffusion equations are chosen in this study for modeling the anomalous mass transport in the rocks. In the case of significantly higher porosity of the altered zone (e.g., this is typical for carbonates) the effective diffusivity here can be much higher than the effective diffusivity of non-altered rocks. By introducing a small parameter that is the ratio of effective diffusivities in the non-altered and altered regions and applying the technique of perturbations, approximate analytical solutions for concentrations in the altered zone bordering the fracture and in the intact surrounding rocks are obtained. Based on these solutions, different regimes of diffusion into the rocks with different physical properties are modeled and analyzed. It is shown that, using experimentally obtained data, the orders of the fractional derivatives in the differential equations can be readily calibrated for the every specific rock.

Keywords Solute transport · Asymptotic solution · Non-fickian diffusion · Porous medium · Altered zone · Fractional derivative · Laplace transform

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1 Introduction

Flow and solute transport in fractured porous rocks has gained increasing interest in the last few decades mostly due to concerns of the possible contamination of subsurface systems with hazardous materials. The fractured porous medium is made up of ordinary porous rocks with fractures in between them. In this medium, the contaminant is transported over long distances by the fluid flow along the fractures; simultaneously, it slowly diffuses into the bordering porous blocks. Penetration of the contaminant from water flowing along the fractures into the porous rock between the conducting fractures is the most important retardation mechanism. For instance, Neretnieks (1980) and Tang et al. (1981) have shown that this retardation effect can be tremendous for absorbing radioactive nuclides, allowing them to decay to insignificance. This study focuses only on one, though very important, factor that affects the overall mass transport in the fractured porous media; namely, on the contaminant diffusion from the fracture into the bordering rock matrix and its peculiarities. Field observations (Sato 1999; Sidle et al. 1998; Alexander 1992; Waber et al. 1998) show that the rock along fracture surfaces can be significantly altered. For example, in the case of carbonates, due to the mineral dissolution, the porosity of the rock matrix bordering the fractures can be much greater than within the intact regions, and this can substantially affect the diffusive transport of contaminants into surrounding rocks (Park et al. 2001; Steefel and Lichtner 1994, 1998a, b; Polak et al. 2003). A schematic of the process of diffusion from a fracture into the porous matrix with altered zone bordering the fracture is presented in Fig. 1. Conventional mathematical models of contaminant diffusion in the porous rocks are based on Fick's equation. However, recent experimental studies of the contaminant diffusion in rock samples with narrow alteration zones along the hydrothermal veins, extracted from the Kamaishi Mine, Iwate Prefecture, Japan, demonstrate the anomalous decay of concentration with distance from the vein, different from what can be predicted by Fick's equation (Yamamoto and Tsuchiya 2004). In these experiments, the novel thermo-luminescence technique (Tsuchiya et al. 2000; Tsuchiya and Nakatsuka 2002) coupled with the spectroscopic analysis of thermo-luminescence was applied as a geochemical sensor to evaluate the mass transport from the vein into the rock matrix. Experimental results for spatial distribution of concentration in a sample of porous rock with an altered narrow region bordering the fracture are represented by circles in Fig. 2. The predicted concentration obtained by solving the conventional diffusion equation based on Fick's law is presented in this figure by a dashed line. As it can be readily seen, Fick's law does not lead to the correct description of the contaminant concentration in the rock sample. In the field experiments carried out by Becker and Shapiro (2000), Haggerty et al. (2000), and Reimus et al. (2003) for the solute transport in highly heterogeneous media, the solute concentration profiles exhibited faster-than-Fickian growth rates, skewness, and sharp leading edges. These effects cannot be predicted by conventional mass transport equations. It was demonstrated in a number of publications (e.g. Benson et al. 2000a, 2001; Schumer et al. 2003; Meerschaert et al. 1999; Herrick et al. 2002; Chao et al. 2000; Boggs et al. 1992, 1993; Fomin et al. 2005) that fractional differential equations can simulate the anomalous character of solute transport in highly heterogeneous media. The anomalous character of diffusion can be mostly attributed to the complex heterogeneous structure of the rock matrix, which can be considered as a fractal, and also to the complex mechanisms of sorption of solute on the solid matrix. Diffusion in the media of fractal geometry was investigated extensively during the recent years. Relatively full review of different approaches to this problem can be found, for example, in Havlin and Ben-Avraham (2002). In Fomin et al. (2008a, b), it was mathematically proved that diffusion on fractals should be modeled by the fractional differential equation order of which depends on fractal dimension of the medium. A continuous time

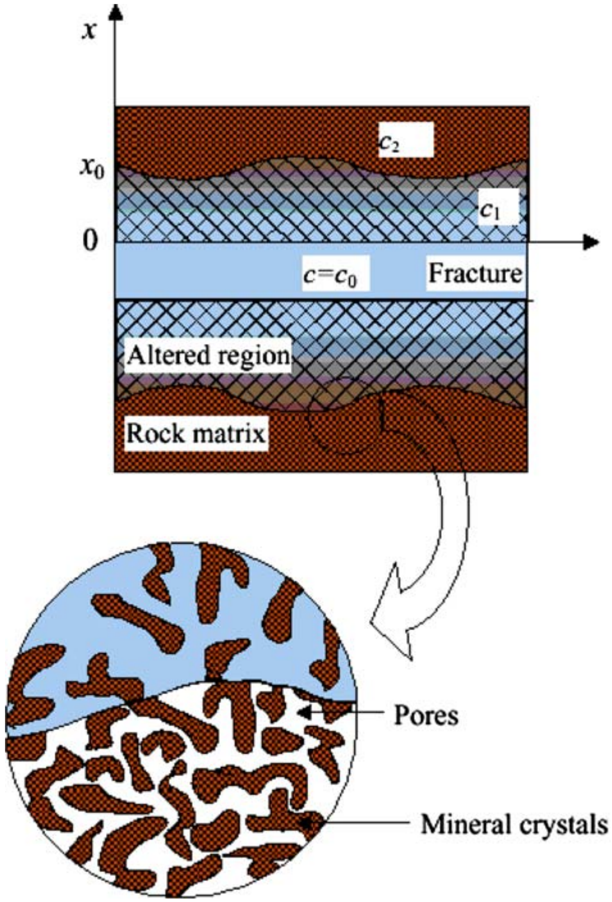

Fig. 1 A schematic of the process of diffusion from a fracture into the porous matrix with altered zone bordering the fracture

random walk (CTRW) formalism has been previously applied to quantify chemical transport in the porous and fractured geological formations (Berkowitz and Scher 1998, 1997, 1995; Margolin and Berkowitz 2000; Berkowitz et al. 2000). These studies demonstrated the relevance and effectiveness of the CTRW approach by analyzing numerical simulations, laboratory, and field measurements. Numerous authors (e.g. Hilfer and Anton 1995; Barkai et al. 2000) showed that, in the asymptotic case (large time and/or distances), the CTRW converges to fractional-order differential equations. Fractional differential equations, which may be viewed as long-time and long-space limit of CTRW, were successfully applied to describe anomalous diffusion phenomena in many areas (Metzler and Compte 2000; Metzler and Klafter 2000; Klafter et al. 1990; Meerschaert et al. 2002a, b, 2001; Saichev and Zaslavsky 1997; Compte 1996; Benson et al. 2000a, b, 2001; del-Castillo-Negrete et al. 2003; Redner 1990; Havlin and Ben-Avraham 2002; Giona and Roman 1992; Fomin et al. 2005). As it was pointed out, "…fractional differential equations have two advantages over a random walk approach: first, they allow one to explore various boundary conditions and, second, to study diffusion and/or relaxation phenomena in external fields. Both possibilities

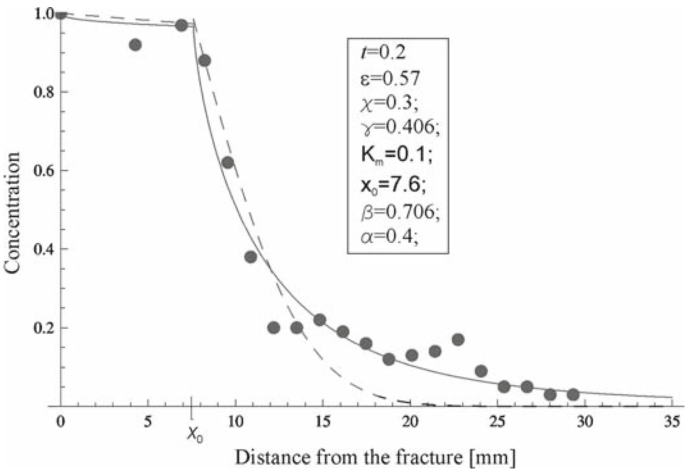

Fig. 2 Relative concentration of the solute in the rock sample: comparison of the computed results with experiment data (Solid line—non-Fickian anomalous diffusion modeled by fractional differential equations, dashed line—Fickian diffusion modeled by classical diffusion equations when $\chi = \gamma = \beta = \alpha = 1$)

are difficult to realize in the framework of CTRW" (Chechkin et al. 2002). In this article, the approach is based on application of fractional differential equations. The reported evidences of the anomalous character of diffusion motivated us to apply the non-Fickian law of diffusion with fractional order derivatives for analyzing the experimental data obtained by Yamamoto and Tsuchiya (2004), who studied diffusion in a rock matrix composed of two regions (a highly porous altered zone adjacent to the fracture and an intact, less porous rock).

2 Governing Equations

One-dimensional diffusion problem in the porous medium, when mass transport takes place in the direction of x-axis, can be described by the following equation $\frac{\partial c}{\partial \tau} = -\frac{\partial}{\partial x}(J_c)$, where J_c is the diffusion flux, and c is the solute concentration, and τ is the time. Apparently, the complexity of the porous matrix may lead to the sub-diffusive transport in the porous medium. The latter phenomenon can be modeled by introducing the fractional time derivatives in the equation of mass transport. In general, however, it cannot be ruled out that situations may occur when dispersion in the porous medium exhibits a super-diffusive behavior. This can be modeled by spatial fractional derivatives. Therefore, in order to account for both phenomena, the following expression for the mass flux will be considered:

$$J_c = -d\frac{\partial^{1-\gamma}}{\partial \tau^{1-\gamma}}\left(\frac{\partial^{\beta} c}{\partial x^{\beta}}\right), \quad 0 < \gamma \leq 1,\ 0 < \beta \leq 1, \tag{1}$$

where d is the effective diffusivity of the porous medium and parameters, γ and β, indicate the order of the temporal and spatial fractional derivatives, respectively. For example, $\gamma = \beta = 1$ corresponds to Fick's law. According to Caputo's definition, spatial and temporal fractional derivatives in Eq. 1 can be represented by the following expressions (Samko et al. 1993):

$$\frac{\partial^{\beta} c}{\partial x^{\beta}} = \int_0^x \frac{(x-\xi)^{-\beta}}{\Gamma(1-\beta)} \frac{\partial c}{\partial \xi} d\xi, \quad \frac{\partial^{\gamma} c}{\partial \tau^{\gamma}} = \int_0^{\tau} \frac{(\tau-\xi)^{-\gamma}}{\Gamma(1-\gamma)} \frac{\partial c}{\partial \xi} d\xi, \tag{2}$$

where $\Gamma(x)$ is Gamma function (Abramowitz and Stegun 1972). Substituting expression (1) into the equation of mass balance yields

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x}\left(d \frac{\partial^{1-\gamma}}{\partial \tau^{1-\gamma}}\left(\frac{\partial^{\beta} c}{\partial x^{\beta}}\right)\right), \tag{3}$$

Applying to the both sides of Eq. 3, the operation of fractional integration (Samko et al. 1993) leads to the following equation

$$\frac{\partial^{\gamma} c}{\partial \tau^{\gamma}} = \frac{\partial}{\partial x}\left(d \frac{\partial^{\beta} c}{\partial x^{\beta}}\right), \tag{4}$$

Equation 4 can be found in many publications related to anomalous diffusion phenomena and will constitute the basis of our mathematical model of diffusion in a porous matrix bordering a fracture. It is assumed that (i) a semi-infinite porous rock matrix $[0, \infty)$ is composed of two regions of different porosity separated by the sharp interface, which can be approximated by the straight line, e.g., $x = x_0$; (ii) porosity of either region is uniform; (iii) porosity of the altered region $[0, x_0]$ adjacent to the fracture surface $x = 0$ is much higher than the porosity of the intact rock matrix $[x_0, \infty)$. As a result, the effective diffusivity in the former region d_1 is much higher than that in the latter zone d_2 (i.e. $d_1 >> d_2$). Concentration of the diffusing substance c_0 at the surface $x = 0$ is sustained at a uniform level over the entire process. Along with big differences in porosities of the two regions, other physical properties of the porous media within these regions also might be significantly different (e.g., these regions might have different geometries of pores, different types of heterogeneities, different distributions of the pores, and micro-cracks, etc (Yu and Cheng 2002; Katz and Tompson 1985)). As mentioned above, these features can be modeled by fractional derivatives of different orders with respect to time and/or space in the mass flux equations. Accounting for the anomalous sub-diffusive and, for the sake of generality, for the possibly super-diffusive transport in both altered and intact regions, the mathematical model of anomalous diffusion in the porous rocks bordering the fracture (see Fig. 1) can be presented in the following form

$$\frac{\partial^{\chi} c_1}{\partial \tau^{\chi}} = d_1 \frac{\partial}{\partial x}\left[\frac{\partial^{\alpha} c_1}{\partial x^{\alpha}}\right], \quad 0 < x < x_0, \tau > 0; (0 < \alpha \leq 1, \quad 0 < \chi \leq 1); \tag{5}$$

$$\frac{\partial^{\gamma} c_2}{\partial \tau^{\gamma}} = d_2 \frac{\partial}{\partial x}\left[\frac{\partial^{\beta} c_2}{\partial x^{\beta}}\right], \quad x_0 < x < \infty, \tau > 0; (0 < \beta \leq 1, \quad 0 < \gamma \leq 1); \tag{6}$$

$$\tau = 0, c_1 = c_2 = 0; \tag{7}$$

$$x = 0, c_1 = c_0; \tag{8}$$

$$x = x_0, c_1 = c_2, \quad m^{(1)} d_1 \frac{\partial^{1-\chi}}{\partial \tau^{1-\chi}}\left(\frac{\partial^{\alpha} c_1}{\partial x^{\alpha}}\right) = m^{(2)} d_2 \frac{\partial^{1-\gamma}}{\partial \tau^{1-\gamma}}\left(\frac{\partial^{\beta} c_2}{\partial x^{\beta}}\right); \tag{9}$$

$$x \to \infty, c_2 \to 0; \tag{10}$$

where c_1 and c_2 are the concentrations in the altered, $(0, x_0)$, and non-altered, (x_0, ∞), regions of the rock matrix, respectively; τ[T] is time; x[L] is the spatial coordinate, and $d_1[\mathrm{L}^{1+\alpha}/\mathrm{T}^{\chi}]$ and $d_2[\mathrm{L}^{1+\beta}/\mathrm{T}^{\gamma}]$ are the effective diffusivities of solute in the altered and non-altered regions, respectively, and $m^{(1)}$ and $m^{(2)}$ are the porosities of the altered and non-altered regions, respectively. (In the above notation, expressions in square brackets denote dimensions of the variables, i.e., T and L are the dimensions of time and spatial variables, respectively). The fractional derivatives in Eqs. 5 and 6 are defined by expressions (2). The conditions of conjugation on the interface (9) model the mass conservation law on the interface of the two media with different physical properties and represent the fact that the values of concentration and diffusive mass flux, which is defined by Eq. 1, remain the same on the both sides of the interface. It is worth noting that the mathematical model (5)–(10) is one-dimensional. The accuracy of this natural approximation can be readily justified by the fact that concentration gradients in the rock matrix adjacent to the fracture in x-direction are much greater than gradients along the fracture (e.g., Tang et al. 1981; Grisak and Pickens 1981; Rahman et al. 2004; Neretnieks 1980). In order to convert the boundary-value problem (5)–(10) to non-dimensional form, the proper characteristic scales should be defined. Since concentrations in both regions $(0, x_0)$ and (x_0, ∞) are of concern, x_0 can be chosen as a scale for the variable x and, for the same reason, $\tau_0 = (x_0^{1+\beta}/d_2)^{1/\gamma}$ can then be taken as a characteristic scale for the time variable. Based on the above scales, the non-dimensional variables can be introduced as

$$C_i = \frac{c_i}{c_0}; \quad t = \frac{\tau}{\tau_0} = \frac{\tau d_2^{1/\gamma}}{x_0^{(1+\beta)/\gamma}}; \quad X = \frac{x}{x_0}; \quad \varepsilon = \frac{d_2^{\chi/\gamma}}{d_1} x_0^{1+\alpha-(1+\beta)\chi/\gamma};$$
$$K_m = \frac{m^{(2)}}{m^{(1)}}. \tag{11}$$

As a result, the non-dimensional mathematical model of diffusion in the rocks bordering the fracture can be presented in the following form:

$$\varepsilon D_t^{\chi} C_1 = D_X^{\alpha+1} C_1, \quad 0 < X < 1, t > 0; \tag{12}$$
$$D_t^{\gamma} C_2 = D_X^{\beta+1} C_2, \quad X > 1, t > 0; \tag{13}$$
$$t = 0, C_1 = C_2 = 0; \tag{14}$$
$$X = 0, C_1 = 1; \tag{15}$$
$$X = 1, C_1 = C_2, \quad D_t^{1-\chi} D_X^{\alpha} C_1 = \varepsilon K_m D_t^{1-\gamma} D_X^{\beta} C_2; \tag{16}$$
$$X \to \infty, C_2 \to 0; \tag{17}$$

where the following notation for the fractional derivatives defined by Eq. 2 is employed, namely, $D_X^{\alpha} C = \frac{\partial^{\alpha} C}{\partial X^{\alpha}}$, $D_t^{\chi} C = \frac{\partial^{\chi} C}{\partial t^{\chi}}$. In the particular case, when $\chi = \gamma = \alpha = \beta = 1$, the boundary-value problem (12)–(17) admits an exact analytical solution, which is derived in Appendix A. This solution can be used for verifying the accuracy of the approximate asymptotic solution found in the next section.

3 Approximate Solution

Presence of the small parameter ε in Eqs. 12–17 allows application of the method of perturbations for their solution. Solutions can be sought in the form of asymptotic series:

$$C_1(X, t) = \sum_{k=0}^{\infty} U_k(X, t)\varepsilon^k, \quad C_2(X, t) = \sum_{k=0}^{\infty} V_k(X, t)\varepsilon^k. \tag{18}$$

where $U_k(X, t)$ and $V_k(X, t)$ are the unknown functions, which will be defined later. Since the small parameter in the left-hand side of Eq. 12 is the coefficient before the derivative of concentration, C_1, with respect to time, it may happen that the solution for C_1, obtained in the form of series (18), will not satisfy the initial condition (14). This is the so-called outer solution. In order to obtain a uniform approximation, the inner solution that is valid in the vicinity of $t = 0$ should be found. This can be done by selecting a newly scaled time variable, $t^* = t/\phi(\varepsilon)$, where function $\phi(\varepsilon)$ should be determined from the analysis of the problem peculiarities. Finally, the uniform approximation can be formed by adding the inner and outer solutions and then subtracting their common limit. However, since the diffusive transport is a very slow process (it follows from the fact that the characteristic time of diffusion, $\tau_0 = \frac{x_0^2}{d_2}$, is large), early time contamination of the rock by hazardous materials is insignificant. Therefore, longer periods of contamination, when the contaminant in big amounts can penetrate into the intact rock matrix, should be of the major concern. Apparently, in the latter case, the outer solution is sufficiently accurate. Furthermore, by comparison with an exact solution found for $\chi = \gamma = \alpha = \beta = 1$, it will be shown that the outer solution is accurate enough within a wide range of variation of t and even for very short times ($t << 1$). Substituting the asymptotic series (18) into Eqs. 12–17 and collecting terms of the same order leads to the following set of boundary-value problems for U_k and V_k (where $k = 1, 2, 3 \cdots$):

for $k = 0$,

$$D_X^{\alpha+1} U_0 = 0, \quad 0 < X < 1, t > 0; X = 0, U_0 = 1; X = 1, \quad D_X^{\alpha} U_0 = 0; \tag{19}$$

$$D_t^{\gamma} V_0 = D_X^{\beta+1} V_0, \quad 1 < X < \infty, t > 0; t = 0, V_0 = 0; X = 1, V_0 = U_0; \\ X \to \infty, V_0 \to 0; \tag{20}$$

for an arbitrary $k \geq 1$,

$$D_X^{\alpha+1} U_k = D_t^{\chi} U_{k-1}, 0 < X < 1, t > 0; X = 0, U_k = 0; X = 1, \\ D_t^{1-\chi} D_X^{\alpha} U_k = K_m D_t^{1-\gamma} D_X^{\beta} V_{k-1}; \tag{21}$$

$$D_t^{\gamma} V_k = D_X^{\beta+1} V_k, \quad 1 < X < \infty, t > 0; t = 0, V_k = O; \\ X = 1, \; V_k = U_k; X \to \infty, V_k \to 0\cdot \tag{22}$$

From Eq. 19, it immediately follows that $U_0 \equiv 1$. Solution of the boundary-value problem (20) is not so straightforward. Introducing a new independent variable, $\eta = (X-1)t^{-\gamma/(1+\beta)}$, this problem can be converted to the boundary-value problem for the ordinary differential regarding the function V_0 of one variable, $V_0 = V_0(\eta)$. Unfortunately, the resulting equation is rather awkward and cannot be easily integrated analytically. Another approach that can lead to solution is the direct application of Laplace transform with respect to variable t to the Eq. 20 in its original form. Using the well-documented properties of Laplace transform, the differential Eq. 20 can be converted to the following ordinary differential equation

$$s^{\gamma} \bar{V}_0 - \frac{\partial}{\partial X}\left(\frac{\partial^{\beta} \bar{V}_0}{\partial X^{\beta}}\right) = 0, \tag{23}$$

where $\bar{V}_0(X, s) = L[V_0(X, t)]$ is Laplace transform of the function V_0 with respect to the independent variable t. In order to find the unique solution of Eq. 23, we have to account for the boundary conditions for $\bar{V}_0$. One boundary condition follows from the fact that the solution vanishes as $X \to \infty$, and the other can be obtained by applying the Laplace transform to the condition of the constant concentration on the interface (i.e. $X = 1$, $V_0(1, t) = 1$). Laplace transformation gives: $\bar{V}_0(1, s) = s^{-1}$. The problem similar to the boundary-value problem for Eq. 23 is considered in Appendix C. Its solution is determined by Eq. C12:

$$\bar{V}_0(X, s) = s^{-1}[E_{\beta+1}(s^{\gamma}(X-1)^{\beta+`1}) \\ -(s^{\gamma}(X-1)^{\beta+1})^{\beta/(\beta+1)} E_{\beta+1,\beta+1}(s^{\gamma}(X-1)^{\beta+1})] \tag{24}$$

where $E_{\beta+1}(z)$ and $E_{\beta+1,\beta+1}(z)$ are Mittag-Leffler functions (Appendix C). Applying the inverse Laplace transform, denoted by$L^{-1}[\cdot]$, to the Eq. 24 yields:

$$L^{-1}[\bar{V}_0(X,s)] = \{L^{-1}[s^{-1}E_{\beta+1}(s^{\gamma}(X-1)^{\beta+‘1})] \\ -L^{-1}[s^{-1}(s^{\gamma}(X-1)^{\beta+1})^{\beta/(\beta+1)}E_{\beta+1,\beta+1}(s^{\gamma}(X-1)^{\beta+1})]\} \quad (25)$$

Evaluation of the inverse Laplace transform can be performed by using the presentation of Mittag-Leffler functions in a form of power series, consequently applying the inverse Laplace transform to each of the terms in the series. Evaluating the first term in the right-hand side of Eq. 25, gives

$$L^{-1}[s^{-1}E_{\beta+1}(s^{\gamma}X^{\beta+‘1})] = \sum_{j=0}^{\infty}\frac{\left((X-1)^{\beta+1}t^{-\gamma}\right)^j}{\Gamma[(\beta+1)j+1]\Gamma(1-\gamma j)}, \quad (26)$$

The series (26) can be expressed through the new function $W_{a_2,b_2}^{a_1,b_1}(z)$defined in Appendix D. Since in our case $a_1 = 1$, $a_2 = \beta+1$, $b_1 = \gamma$, and $b_2 = 1$, expression (26) can be presented as

$$L^{-1}[s^{-1}E_{\beta+1}(s^{\gamma}(X-1)^{\beta+‘1})] = W_{\beta+1,1}^{1,\gamma}((X-1)^{\beta+1}/t^{\gamma}). \quad (27)$$

It should be noted that function $W_{a_2,b_2}^{a_1,b_1}(z)$ is defined only for $a_2 - b_1 > 0$. In the case under consideration, since $0 < \beta, \gamma < 1$, $a_2 - b_1 = 1+\beta-\gamma > 0$. Analogously to the above, then

$$L^{-1}[s^{-1+\beta\gamma/(\beta+1)}(X-1)^{\beta}E_{\beta+1,\beta+1}(s^{\gamma}X^{\beta+‘1})] \\ = ((X-1)^{\beta+1}/t^{\gamma})^{\beta/(\beta+1)}W_{\beta+1,\beta+1}^{1-\beta\gamma/(\beta+1),\gamma}((X-1)^{\beta+1}/t^{\gamma}). \quad (28)$$

Using correlations (27), (28), and (24), solution of the boundary-value problem (20), $V_0(X,t)$ $= L^{-1}[\bar{V}_0(X,s)]$ can be presented as a function of one variable η, $V_0(X,t) = \omega(\eta)$:

$$V_0(X,t) = \omega(\eta) = W_{\beta+1,1}^{1,\gamma}(\eta^{\gamma}) - \eta^{\gamma\beta/(\beta+1)}W_{\beta+1,\beta+1}^{1-\beta\gamma/(\beta+1),\gamma}(\eta^{\gamma}), \quad (29)$$

where $\eta = (X-1)^{(\beta+1)/\gamma}/t$.

From the Eq. 29, accounting for the definition of Caputo fractional derivative (2), the fractional derivative of $V_0(X,t) = \omega(\eta)$ at $X = 1$ can be presented as

$$D_X^{\beta}V_0\Big|_{X=1} = \frac{\partial^{\beta}V_0}{\partial X^{\beta}}\Big|_{X=1} = t^{-\gamma\beta/(\beta+1)}\frac{\partial^{\beta}\omega(\eta)}{\partial\eta^{\beta}}\Big|_{\eta=0} = \frac{-t^{-\gamma\beta/(\beta+1)}}{\Gamma[1-\gamma\beta/(1+\beta)]}. \quad (30)$$

Once V_0, $D_X^{\beta}V_0\Big|_{X=1}$, and U_0 are found, the boundary-value problem for U_1, which follows from (21), reduces to the following one:

$$D_X^{\alpha+1}U_1 = 0, 0 < X < 1, t > 0; \quad (31)$$

$$X = 0, U_1 = 0; X = 1, \quad D_t^{1-\chi}D_X^{\alpha}U_1 = -\frac{D_t^{1-\gamma}(t^{-\beta\gamma/(1+\beta)})K_m}{\Gamma(1-\gamma\beta/(1+\beta))}. \quad (32)$$

It can be readily shown that $D_t^{\lambda}t^{\mu} = -\frac{\Gamma(\lambda+1)t^{\mu-\lambda}}{\Gamma(1+(\mu-\lambda))}$ and, therefore, the boundary condition for the flux at $X = 1$ can be rewritten in the form

$$X = 1, \quad D_t^{1-\chi}D_X^{\alpha}U_1 = -\frac{t^{-1+\gamma/(1+\beta)}K_m}{\Gamma(\gamma/(1+\beta))}, \quad (33)$$

Applying an operation of fractional integration with respect to time (Samko et al. 1993) to the Eq. 33 yields

$$X = 1, \quad D_X^{\alpha} U_1 = -\frac{t^{-\chi+\gamma/(1+\beta)} K_m}{\Gamma\left(1-\chi+\gamma/(1+\beta)\right)} + At^{-\chi}\cdot \tag{34}$$

where A is a constant of integration, which is due to the initial condition which should vanish. Accounting for the expression (34), where $A = 0$, solution of the problems (31) and (32) is rather straightforward:

$$U_1(X, t) = -\frac{X^{\alpha} t^{-\chi+\gamma/(1+\beta)} K_m}{\Gamma\left[1-\chi+\gamma/(1+\beta)\right]\Gamma(1+\alpha)}\cdot \tag{35}$$

As a result of this solution, the boundary-value problem for V_1, which follows from the formulae (22), where k should be set equal to 1, can be represented as

$$D_t^{\gamma} V_1 = D_X^{\beta+1} V_1, \quad 1 < X < \infty, t > 0; \tag{36}$$

$$t = 0,\ V_1 = 0;\ X = 1,$$

$$V_1 = U_1 = -\frac{t^{-\chi+\gamma/(1+\beta)} K_m}{\Gamma\left[1-\chi+\gamma/(1+\beta)\right]\Gamma(1+\alpha)};\ X \to \infty,\ V_1 \to 0\cdot \tag{37}$$

Solution of the problem (36) and (37) can be sought in the following form:

$$V_1(X, t) = -\frac{K_m t^{-\chi+\gamma/(1+\beta)}}{\Gamma\left(1-\chi+\gamma/(1+\beta)\right)\Gamma(1+\alpha)} f(\eta), \tag{38}$$

where $f(\eta)$ is an unknown function of one variable $\eta = \frac{X-1}{t^{\gamma/(1+\beta)}}$. Analogously to the above, it can be readily shown that

$$f(\eta) = W_{\beta+1,1}^{1-\chi+\frac{\gamma}{1+\beta},\gamma}\left(\eta^{1+\beta}\right) - \eta^{\beta} W_{\beta+1,\beta+1}^{1-\chi+\frac{\gamma(1-\beta)}{1+\beta},\gamma}\left(\eta^{1+\beta}\right)\cdot \tag{39}$$

Finally, solution of the problem in both altered and intact regions with an accuracy of $O(\varepsilon^2)$can be presented in the following form:

$$C_1(X, t) = 1 - \frac{\varepsilon K_m X^{\alpha} t^{-\chi+\gamma/(1+\beta)}}{\Gamma\left[1-\chi+\gamma/(1+\beta)\right]\Gamma(1+\alpha)} + O(\varepsilon^2), \quad 0 < X < 1, t > 0, \tag{40}$$

$$C_2(X, t) = \omega\left(\frac{X-1}{t^{\gamma/(1+\beta)}}\right) - \frac{\varepsilon K_m t^{-\chi+\gamma/(1+\beta)}}{\Gamma\left[1-\chi+\gamma/(1+\beta)\right]\Gamma(1+\alpha)} f\left(\frac{X-1}{t^{\gamma/(1+\beta)}}\right)$$
$$+ O(\varepsilon^2), \quad 1 < X < \infty, t > 0, \tag{41}$$

where ω and f are defined by Eqs. 29 and 39 respectively.

The important particular case, when mass transport exhibits only a subdiffusive character, can be obtained from the solutions (40) and (41) by substituting there and in Eqs. 29 and 39 parameters $\alpha = \beta = 1$. It is interesting to note that, when $\alpha = \beta = 1$, the boundary-value problem (20) for V_0 and the boundary-value problems (36) and (37) for V_1 admit solutions in an integral form. For $\alpha = \beta = 1$, solution of the Eq. 23 in transforms is $\bar{V}_0(X, s) = s^{-1}\exp[-s^{\gamma/2}(X-1)]$ and, hence, application of the inverse Laplace transform $L^{-1}[\bar{V}_0]$ leads to the following expression:

$$V_0(X,t) = \frac{1}{\pi}\int_0^t d\tau \int_0^\infty e^{-\tau\xi}\exp[-(X-1)\xi^{\gamma/2}\cos(\frac{\gamma\pi}{2})]\sin[(X-1)\xi^{\gamma/2}\sin(\frac{\gamma\pi}{2})]d\xi$$
$$= 1 - \frac{1}{\pi}\int_0^\infty \frac{e^{-t\xi}}{\xi}\exp[-(X-1)\xi^{\gamma/2}\cos(\frac{\gamma\pi}{2})]\sin[(X-1)\xi^{\gamma/2}\sin(\frac{\gamma\pi}{2})]d\xi = \quad (42)$$

Analogously to the above, if $\alpha = \beta = 1$, application of Laplace transform to the problems (36) and (37), gives $\bar{V}_1(X,s) = -K_m s^{-1+\chi-\gamma/2}\exp[-s^{\gamma/2}(X-1)]$. Hence, the inverse transformation leads to the formula

$$V_1(X,t) = -\frac{K_m}{\pi\Gamma(1-\chi+\gamma/2)}\int_0^\infty \exp[-(X-1)\xi^{\gamma/2}\cos(\frac{\gamma\pi}{2})]$$
$$\times \sin[(X-1)\xi^{\gamma/2}\sin(\frac{\gamma\pi}{2})]d\xi \int_0^t e^{-\tau\xi}(t-\tau)^{-\chi+\gamma/2}d\tau \quad (43)$$

So in the latter case, Eq. 41 can be replaced by

$$C_2(X,t) = V_0(X,t) + V_1(X,t)\varepsilon \quad (44)$$

where V_0 and V_1 are defined by the integrals (42) and (43).

It can be easily shown (Appendix B) that in the particular case of Fickian diffusion, when $\gamma = \chi = \alpha = \beta = 1$, Eqs. 40 and 41 can be substantially simplified:

$$C_1(X,t) = 1 - \frac{\varepsilon K_m X}{\sqrt{\pi t}} + O(\varepsilon^2), \quad (45)$$

$$C_2(X,t) = \mathrm{erfc}\left(\frac{X-1}{2\sqrt{t}}\right) - \frac{\varepsilon K_m}{\sqrt{\pi t}}\exp\left[-\frac{(X-1)^2}{4t}\right] + O(\varepsilon^2)\cdot \quad (46)$$

4 Numerical Results and Discussion

Particular solutions (42)–(46) can be used for testing the accuracy of the general solutions (40) and (41). The numerical experiments with Eqs. 40, 41, 39, and (29) show that, in the particular case, when $\gamma = \chi = \alpha = \beta = 1$, the computed functions ω and f coincide up to the 10th decimal place with their exact values $\mathrm{erfc}(\eta/2)$ and $\exp(-\eta^2/4)$, respectively. Hence, for $\gamma = \chi = \alpha = \beta = 1$, solutions (40) and (41) coincide with solutions (45) and (46).

As mentioned above, the formulae (40) and (41) represent the outer asymptotic solutions of the boundary-value problem (12)–(17). Therefore, it might be expected that these solutions are only valid for sufficiently large times. However, numerical computations demonstrate that these solutions are accurate enough for all finite times and can be used even for relatively short durations ($t < 1$). The applicability of the outer asymptotic solutions for modeling diffusion at the initial moments of time ($t < 1$) can be justified by comparing these solutions with exact solutions (A5) and (A6) obtained in Appendix A for the case when $\gamma = \chi = \alpha = \beta = 1$. The numerical computations based on the approximate Eqs. 42 and 43 and on exact formulae (A5) and (A6) are presented in Fig. 3a–c by dashed and solid curves, respectively. Observing the graphs in Fig. 3a, which correspond to $\varepsilon = 0.01$, it can be readily seen that for very short values of parameter ε, the exact (solid lines) and asymptotic (dashed lines) solutions nearly coincide already at very short times ($t = 0.02$). For the greater values of $\varepsilon(\varepsilon = 0.05)$, the discrepancy between these solutions slightly increases for the very short times. However, starting from $t = 0.08$, the agreement between the asymptotic and exact

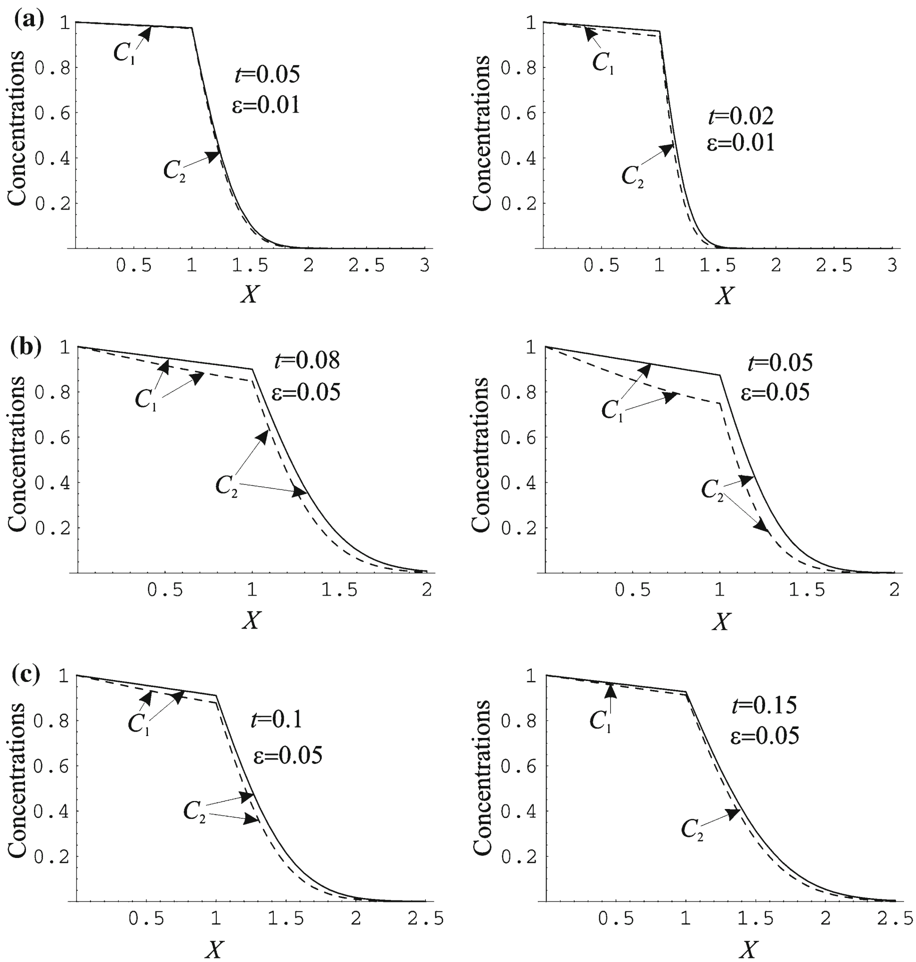

Fig. 3 (**a–c**) Comparison of exact (A5), (A6), and asymptotic solutions (45), (46) for Fickian diffusion at short times

solutions is already good, and for $t = 0.15$, the solutions are again in perfect consistency (see Fig. 3b, c). These results indicate that the obtained asymptotic solutions are suitable for modeling the non-Fickian diffusion shortly after the onset of diffusion. It is interesting to note that accuracy of the approximate solution is sufficiently good even for ε close to unity since every term of asymptotic expansion (except the leading term) is factored by K_m, which is less than unity for the process under consideration. Furthermore, each k-th term in the asymptotic expansion is proportional to the expression $\varepsilon^k t^{-k\sigma}$, where the value of $\sigma > 0$ can be found by constructing the next terms in the asymptotic expansions. Therefore, even assuming hypothetically that $\varepsilon = K_m = 1$, there exists such a moment of time starting from which the accuracy of the asymptotic formulae will be sufficiently good. This fact is illustrated by computations presented in Fig. 3, though the computations are made for the small values of ε.

Parameters α, β, γ, and χ in the obtained solutions can be defined by accounting for the typical physical properties of the specific rock. If the spatial distribution of concentration in the rock is measured experimentally at the given moment of time, then these unknown parameters can be readily determined by comparing the experimentally and theoretically obtained concentration distributions. This process is known as calibration of the model for the specific rock formation. It can be performed, for example, by minimizing the root mean square deviation, D, between the computed values and experimental data,

$$D = \left[\sum_{i=1}^{m} \left(C_1(X_i, t_0) - C_i^* \right)^2 + \sum_{i=m+1}^{n} \left(C_2(X_i, t_0) - C_i^* \right)^2 \right]^{1/2} \tag{47}$$

where C_i^* $(i = 1, 2, \ldots, n)$ are the experimentally measured values of concentration at n points $X = X_i$ of the rock sample, the value of summation index $i = m$ corresponds to location of the altered-intact interface between altered and intact zones (i.e. $X = X_m = 1$), C_1 and C_2 are computed by the formulae (40) and (41), respectively. The minimum of D and the corresponding values of controlling parameters α, β, γ, and χ can be easily computed by using the standard numerical optimization operators available in *Mathematica* computer algebra system. For instance, considering the experimental results of Yamamoto and Tsuchiya (2004) (the contaminant diffusion in rock samples with narrow alteration zones along the hydrothermal veins), which are indicated by dots in Fig. 2, it can be readily seen that the root mean square deviation between the computed and experimental data, D, reaches its minimal value 0.057 at $\beta = 0.7$, $\gamma = 0.4$, $\alpha = 0.4$, and $\chi = 0.3$. The corresponding concentration distribution obtained from the formulae in the solutions (40) and (41), which is presented by a solid line in Fig. 2, demonstrates a very good agreement with experimental results. For the Fickian diffusion (solutions (45) and (46)), the root mean square deviation $D = 0.09$, which is almost two times bigger than in the case of non-Fickian diffusion with optimal values of controlling parameters β, γ, α, and χ. Hence, it can be concluded that for the rock sample from the Kamaishi Mine, Iwate Prefecture, Japan, the mass flux in the narrow altered zone can be modeled by the fractional derivatives of order $\alpha = 0.4$, $\chi = 0.3$, whereas, for the diffusive transport in the intact rock, the spatial and temporal fractional derivatives should be defined by the parameters $\beta = 1$ and $\gamma = 0.5$, respectively. Sensitivity of the asymptotic solutions (40) and (41) to the variation of parameters α and β, which define the order of the spatial fractional derivatives, is illustrated in Fig. 4a, b. For the fractional derivatives of the smaller order, the graphs of solutions demonstrate a sharp decline of concentration in the intact rocks near the altered region. In this case, the concentration curves have greater skewness and heavier tails. This is consistent with results of previous studies of fractional order equations. Figure 4a demonstrates that accounting for the non-Fickian transport in the intact rock will affect diffusion in the altered zone even in the case when diffusion in the altered zone is modeled by of the Fick's law ($\alpha = 1$). Although the concentration profile in the altered region in the latter case is linear, it does not exactly follow the conventional Fickian distribution presented by the solid line. For the case of Fickian diffusion in the altered region (Fig. 4a), it is interesting to note that at the greater times ($t > 1$) Fickian diffusion leads to a higher concentration in the altered region and in the intact rocks near this region, whereas for the shorter times ($t < 0.1$) the Fick's law leads to the lower values of concentration in the altered zone and higher values in the intact rock. In the case when diffusion in the altered region is non-Fickian (Fig. 4b), concentration curves in the altered zone also demonstrate some moderate skewness, though this effect is not so pronounced as in the intact region.

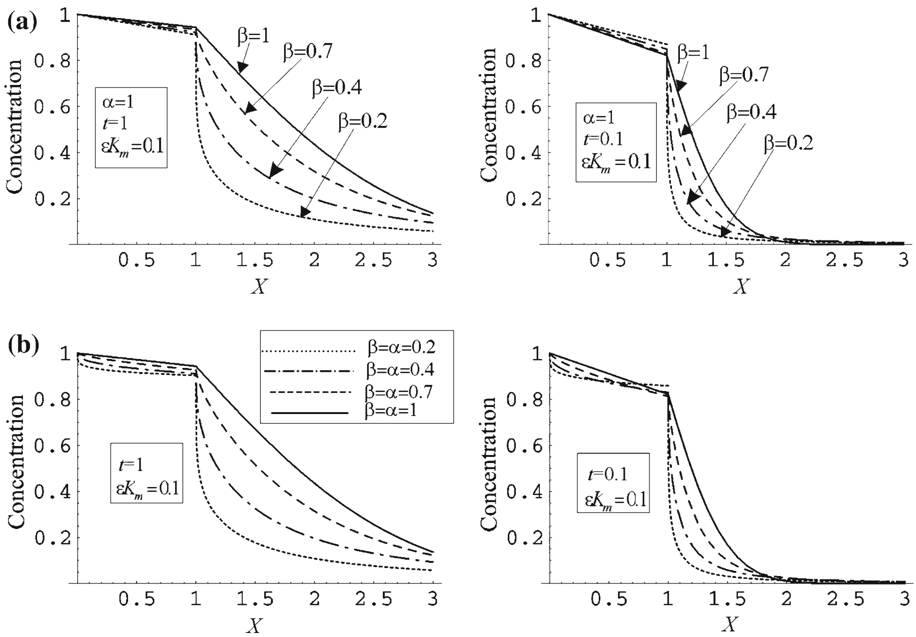

Fig. 4 (**a, b**) Variation of concentration in the direction perpendicular to the fracture computed by Eqs. 40 and 41: illustration of sensitivity of the non-Fickian model to variation of the orders of fractional derivatives

5 Conclusions

The following conclusions can be drawn:

Using the fractional order diffusion equations, the non-Fickian anomalous mass transport in the porous rocks with altered region bordering the fracture is modeled; closed-form solutions of the governing fractional differential equations are obtained.

The accuracy of the outer asymptotic solutions of non-Fickian diffusion for small times is proved by comparison with exact analytical solutions available for the particular case of Fickian diffusion ($\gamma = \chi = \beta = \alpha = 1$). This result confirms the applicability of the obtained solutions for modeling solute transport in a heterogeneous porous medium of complex geometry for all the moments of time of practical importance.

Introducing a fractional derivative into the equation of mass transport in a porous medium leads to the model that is capable to describe the mechanisms of anomalous diffusion. This model can be properly calibrated for simulating diffusion in the specific rock formation by choosing the appropriate order of fractional derivative, which provides the best fit between the measured and calculated concentration distributions.

The complex phenomena of anomalous diffusion in the heterogeneous rock matrix can be effectively modeled by choosing the proper values of parameters β, α, γ, and χ, which simulate the properties of the porous media and solute.

Appendix A: An Exact Solution of the Fickian Diffusion Problem ($\alpha = \beta = \chi = \gamma = 1$, $K_m = 1$)

In the particular case when $\alpha = \beta = \chi = \gamma = 1$, the boundary-value problem (12)–(17) can be solved by Laplace transformation with respect to t. For Laplace transforms, the problem

(12)–(17) reduces to

$$\varepsilon s\overline{C}_1 = \frac{d^2\overline{C}_1}{dX^2}, s\overline{C}_2 = \frac{d^2\overline{C}_2}{dX^2}, \tag{A1}$$

$$X = 0, \overline{C}_1 = 1/s;\ X = 1, \overline{C}_1 = \overline{C}_2, \quad \partial\overline{C}_1/\partial X = \varepsilon(\partial\overline{C}_2/\partial X);\ X \to \infty, \overline{C}_2 \to 0; \tag{A2}$$

where a bar above a variable indicates a function after application of Laplace transform L, e.g., $\overline{C} = L[C]$, and s is the Laplace variable, which corresponds to the variable t.

Solution of Eq. A1 with boundary conditions (A2) is rather straightforward:

$$s\overline{C}_1 = \frac{(1-\sqrt{\varepsilon})e^{-\sqrt{s}[1+\sqrt{\varepsilon}(1-X)]} + (1+\sqrt{\varepsilon})e^{-\sqrt{s}[1-\sqrt{\varepsilon}(1-X)]}}{(1-\sqrt{\varepsilon})e^{-\sqrt{s}(1+\sqrt{\varepsilon})} + (1+\sqrt{\varepsilon})e^{-\sqrt{s}(1-\sqrt{\varepsilon})}}, \quad 0 < X < 1, \tag{A3}$$

$$s\overline{C}_2 = \frac{2e^{-\sqrt{s}X}}{(1-\sqrt{\varepsilon})e^{-\sqrt{s}(1+\sqrt{\varepsilon})} + (1+\sqrt{\varepsilon})e^{-\sqrt{s}(1-\sqrt{\varepsilon})}}, \quad X > 1, \tag{A4}$$

Converting Eq. A4 to the following form

$$\begin{aligned} s\overline{C}_2 &= \frac{e^{-\sqrt{s}(X-1+\sqrt{\varepsilon})}}{(1+\sqrt{\varepsilon})} \frac{2}{1+[(1-\sqrt{\varepsilon})/(1+\sqrt{\varepsilon})]e^{-2\sqrt{\varepsilon s}}} \\ &= 2\frac{e^{-\sqrt{s}(X-1+\sqrt{\varepsilon})}}{(1+\sqrt{\varepsilon})} \sum_{k=0}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k e^{-2k\sqrt{\varepsilon s}} \\ &= \frac{2}{(1+\sqrt{\varepsilon})} \sum_{k=0}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k \exp[-\sqrt{s}(X-1+\sqrt{\varepsilon}+2k\sqrt{\varepsilon})]. \end{aligned}$$

and applying to it the inverse Laplace transform, L^{-1}, yields

$$C_2(X,t) = \frac{2}{(1+\sqrt{\varepsilon})} \sum_{k=0}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k \operatorname{erfc}\left[\frac{X-1+\sqrt{\varepsilon}(1+2k)}{2\sqrt{t}}\right]. \tag{A5}$$

Analogously, since Eq. A3 can be rewritten as

$$\begin{aligned} s\overline{C}_1 = &\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}} e^{-\sqrt{s\varepsilon}(2-X)} \sum_{k=0}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k e^{-2k\sqrt{\varepsilon s}} \\ &+ e^{-\sqrt{s\varepsilon}X} \sum_{k=0}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k e^{-2k\sqrt{\varepsilon s}}, \end{aligned}$$

its inverse Laplace transformation gives

$$\begin{aligned} C_1(X,t) = \operatorname{erfc}\left[\frac{\sqrt{\varepsilon}X}{2\sqrt{t}}\right] + \sum_{k=1}^{\infty} (-1)^k \left(\frac{1-\sqrt{\varepsilon}}{1+\sqrt{\varepsilon}}\right)^k \left\{\operatorname{erfc}\left[\frac{\sqrt{\varepsilon}(2k+X)}{2\sqrt{t}}\right]\right. \\ \left. - \operatorname{erfc}\left[\frac{\sqrt{\varepsilon}(2k-X)}{2\sqrt{t}}\right]\right\}. \end{aligned} \tag{A6}$$

Formulae (A5) and (A6) present the exact closed-form solution of the boundary-value problem (12)–(17) for the case of Fickian diffusion when $\alpha = \beta = \chi = \gamma = 1$.

Appendix B: An Approximate Solution for the Fickian Diffusion ($\alpha = \beta = \chi = \gamma = 1$, $K_m = 1$)

An approximate solution (45), (46) of the boundary-value problem (12)–(17), for the particular case when $\alpha = \beta = \chi = \gamma = 1$, is obtained by using the perturbation technique, similar to how it was done above. This means that from Eqs. 19 and 20 it follows that $U_0 \equiv 1$ and $V_0 = \operatorname{erfc}\left(\frac{X-1}{2\sqrt{t}}\right)$. Evaluating Eq. 21 for $k \geq 1$ gives the following recurrent formula:

$$U_k(X,t) = \frac{\partial}{\partial t}\int_0^X (X-\xi)U_{k-1}d\xi + \left.\frac{\partial V_{k-1}}{\partial X}\right|_{X=1} X. \tag{B1}$$

From Eq. 22, accounting for the Duhamel's theorem (Carslaw and Jaeger 1959), it follows that

$$V_k(X,t) = \frac{\partial}{\partial t}\int_0^t U_k(X,\tau)\operatorname{erfc}\left(\frac{X-1}{2\sqrt{t-\tau}}\right)d\tau. \tag{B2}$$

Equations B1 and B2 in the particular case when k=1 give

$$U_1 = -\frac{X}{\sqrt{\pi t}},$$
$$V_1(X,t) = -\frac{\partial}{\partial t}\int_0^t \frac{X}{\sqrt{\pi t}}\operatorname{erfc}\left(\frac{X-1}{2\sqrt{t-\tau}}\right)d\tau = -\frac{1}{\sqrt{\pi t}}e^{-\frac{(X-1)^2}{4t}}.$$

As a result, with an accuracy of $O(\varepsilon^2)$, the approximate solution can be written as

$$C_1 = 1 - \frac{X}{\sqrt{\pi t}}\varepsilon + O(\varepsilon^2), \tag{B3}$$
$$C_2(X,t) = \operatorname{erfc}\left(\frac{X-1}{2\sqrt{t-\tau}}\right) - \frac{\varepsilon}{\sqrt{\pi t}}e^{-\frac{(X-1)^2}{4t}} + O(\varepsilon^2). \tag{B4}$$

Appendix C: Solution of the Boundary-Value Problem for the Eq. 23

Denoting for simplicity in Eq. 23 and corresponding boundary conditions, $p = \bar{V}_0$, $p_0 = s^{-1}$, $\lambda = s^\gamma$, and $\tilde{X} = X - 1$, leads to the following boundary-value problem:

$$\frac{d}{d\tilde{X}}\left(\frac{d^\beta p}{d\tilde{X}^\beta}\right) - \lambda p = 0; \quad 0 < \beta < 1, \tag{C1}$$
$$\tilde{X} = 0,\ p = p_0; \quad \tilde{X} \to \infty,\ p \to 0 \tag{C2}$$

where $\frac{d^\beta p}{d\tilde{X}^\beta}$ is the fractional derivative of the order β.

After application of Laplace transform with respect to the variable $\tilde{X}$, Eq. C1 takes the following form

$$s[s^\beta \hat{p} - s^{\beta-1}p_0] - q_0 - \lambda\hat{p} = 0, \tag{C3}$$

where $\hat{p} = L[p]$ is Laplace transform of function p regarding the spatial variable X and $q_0 = \left.\frac{d^\beta p}{dX^\beta}\right|_{X=1}$ is an unknown constant. Equation C3 gives

$$\hat{p} = p_0\frac{s^\beta}{s^{\beta+1} - \lambda} + q_0\frac{1}{s^{\beta+1} - \lambda}. \tag{C4}$$

At this point, it is convenient to introduce Mittag-Leffler functions defined by the series that are valid in the whole complex plane C (Samko et al. 1993):

$$E_\alpha(z) \equiv \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + 1)}; \quad E_{\alpha,\beta}(z) \equiv \sum_{n=0}^{\infty} \frac{z^n}{\Gamma(\alpha n + \beta)}, \quad \alpha > 0, \beta > 0, z \in \boldsymbol{C}. \tag{C5}$$

Mittag-Leffler functions are connected to the Laplace integral through equations

$$\begin{aligned} L[E_\alpha(-\lambda t^\alpha)] &= s^{\alpha-1}/(s^\alpha + \lambda),\ Res > |\lambda|^{1/\alpha}, \\ L[t^{\beta-1}E_{\alpha,\beta}(-\lambda t^\alpha)] &= s^{\alpha-\beta}/(s^\alpha + \lambda),\ Res > |\lambda|^{1/\alpha}. \end{aligned} \tag{C6}$$

Accounting for the relationships (C6), Eq. C3 yields

$$p(\tilde{X}, \lambda) = p_0 E_{\beta+1}(\lambda \tilde{X}^{\beta+1}) + q_0 \tilde{X}^\beta E_{\beta+1,\beta+1}(\lambda \tilde{X}^{\beta+1}). \tag{C7}$$

Taking into account the properties of Mittag-Leffler functions (Samko et al. 1993), it can be readily shown that

$$\lambda \tilde{X}^\beta E_{\beta+1,\beta+1}(\lambda \tilde{X}^{\beta+1}) = \frac{d}{d\tilde{X}}[E_{\beta+1}(\lambda \tilde{X}^{\beta+1})]. \tag{C8}$$

Formula (C7) defines the general solution of Eq. C1. In order to find the solution, which satisfies conditions at infinity, $P \to 0$, $\tilde{X} \to \infty$, the following asymptotic representations of Mittag-Leffler functions can be utilized:

$$\begin{aligned} E_{\alpha,\beta}(z) &= \frac{z^{(1-\beta)/\alpha}}{\alpha} \exp(z^{1/\alpha}) - \sum_{k=1}^{\infty} \frac{z^{-k}}{\Gamma(\beta - k\alpha)}, \quad |z| \to \infty, |\arg z| < \alpha\pi/2, \\ E_{\alpha,\beta}(z) &= -\sum_{k=1}^{\infty} \frac{z^{-k}}{\Gamma(\beta - k\alpha)}, |z| \to \infty, \alpha\pi/2 < \arg z < 2\pi - \alpha\pi/2. \end{aligned} \tag{C9}$$

where $0 < \alpha < 2$.

From the Eqs. C7–C9, it follows that

$$\lim_{\tilde{X}\to\infty} p(\tilde{X}, \lambda) = (p_0 + q_0 \lambda^{-\beta/(1+\beta)}) \lim_{\tilde{X}\to\infty} [(\beta+1)^{-1} \exp(\lambda^{1/(1+\beta)} \tilde{X})] = 0. \tag{C10}$$

The last condition can be satisfied, if the expression $(p_0 + q_0\lambda^{-\beta/(1+\beta)})$ is equal to zero. Therefore, $q_0 = -p_0\lambda^{\beta/(1+\beta)}$ and solution (C7) of the boundary-value problem (C1) and (C2) can be presented as

$$p(\tilde{X}, \lambda) = p_0 \left[E_{\beta+1}(\lambda \tilde{X}^{\beta+1}) - \lambda^{\beta/(1+\beta)} \tilde{X}^\beta E_{\beta+1,\beta+1}(\lambda \tilde{X}^{\beta+1}) \right]. \tag{C11}$$

Hence, returning back from $p(\tilde{X}, \lambda)$ to the variable $\bar{V}_0(X, s)$, Eq. C11 yields

$$\begin{aligned} \bar{V}_0(X, s) &= s^{-1}[E_{\beta+1}(s^\gamma (X-1)^{\beta+‘1}) \\ &\quad - (s^\gamma (X-1)^{\beta+1})^{\beta/(\beta+1)} E_{\beta+1,\beta+1}(s^\gamma (X-1)^{\beta+1})] \end{aligned} \tag{C12}$$

Appendix D: Definition of the Function $W_{a_2,b_2}^{a_1,b_1}(z)$

Let us consider a series

$$W_{a_2,b_2}^{a_1,b_1}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(a_2 k + b_2)\Gamma(a_1 - b_1 k)}, \quad a_2, b_2, b_1 > 0. \tag{D1}$$

Using the Stirling's formula for the Gamma function (Abramowitz and Stegun 1972),

$$\Gamma(z+1) = \sqrt{2\pi}\,|z|^{z+1/2}\exp(-z)[1+O(|z|^{-1})], \tag{D2}$$

it can be shown that

$$\begin{aligned} &|\Gamma(a_2k+b_2)\Gamma(a_1-b_1k)| \\ &\quad\sim (\sqrt{2\pi})^{2-a_2+b_1}\left(a_2^{a_2}b_1^{-b_1}\right)^k a_2^{b_2-1/2}b_1^{a_1-1/2}(k!)^{a_2-b_1}k^{b_2+a_1-1-(a_2-b_1)/2}. \end{aligned} \tag{D3}$$

Substituting formula (D3) into the series (D1), it can be readily seen that the series absolutely converges along with the following series

$$\sum_{k=0}^{\infty} u_k = \sum_{k=0}^{\infty} \frac{\left|\hat{z}\right|^k}{(k!)^{a_2-b_1}k^{\chi}}, \tag{D4}$$

where $\hat{z} = (zb_1^{b_1}/a_2^{a_2})$, $\chi = b_2 + a_1 - 1 - (a_2 - b_1)/2$.

Apparently, for the series (D4), the following relationship can be easily validated:

$$k\left(\frac{u_k}{u_{k+1}} - 1\right) \sim \frac{k^{1+a_2-b_1}}{\left|\hat{z}\right|}\left(1 - \left|\hat{z}\right| k^{-(a_2-b_1)}\right), \quad k \to \infty. \tag{D5}$$

From the formula (D5), it follows that if $(a_2 - b_1) > 0$, then, for any positive constant A and $\hat{z} < \infty$, there exists a number N, such that the following inequality is satisfied

$$k\left(\frac{u_k}{u_{k+1}} - 1\right) \geq A > 1, \quad (k > N)\,. \tag{D6}$$

Therefore, according to the Raabe's test (Arfken 1985), series (D4) and (D1) converge for any finite z. If $(a_2 - b_1) < 0$, the series (D4) diverges and, therefore, the series(D1) does not converge absolutely. If $a_2 = b_1$, the series (D4) converges only when $\left|\hat{z}\right| < 1$ and, consequently, the series (D1), converges absolutely only for $|z| < 1$. Thus, if $a_2 > b_1$, the series (D1) converges absolutely and, therefore, function $W_{a_2,b_2}^{a_1,b_1}(z)$ is defined for any finite z.

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