

# On the Transient Non-Fickian Dispersion Theory

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(Received: 20 June 1995; in final form: 11 December 1995)

**Abstract.** The Fickian dispersion equation is the basic relationship used to describe the nonconvective mass flux of a solute in a porous medium. This equation prescribes a linear relationship between the dispersive mass flux and the concentration gradient. An important characteristic of the Fickian relationship is that it is independent of the history of dispersion (e.g. the time rate of change of the dispersion flux). Also, the dispersivities are supposed to be medium constants and invariant with temporal and spatial scales of observation. It is believed that in general these restrictions do not hold. A number of authors have proposed various alternative relationships. For example, differential equations have been employed that prescribe a relationship between the dispersion flux and its time and space derivatives. Also, stochastic theories result in integro-differential equations in which dispersion tensor grow asymptotically with time or distance. In this work, three different approaches, which lead to three different non-Fickian equations with a transient character, are discussed and their primary features and differences are highlighted. It is shown that an effective dispersion tensor defined in the framework of the transient non-Fickian theory, grows asymptotically with time and distance; a result which also follows from stochastic theories. Next, principles of continuum mechanics are employed to provide a solid theoretical basis for the non-Fickian transient dispersion theory. The equation of motion of a solute in a porous medium is used to provide a rigorous derivation of various dispersion relationships valid under different conditions. Under various simplifying assumptions, the generalized theory is found to agree with the conventional Fickian theory as well as several other non-Fickian relationships found in the literature. Moreover, it is shown that for nonconservative solutes, the traditional dispersion tensor is affected by the rate of mass exchange of the solute.

**Key words:** solute transport, Fick's law, dispersion, dispersivity, equation of motion, non-Fickian dispersion equation, scale effects.

## 1. Notation

- A measure of auto-correlation strength in Scheidegger's equation, [T]
- A three-dimensional counterpart of A, [T]
- $A^*$  relative free energy per unit mass of a solute, [ $L^2T^{-2}$ ]
- C concentration of a solute, [ $ML^{-3}$ ]
- D dispersion tensor, [ $L^2T^{-1}$ ]
- $D_0$  modified dispersion tensor in Tompson's theory, [ $L^2T^{-2}$ ]
- $D_m$  effective diffusion coefficient, [ $L^2T^{-1}$ ]
- f modified dispersion flux vector, [ $LT^{-1}$ ]
- g gravity vector, [ $LT^{-2}$ ]

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<b>I</b>	unit tensor, [–]
<i>J</i>	solute dispersion flux in one dimension, [ML <sup>-2</sup> T <sup>-1</sup> ]
<b>J</b>	solute dispersion flux vector, [ML <sup>-2</sup> T <sup>-1</sup> ]
<b>q</b>	Darcy velocity, [LT <sup>-1</sup> ]
$\hat{r}$	rate of exchange of mass for a nonconservative solute, [T <sup>-1</sup> ]
<b>R</b>	resistance (to dispersion) tensor, [M <sup>-1</sup> L <sup>3</sup> T <sup>1</sup> ]
<b>s</b>	source term due to diffusion in equation of motion of a solute, [L <sup>-1</sup> T <sup>-1</sup> ]
<i>t</i>	time, [T]
$\hat{T}$	resistance force (per unit mass) exerted on a component by all other components of the porous medium, [LT <sup>-2</sup> ]
<b>u<sup>s</sup></b>	relative velocity of the solute, [LT <sup>-1</sup> ]
<b>v</b>	fluid velocity vector, [LT <sup>-1</sup> ]
<i>v</i>	magnitude of fluid velocity vector, [LT <sup>-1</sup> ]

*Greek Symbols:*

$\alpha_L$	longitudinal dispersivity, [L]
$\alpha_T$	transversal dispersivity, [L]
$\beta$	a new dispersivity coefficient in Scheidegger's equation, [L]
$\beta_1$	and $\beta_2$ modified dispersivities in Tompson's theory, [–]
$\eta$	a tensor property in Tompson's theory, [L <sup>-2</sup> ]
$\mu_*^s$	relative chemical potential of a solute, [L <sup>2</sup> T <sup>-2</sup> ]
$\rho$	mass density of fluid, [ML <sup>-3</sup> ]
$\sigma$	stress tensor, [ML <sup>-1</sup> T <sup>-2</sup> ]
$\tau_*^s$	nonequilibrium part of the solute resistance force $\hat{T}^s$ , [LT <sup>-2</sup> ]
$\omega$	solute mass fraction, [–]

*Superscripts:*

<i>T</i>	transpose of a vector or a tensor
<i>w</i>	pure water component of the fluid phase
<i>s</i>	solute components of the fluid phase

## 2. Introduction

The fundamental equation governing the spreading of solutes in a porous medium is the equation of conservation of mass

$$\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v}C) + \nabla \cdot \mathbf{J} = \hat{r}, \quad (1)$$

where  $C$  is the solute concentration,  $\mathbf{v}$  is the mean flow velocity,  $\mathbf{J}$  is the dispersive mass flux, and  $\hat{r}$  is the rate of solute mass exchange. The velocity is commonly assumed to be either known as a constant or calculated from the fluid flow equation. Obviously, an additional equation is needed to relate  $\mathbf{J}$  to other system variables.

The equation most widely used to describe the dispersion flux of solutes in a porous medium is an extension of the Fick's law of diffusion

$$\mathbf{J} = -\mathbf{D} \cdot \nabla C, \quad (2)$$

where  $\mathbf{D}$  is the dispersion tensor. According to this equation, the dispersive mass flux of a solute is proportional to the solute concentration gradient. The dispersion tensor is assumed to be independent of the solute concentration and its gradient. It is, however, considered to be a function of the flow velocity,  $\mathbf{v}$ , according to the relation

$$\mathbf{D} = (D_m + \alpha_T \nu) \mathbf{I} + (\alpha_L - \alpha_T) \mathbf{v} \mathbf{v}^T / \nu, \quad (3)$$

where  $D_m$  is the effective molecular diffusion coefficient,  $\alpha_T$  and  $\alpha_L$  are the transversal and longitudinal dispersivities, respectively,  $\mathbf{I}$  is unit tensor,  $\nu$  is the magnitude of fluid velocity, and the superscript  $T$  denotes the transpose of a vector (or a tensor). The dispersivities  $\alpha_T$  and  $\alpha_L$  are supposed to be medium constants. Combination of (1) and (2), for a conservative solute, yields the well-known advection-dispersion equation:

$$\frac{\partial C}{\partial t} + \nabla \cdot (\mathbf{v}C) - \nabla \cdot (\mathbf{D} \cdot \nabla C) = 0. \quad (4)$$

Equations (3) and (4) have been shown to give satisfactory results for 'perfectly homogeneous' media. Such media, however, can only be constructed in the laboratory and the Fickian dispersion equation, as any other phenomenological relationship, has certain limitations when applied to real media. Small-scale and large-scale heterogeneities in the porous matrix and/or fluid properties are the main sources of deviations from the so-called 'Fickian dispersion behavior'. A more theoretical objection is that the parabolic Equation (4) prescribes an infinite speed of propagation of solutes; a property which is physically unacceptable.

Commonly, two kinds of deviations from the Fickian behavior are encountered. The first kind regards the dependence of the dispersion tensor on flow velocity. In this case, the form of Equations (2) and (3) remains valid, but dispersivity coefficients are not found to be medium constants. Indeed Equation (3) is an empirical relationship and only an approximation. For example, for a given range of Peclet numbers, a (weak) dependence of both longitudinal and transversal dispersivities on velocity is observed (Bear, 1972). This deviation, however, is often considered not to be important for practical situations. A more serious shortcoming is that the values of longitudinal and transversal dispersivities often increase with the distance and/or with time (i.e. depends on the spatial and/or temporal scale of observation, respectively). They approach, however, some asymptotic values at large distances and/or times. This is a well-known phenomenon and has been investigated by many researchers (e.g. Matheron and de Marsily, 1980; Dagan, 1989).

In the second kind of deviations, the linear relationship between the dispersive mass flux  $\mathbf{J}$  and the solute concentration gradient breaks down; often additional terms have to be introduced into equation (2). For example, when large concentration gradients exist, nonlinear effects become important and (2) will have to be replaced with a non-linear relationship for  $\mathbf{J}$  (see Hassanizadeh and Leijnse, 1995). Another example regards generalizations of (2) or (4) such that the history of  $\mathbf{J}$  is brought into consideration. For example, Tompson (1988) and Strack (1992) have proposed theories in which the dispersion equation (2) is replaced by a differential equation for  $\mathbf{J}$ . Thus, the transport process is modelled by a set of coupled differential equations.

In more general cases, both of Equations (2) and (3) may prove deficient. In such cases, instead of the differential equation (4), either a set of coupled differential equations or a single integro-differential equation may be needed to describe the transport process. Examples of the latter kind of theories are found in the works of, among others, Cushman and Ginn (1993) and Neuman (1993), who obtain non-local dispersion theories. According to these theories, the dispersion properties of a medium are affected by the history of motion and the history of concentration gradient at all points of the medium.

In this article, a theoretical basis for a number of generalized dispersion theories is provided. First, three different approaches for modelling transient non-Fickian dispersion, followed by Scheidegger, Tompson, and Strack, are discussed and their differences are identified. Also, the correspondences of the transient non-Fickian dispersion with stochastic nonlocal dispersion theories are discussed. Next, a generalized relationship for the dispersion flux vector,  $\mathbf{J}$ , is derived. The derivation is based on a thermodynamic theory of flow and dispersion developed by Hassanizadeh (1986a,b). It is shown that, just the same way that Darcy's equation is a modified form of the equation of motion for a fluid flowing in a porous medium, various equations of dispersion can be obtained from the equation of motion for a solute. The resulting dispersion theory has a unifying character and is capable of removing both kinds of shortcomings discussed above.

### 3. Autocorrelation and Time-Dependent Dispersion Flux

The Fickian dispersion equation (2) describes the spreading of solutes as a result of microscale variations in the mean flow velocity of the fluid phase. It can be shown that this equation implies a random distribution of microscale velocity (see, e.g., Scheidegger, 1958; De Josselin de Jong, 1958). In the context of random-walk models, equation (4) (and therefore (2)) corresponds to the case that there is no correlation between the directions that a fluid particle possesses in subsequent time steps. If, however, one assumes that there exists a correlation between what happens to a particle in subsequent time steps, a different differential equation for dispersion will be obtained. This case is referred to as 'autocorrelation'. Scheidegger has shown that when autocorrelation is taken into account, then, instead of the parabolic

equation (4), an hyperbolic equation is obtained. He derives the following equation for the case of one-dimensional transport with a constant velocity (Scheidegger, 1960, p. 261):

$$\frac{\partial C}{\partial t} + \nu \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = -A \left( \frac{\partial^2 C}{\partial t^2} + 2\nu \frac{\partial^2 C}{\partial t \partial x} + \nu^2 \frac{\partial^2 C}{\partial x^2} \right), \quad (5)$$

where  $A$  is a new coefficient which is related to a certain measure of the correlation strength. Scheidegger (1958), obtains the following relationships for  $D$  and  $A$ :

$$D = \alpha_L \nu, \quad (6a)$$

$$A = \frac{\beta}{\nu}, \quad (6b)$$

where both  $\alpha_L$  and  $\beta$  have dimensions of length and are assumed to be medium constants.

Scheidegger refers to the spreading of particles under the auto-correlation assumption as 'dispersion with memory' and suggests that the dispersion in such a porous medium resembles the 'random walk of a drunkard . . . with some memory' (Scheidegger, 1960, sec. 8.2.3). In this theory,  $A$  serves as a relaxation coefficient.

Equation (5) has the form of the telegraph equation and, as compared to the commonly-employed advection-dispersion equation (4), has the advantage that the speed of propagation of particles is finite. In fact, two real characteristics for Equation (5) are found to be  $\nu \pm \sqrt{D/A}$  (C. J. van Duijn, personal communications). Obviously, the characteristics are both positive if the following restriction is fulfilled (the second alternative is based on relations (6a) and (6b)):

$$\frac{D}{A} < \nu^2 \quad \text{or} \quad \frac{\alpha_L}{\beta} < 1. \quad (7)$$

Under these conditions, a sharp front moving into a porous medium will have a sharp cut-off at both the leading and the tailing edges (as illustrated in Figure 1).

One can show that equation (5) may be obtained from the equation of mass balance for a solute (i.e. Equation (1)), only if the following relationship for the dispersion flux is assumed. (Note that Scheidegger did not give this equation.)

$$J = -D \frac{\partial C}{\partial x} - A \frac{\partial J}{\partial t} - A\nu \frac{\partial J}{\partial x}. \quad (8)$$

Obviously, Equation (8) is a generalized form of the Fickian dispersion equation (2) for the one-dimensional case. Only if the last two terms on the right-hand side of (8) are negligible will the Fickian approximation be valid.

Basically, Equation (8) must be seen as the governing equation for the dispersion flux  $J$ . Because  $J$  can also be regarded as the (dispersive or relative) momentum

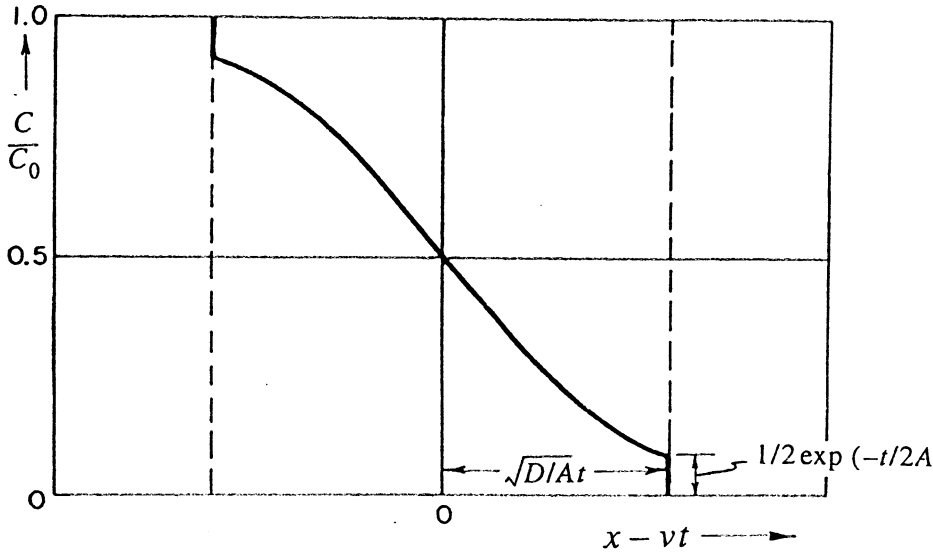


Figure 1. Shape of a typical concentration front during miscible displacement in a porous medium with autocorrelation (after Scheidegger, 1958).

of the solute, one should be able to derive (8) from the equation of motion (balance of momentum) of the solute. Such an approach was adopted by Tompson and Gray (1986) who provide a rigorous development of a 'second-order dispersion theory'. In their approach, they discard the Fickian relation (2) and the mass balance equation (1) is recast in a different form:

$$\rho \frac{\partial \omega}{\partial t} + \rho \nabla \cdot (\mathbf{v}\omega) + \rho \nabla \cdot \mathbf{f} = \rho D_m (1 - B) \nabla^2 \omega, \quad (9)$$

where  $\rho$  denotes the fluid mass density,  $\omega$  is the solute mass fraction defined by

$$\omega = \frac{C}{\rho}, \quad (10)$$

$B$  is a positive constant smaller than 1, and  $\mathbf{f}$  is equal to the average of product of microscale mass fraction and velocity fluctuations and is related to the dispersion flux  $\mathbf{J}$  by

$$\mathbf{J} = \rho \mathbf{f} - \rho D_m \nabla \omega. \quad (11)$$

For an incompressible fluid (constant  $\rho$ ) and if  $B = 0$ , Equations (9) and (1) would be identical. Clearly,  $\mathbf{f}$  does not include the effect of molecular diffusion. Tompson and Gray (1986) derive an equation for  $\mathbf{f}$  by combining the microscale equations of momentum dispersion for the fluid with the mass balance for the solute, and by averaging the resulting relationship. In their development, they assume that the

fluid is incompressible. The resulting equation, after introducing some constitutive and/or simplifying assumptions, reads (Equation (74) in Tompson and Gray, 1986):

$$\frac{\partial \mathbf{f}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{f} + \mathbf{f} \cdot \nabla \mathbf{v} + \mathbf{D}_0 \cdot \nabla \omega = D_m \mathbf{s}, \quad (12)$$

where  $\mathbf{D}_0$  is related to the dispersion of momentum of the fluid that results directly from the winding microscopic flow patterns induced by the grain structure of the medium. The term  $\mathbf{s}$  is identified as a source of momentum due to the spreading by molecular diffusion. Additional constitutive equations are needed for  $\mathbf{D}_0$  and  $\mathbf{s}$ . Tompson (1988) proposes the following relationships:

$$\mathbf{D}_0 = \beta_1 \nu^2 \mathbf{I} + \beta_2 \mathbf{v} \mathbf{v}^T, \quad (13)$$

$$\mathbf{s} = -\boldsymbol{\eta} \cdot \mathbf{f}, \quad (14)$$

where  $\beta_1$  and  $\beta_2$  are dimensionless coefficients assumed to be medium constants, and  $\boldsymbol{\eta}$  is considered to be a positive definite tensor given as a function of the flow velocity  $\mathbf{v}$ . Substitution of (14) in (12) yields

$$((\nabla \mathbf{v})^T + D_m \boldsymbol{\eta}) \cdot \mathbf{f} = -\mathbf{D}_0 \cdot \nabla \omega - \frac{\partial \mathbf{f}}{\partial t} - \mathbf{v} \cdot \nabla \mathbf{f}. \quad (15)$$

Equation (15) is an interesting result and it can be readily verified that this equation is a generalized form of Equation (8) which is implied by Scheidegger's theory. An equivalence between Equations (8) and (15), however, can be established only if molecular diffusion effects are negligible so that  $\rho \mathbf{f}$  in (15) may be replaced with  $\mathbf{J}$ .

Tompson (1988) has shown that, under the assumption of constant flow velocity, for an isotropic medium (thus  $\boldsymbol{\eta} = \eta \mathbf{I}$ ), and assuming that  $\mathbf{f}$  is zero at some reference or initial time, Equation (15) can be integrated to yield:

$$\mathbf{f} = - \int_0^t e^{\eta D_m (t-\tau)} (\beta_1 \nu^2 \mathbf{I} + \beta_2 \mathbf{v} \mathbf{v}^T) \cdot \nabla \omega \, d\tau. \quad (16)$$

This is an important result which indicates that in general the dispersive flux is not directly proportional to the gradient of mass fraction (or concentration), as suggested by the traditional Fickian formulation (2). Rather, as pointed out by Tompson (1988), the dispersive mass flux 'is influenced by the weighted contributions from all previous mass fraction gradients through a convolution or "memory" integral'. It would be momentarily shown that this effect ties in with the scale-dependence of dispersion, which also appears in stochastic theories.

Tompson (1988) has shown that linearization of (16), for cases of large  $\eta D_m$ , results in a non-Fickian relationship for  $\mathbf{f}$ :

$$\mathbf{f} = \frac{1}{\eta D_m} (\beta_1 \nu^2 \mathbf{I} + \beta_2 \mathbf{v} \mathbf{v}^T) (1 - e^{-\eta D_m t}) \cdot \nabla \omega. \quad (17)$$

Comparison of the one-dimensional version of (15) with Equations (6b) and (8), results in the following relationship between  $\eta$  and  $\beta$  (the coefficient in Scheidegger's theory):

$$\eta = \frac{\nu}{\beta D_m}. \quad (18)$$

Combination of (18) and (17) and subsequent substitution in (11), and comparison of the result with the Fickian dispersion equation (2) results in the definition of a generalized dispersion tensor given by:

$$\mathbf{D} = D_m \mathbf{I} + \beta(\beta_1 \nu \mathbf{I} + \beta_2 \mathbf{v} \mathbf{v}^T / \nu)(1 - e^{-\nu t / \beta}). \quad (19)$$

Comparison of this result with (3) makes it clear that according to the transient non-Fickian theory, transversal and longitudinal dispersivities are not constant but they grow as a function of time (or distance  $\nu t$ ) and approach the asymptotic values  $\beta\beta_1$  and  $\beta(\beta_1 + \beta_2)$ , respectively. Note that this result is based on successive approximations of the original Equation (15). The full theory accounts for more general spatial and temporal scale effects.

Relationships similar to (16) have been derived by means of stochastic theories applied to porous media with local heterogeneities. Examples are found in the works of Cushman and Ginn (1993) and Neuman (1993). For example, a generalization of (16) is obtained by Cushman and Ginn (1993):

$$\mathbf{f} = - \int_0^t \int_{R^3} \mathbf{D}(\mathbf{y}, t, \tau) \cdot \nabla_{\mathbf{x}-\mathbf{y}} G(\mathbf{x} - \mathbf{y}, t - \tau) \, d\mathbf{y} \, d\tau, \quad (20)$$

where  $G$  is a conditional probability which plays the role of concentration. Here, the dispersion flux is not only nonlocal in time but also in space: it depends on two points in space. The dispersion tensor  $\mathbf{D}$  is left unspecified here. A more general equation for the dispersive flux, applicable to the case of flow with a random nonstationary velocity field, is derived by Neuman (1993). His result for the case of a divergence-free velocity field reduces to

$$\mathbf{Q} = \int_{t_0}^t \int \overline{\mathbf{C}}(\mathbf{x}, t | \chi, \tau) \left( \overline{\mathbf{v}'(\mathbf{x}, t) \mathbf{v}'^T(\chi, \tau)} \right) \cdot \nabla_{\chi} \overline{\mathbf{C}}(\chi, \tau) \, d\chi \, d\tau, \quad (21)$$

where  $\mathbf{Q}$  is the large-scale dispersion flux and the overbar denotes the ensemble mean (of the concentration or of the covariance tensor of velocity fluctuations). Comparison of (16), (20), and (21) shows that there is a definite correspondence between the transient dispersion theory introduced here and the nonlocal dispersion theories.

It is worth noting that equation (15) derived by Tompson (1988), when combined with mass balance equation (9), will lead to a telegraph equation only if the molecular diffusion term is neglected. Otherwise, the resulting equation of transport will have no positive characteristics, and the speed of propagation of particles will be infinite.

Recently, Strack (1992) has employed an equation similar to (8), but in three-dimensional form, in order to model the non-Fickian behavior of transport in porous media with small-scale heterogeneities:

$$\mathbf{J} = -\mathbf{D} \cdot \nabla C - \mathbf{A} \cdot \frac{\partial \mathbf{J}}{\partial t}, \quad (22)$$

in which  $\mathbf{A}$  is a tensor which is the three-dimensional equivalent of the coefficient  $A$  in equation (5), in the work of Scheidegger, and is related to the inverse of  $\eta$  that appears in (14) in the theory of Tompson (1988). Comparison of this equation with (8), implied by Scheidegger, and with (15), derived by Tompson, reveals that Strack does not include the divergence term  $\mathbf{v} \cdot \nabla \mathbf{J}$ . Strack (1992) applies this equation to the case of one-dimensional steady-state flow for which case he obtains the following transport equation (to be compared with (5)):

$$\frac{\partial C}{\partial t} + \nu \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = -A \left( \frac{\partial^2 C}{\partial t^2} + \nu \frac{\partial^2 C}{\partial t \partial x} \right). \quad (23)$$

The motivation of Strack in employing this equation has been to obtain a finite velocity for the movement of the dispersion front. But, the characteristics of this equation are found to be  $\nu \pm \sqrt{\nu^2 + D/A}$ . This means that Equation (23) has only one positive characteristic. Thus, during the movement of a sharp front in a column, only the leading edge will have a sharp cut-off and the tailing edge will be smoothed under all conditions (see Figures 3.13 and 3.14 in the work of Maas, 1994, who uses Strack's theory).

Contrary to Scheidegger, Strack (1992) does not consider the additional term in equation (22) to be due to memory effects, but refers to it as 'an inertial term similar to that used in the constitutive equation for heat flow presented by Glass *et al.* (1987)'. He submits that this inertial effect is expected to be important close to a contamination source.

In the following sections, we examine the theoretical foundation of Equations (8), (15), and (22). The equations discussed above are derived from the principle of conservation of momentum of solutes. The conditions under which these equations are valid are identified. In particular, it will be determined whether the non-Fickian dispersion equation is applicable to reacting solutes and/or deformable porous media.

#### 4. Equation of Motion for a Solute

Consider a porous medium saturated with water containing a reacting and/or decaying solute. The water phase is considered to consist of two components; (pure) water and a reacting solute. To describe the movement of water and the solute, equations of mass and momentum conservation for each component are needed. These are (cf. Hassanizadeh, 1986a):

*Equations of Mass Balance:*

$$\frac{\partial(n\rho\omega^w)}{\partial t} + \nabla \cdot (n\rho\omega^w \mathbf{v}^w) = n\rho\omega^w \hat{r}^w, \quad (24)$$

$$\frac{\partial(n\rho\omega^s)}{\partial t} + \nabla \cdot (n\rho\omega^s \mathbf{v}^s) = n\rho\omega^s \hat{r}^s. \quad (25)$$

*Equations of Momentum Balance (or motion):*

$$\begin{aligned} \frac{\partial(n\rho\omega^w \mathbf{v}^w)}{\partial t} + \nabla \cdot (n\rho\omega^w \mathbf{v}^w \mathbf{v}^w) - \nabla \cdot \boldsymbol{\sigma}^w - n\rho\omega^w \mathbf{g} \\ = n\rho\omega^w (\hat{\mathbf{T}}^w + \hat{r}^w \mathbf{v}^w), \end{aligned} \quad (26)$$

$$\begin{aligned} \frac{\partial(n\rho\omega^s \mathbf{v}^s)}{\partial t} + \nabla \cdot (n\rho\omega^s \mathbf{v}^s \mathbf{v}^s) - \nabla \cdot \boldsymbol{\sigma}^s - n\rho\omega^s \mathbf{g} \\ = n\rho\omega^s (\hat{\mathbf{T}}^s + \hat{r}^s \mathbf{v}^s), \end{aligned} \quad (27)$$

where superscripts  $w$  and  $s$  stand for pure water and solute components, respectively,  $\omega$  is mass concentration of a component,  $\mathbf{v}$  is velocity of a component,  $\boldsymbol{\sigma}$  is the stress tensor,  $\mathbf{g}$  is the gravity vector,  $\hat{r}$  is the rate of exchange of mass of a component with other components and the solid phase (and/or the rate of decay), and  $\hat{\mathbf{T}}$  is the force exerted on a component by all other components and the solid phase.

Now, multiply Equations (24) and (25) by  $\mathbf{v}^w$  and  $\mathbf{v}^s$ , respectively, and subtract the results from (26) and (27) to obtain:

$$n\rho\omega^w \frac{\partial \mathbf{v}^w}{\partial t} + n\rho\omega^w \mathbf{v}^w \cdot \nabla \mathbf{v}^w - \nabla \cdot \boldsymbol{\sigma}^w - n\rho\omega^w \mathbf{g} = n\rho\omega^w \hat{\mathbf{T}}^w, \quad (28)$$

$$n\rho\omega^s \frac{\partial \mathbf{v}^s}{\partial t} + n\rho\omega^s \mathbf{v}^s \cdot \nabla \mathbf{v}^s - \nabla \cdot \boldsymbol{\sigma}^s - n\rho\omega^s \mathbf{g} = n\rho\omega^s \hat{\mathbf{T}}^s. \quad (29)$$

In the study of dispersion, one is commonly interested in the relative motion of a solute with respect to the other component. Thus, we now develop an equation of

relative momentum balance for the solute. Multiply Equation (28) by  $\omega^s/\omega^w$  and subtract the result from Equation (29) to obtain

$$\begin{aligned} n\rho\omega^s \frac{\partial(\mathbf{v}^s - \mathbf{v}^w)}{\partial t} + n\rho\omega^s(\mathbf{v}^s \cdot \nabla \mathbf{v}^s - \mathbf{v}^w \cdot \nabla \mathbf{v}^w) \\ = \left( \nabla \cdot \boldsymbol{\sigma}^s - \frac{\omega^s}{\omega^w} \nabla \cdot \boldsymbol{\sigma}^w \right) + n\rho\omega^s(\hat{\mathbf{T}}^s - \hat{\mathbf{T}}^w). \end{aligned} \quad (30)$$

In the remainder of this study, we confine our attention to the cases where the solute concentration is low enough so that the water phase density,  $\rho$ , will not be affected by changes in the solute concentration. Then, one will have

$$\omega^s \ll 1, \quad \omega^w \approx 1 \quad \text{and} \quad \rho \approx C^w. \quad (31)$$

Also, the water phase velocity,  $\mathbf{v}$  as defined below, may be assumed to be equal to the velocity of the water component,  $\mathbf{v}^w$ :

$$\mathbf{v} = \omega^s \mathbf{v}^s + \omega^w \mathbf{v}^w, \quad \text{with} \quad \mathbf{v} \approx \mathbf{v}^w \quad \text{for small} \quad \omega^s. \quad (32)$$

Therefore, for low solute concentration, the relative solute velocity,  $\mathbf{u}^s$ , and the dispersive mass flux,  $\mathbf{J}$ , may be defined by

$$\mathbf{u}^s = \mathbf{v}^s - \mathbf{v} \cong \mathbf{v}^s - \mathbf{v}^w, \quad (33)$$

$$\mathbf{J} = n\rho\omega^s \mathbf{u}^s = n\rho\omega^s(\mathbf{u}^s - \mathbf{v}^w). \quad (34)$$

From averaging theories, one can show that the macroscale dispersion flux  $\mathbf{J}$  defined here is equal to the average of product of microscale concentration and velocity fluctuations. With these definitions and assumptions, the equation of solute mass balance, (25), becomes

$$\frac{\partial(n\rho\omega^s)}{\partial t} + \nabla \cdot (n\rho\omega^s \mathbf{v}^w) + \nabla \cdot \mathbf{J} = n\rho\omega^s \hat{r}^s. \quad (35)$$

Also, with the aid of definitions (31) to (33) and chain rule of differentiation, the left hand side of (30) may be rearranged to

$$\begin{aligned} \text{L.H.S.} = & \frac{\partial \mathbf{J}}{\partial t} - \mathbf{u}^s \frac{\partial(n\rho\omega^s)}{\partial t} + \mathbf{v}^w \cdot \nabla \mathbf{J} - \mathbf{u}^s \mathbf{v}^w \cdot \nabla(n\rho\omega^s) + \\ & + \mathbf{J} \cdot \nabla \mathbf{v}^w + \mathbf{J} \cdot \nabla \mathbf{u}^s. \end{aligned} \quad (36)$$

The second and the fourth terms in this equation can be combined and, with the aid of the mass balance for the solute, (35), they are reduced to:

$$\frac{\partial(n\rho\omega^s)}{\partial t} + \mathbf{v}^w \cdot \nabla(n\rho\omega^s) = -\nabla \cdot \mathbf{J} - n\rho\omega^s \nabla \cdot \mathbf{v}^w + n\rho\omega^s \hat{r}^s. \quad (37)$$

Substitution of (37) in (36), yields

$$\begin{aligned} \text{L.H.S.} = & \frac{\partial \mathbf{J}}{\partial t} + \mathbf{v}^w \cdot \nabla \mathbf{J} + \mathbf{J} \cdot \nabla \mathbf{v}^w + \\ & + \mathbf{u}^s (\nabla \cdot \mathbf{J} + n\rho\omega^s \nabla \cdot \mathbf{v}^w - n\rho\omega^s \hat{\mathbf{r}}^s) + \mathbf{J} \cdot \nabla \mathbf{u}^s. \end{aligned} \quad (38)$$

This equation can be recasted in the following form with the use of relation (34), the chain rule of differentiation, and the fact that for low solute concentrations,  $\mathbf{v}$  may be approximated with  $\mathbf{v}^w$ .

$$\text{L.H.S.} = \frac{\partial \mathbf{J}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{J} + \mathbf{J} \cdot \nabla \mathbf{v} + \nabla \cdot \left( \frac{\mathbf{J}\mathbf{J}}{n\rho\omega^s} \right) + \mathbf{J}\nabla \cdot \mathbf{v} - \mathbf{J}\hat{\mathbf{r}}^s. \quad (39)$$

Upon substitution of this term in the left hand side of (30), the following equation of motion for the solute is obtained:

$$\begin{aligned} \frac{\partial \mathbf{J}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{J} + \mathbf{J} \cdot \nabla \mathbf{v} + \nabla \cdot \left( \frac{\mathbf{J}\mathbf{J}}{n\rho\omega^s} \right) + \mathbf{J}\nabla \cdot \mathbf{v} - \mathbf{J}\hat{\mathbf{r}}^s \\ = \nabla \cdot \hat{\boldsymbol{\sigma}}^s + n\rho\omega^s (\hat{\mathbf{T}}^s - \hat{\mathbf{T}}^w) + \boldsymbol{\sigma}^w \cdot \nabla \left( \frac{\omega^s}{\omega^w} \right), \end{aligned} \quad (40)$$

where

$$\hat{\boldsymbol{\sigma}}^s = \boldsymbol{\sigma}^s - \left( \frac{\omega^s}{\omega^w} \right) \boldsymbol{\sigma}^w. \quad (41)$$

From the constitutive theory, the following constitutive equations can be obtained for  $\hat{\boldsymbol{\sigma}}^s$  and  $(\hat{\mathbf{T}}^s - \hat{\mathbf{T}}^w)$  (Equations (46c) and (47b) in Hassanizadeh, 1986b):

$$\hat{\boldsymbol{\sigma}}^s = -[n\rho\omega^s(\mu_*^s - A_*^s)]\mathbf{I}, \quad (42)$$

$$\begin{aligned} n\rho\omega^s(\hat{\mathbf{T}}^s - \hat{\mathbf{T}}^w) \\ = \nabla[n\rho\omega^s(\mu_*^s - A_*^s)] - n\rho\omega^s \nabla \mu_*^s - \boldsymbol{\sigma}^w \cdot \nabla \left( \frac{\omega^s}{\omega^w} \right) + n\rho\omega^s \tau_*^s, \end{aligned} \quad (43)$$

where  $\mu_*^s$  is the relative chemical potential of the solute,  $A_*^s$  is the relative Helmholtz free energy of the solute (both relative to the pure water component), and  $\tau_*^s$  is the nonequilibrium component of the resistance force. Note that these equations are not empirically motivated or 'clever' intuitive assumptions; these are obtained as a result of the application of the second law of thermodynamics and other physical and mathematical principles (For details of development of the constitutive relationships see Hassanizadeh, 1986b.) The nonequilibrium part of the resistance force in Equation (43),  $\tau_*^s$ , is a dissipative force and is present only if there is solute dispersion. The other forces in (43), however, will act even if there is no

movement. Both  $\mu_*^s$  and  $A_*^s$  are functions of mass fraction  $\omega^s$ , mass density  $\rho$ , and temperature only. The functional dependence of  $\tau_*^s$  will be discussed shortly.

Substitution of (42) and (43) in (40), and collecting terms results in the following equation:

$$\begin{aligned} \frac{\partial \mathbf{J}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{J} + \mathbf{J} \cdot \nabla \mathbf{v} + \nabla \cdot \left( \frac{\mathbf{J}\mathbf{J}}{n\rho\omega^s} \right) + \mathbf{J}\nabla \cdot \mathbf{v} + n\rho\omega^s \nabla \mu_*^s \\ = n\rho\omega^s \tau_*^s + \mathbf{J}\hat{\mathbf{r}}^s. \end{aligned} \quad (44)$$

This equation is clearly an expression of balance of forces. The first five terms on the left-hand side of (44) account for the inertia of the solute movement. The last term on the left hand side (the gradient of macroscopic chemical potential) is the driving force for the dispersion of the solute. Solutes will disperse from areas of high chemical potential to areas of low chemical potential. It is important to emphasize that the macroscopic chemical potential includes the sub-scale kinetic energy associated with microscale velocity fluctuations (see Hassanizadeh, 1986a,b). Thus, the higher the microscale velocity fluctuations, the greater the ability of the solute to disperse itself. This driving force (i.e., the gradient of macroscopic chemical potential) is opposed by the resistance of the medium to the movement (the dispersion) of the solute,  $\tau_*^s$ , and has to supply the inertia of the moving solute mass. The momentum supply term  $\mathbf{J}\hat{\mathbf{r}}^s$ , associated with the rate of solute mass exchange, may provide additional resistance to dispersion (in the case of negative mass supply) or additional driving force (in the case of positive mass supply).

To develop the theory further, one has to make assumptions about the functional dependence of  $\tau_*^s$ . This resistance force will be nonzero only if the solute moves with respect to the pure water component and the solid phase. Therefore, it is bound to depend on relative velocities of the solute with respect to water and solid:  $\mathbf{v}^s - \mathbf{v}^w$ , and  $\mathbf{v}^s - \mathbf{v}^{\text{solid}}$ . But, with the aid of definitions (33) and (34), these two terms can be written in terms of  $\mathbf{J}$  and the Darcy velocity,  $\mathbf{q} = n(\mathbf{v} - \mathbf{v}^{\text{solid}})$ :

$$\mathbf{v}^s - \mathbf{v}^w \cong \mathbf{v}^s - \mathbf{v} = \mathbf{J}/(n\rho\omega^s), \quad (45)$$

$$\mathbf{v}^s - \mathbf{v}^{\text{solid}} = (\mathbf{v}^s - \mathbf{v}) + (\mathbf{v} - \mathbf{v}^{\text{solid}}) = \mathbf{J}/(n\rho\omega^s) + \mathbf{q}/n. \quad (46)$$

The resistance force may also depend on the solute concentration and on the porosity. Thus, one may propose the following constitutive equation for  $\tau_*^s$ :

$$\tau_*^s = \tau_*^s(n, \rho, \omega^s, \mathbf{J}, \mathbf{q}). \quad (47)$$

The next step in the development of a general dispersion equation similar to (15) is to simplify the functional dependence of  $\tau_*^s$  in (47). As a first-order

approximation, a linear form for  $\tau_*^s$  will be sought. Thus, we assume that  $\tau_*^s$  depends on  $\mathbf{J}$  linearly but is still an unknown function of  $\mathbf{q}$ :

$$\tau_*^s = -\mathbf{R}(n, \rho, \omega^s, \mathbf{q}) \cdot \mathbf{J}, \quad (48)$$

where  $\mathbf{R}$  is a resistivity tensor which still could be a nonlinear function of  $\mathbf{q}$ . The negative sign ensures that  $\mathbf{R}$  will be positive semidefinite (Hassanizadeh, 1986b).

Substitute (48) in (44) and apply the chain rule of differentiation to the last term in the left-hand side of that equation. The result, for isothermal conditions, may be written in the following form:

$$\begin{aligned} & (n\rho\omega^s\mathbf{R} + \nabla\mathbf{v} + (\nabla \cdot \mathbf{v})\mathbf{I} - \hat{r}^s\mathbf{I}) \cdot \mathbf{J} \\ &= -n\rho\omega^s \frac{\partial\mu_*^s}{\partial\omega^s} \nabla\omega^s - \frac{\partial\mathbf{J}}{\partial t} - \mathbf{v} \cdot \nabla\mathbf{J} - \nabla \cdot \left( \frac{\mathbf{J}\mathbf{J}}{n\rho\omega^s} \right). \end{aligned} \quad (49)$$

This equation must be seen as a governing relationship for the dispersion mass flux,  $\mathbf{J}$ . Together with the conservation of mass for solute, Equation (35), and assuming that the flow velocity field is known, we have a determinate set of equations to solve for the mass concentration  $C$ . Equation (49), however, is too general and, depending on the conditions imposed, various simplified forms may be obtained. In the next section, a number of important cases are considered.

## 5. Simplifications of the Equation of Motion

Equation (49) is a fundamental relationship for describing the dynamics of solute dispersion in a porous medium. Various equations proposed by different authors, discussed earlier in this work, can be derived from this relationship under different assumptions. A number of cases are considered.

### 5.1. FICKIAN DISPERSION

The simplest equation of dispersion is obtained by neglecting all inertia terms (those involving the derivatives of flow velocity or dispersion flux) and the mass exchange term in (49). Strictly speaking, this would mean that the flow and transport should be uniform in time and space and the solute should be conservative (no adsorption or decay). The resulting equation will be:

$$n\rho\omega^s\mathbf{R} \cdot \mathbf{J} = -n\rho\omega^s \frac{\partial\mu_*^s}{\partial\omega^s} \nabla\omega^s, \quad (50)$$

which can be recast in the form of the well-known Fickian dispersion equation

$$\mathbf{J} = -n\rho\mathbf{D} \cdot \nabla\omega^s, \quad (51)$$

where  $\mathbf{D}$  is the dispersion tensor given by

$$\mathbf{D} = \frac{1}{n\rho} \frac{\partial \mu_*^s}{\partial \omega^s} \mathbf{R}^{-1}. \quad (52)$$

The dispersion tensor may be a function of  $\mathbf{q}$  (e.g. as in Equation (3)), but it is commonly considered to be independent of mass fraction and  $\mathbf{J}$ .

## 5.2. THE EFFECT OF MASS EXCHANGE

It is commonly assumed that the Fickian dispersion equation is valid regardless of whether there is solute mass exchange between the flowing fluid and the solid phase (sorption or precipitation/dissolution) or solid aggregates (diffusion into stagnant pores). However, it is clear from Equation (49) that in such cases, the dispersive mass flux may be affected by the mass exchange process. In Equation (49), neglect all the inertial terms to obtain:

$$(n\rho\omega^s \mathbf{R} - \hat{r}^s \mathbf{I}) \cdot \mathbf{J} = -n\rho\omega^s \frac{\partial \mu_*^s}{\partial \omega^s} \nabla \omega^s. \quad (53)$$

Take the inner product of this equation with  $\mathbf{R}^{-1}$  and employ the definition (52) to obtain

$$(\mathbf{I} - \hat{r}^s \mathbf{A}) \cdot \mathbf{J} = -n\rho \mathbf{D} \cdot \nabla \omega^s, \quad (54)$$

where  $\mathbf{A}$  is a new dispersion parameter defined by

$$\mathbf{A} = \frac{1}{n\rho\omega^s} \mathbf{R}^{-1} = \left( \frac{\partial \mu_*^s}{\partial \ln \omega^s} \right)^{-1} \mathbf{D}. \quad (55)$$

Equation (54) may be written in the form of Fickian dispersion equation if an effective dispersion coefficient,  $\mathbf{D}_{\text{eff}}$ , is defined by

$$\mathbf{D}_{\text{eff}} = (\mathbf{I} - \hat{r}^s \mathbf{A})^{-1} \cdot \mathbf{D}. \quad (56)$$

This relationship indicates that, as compared with conservative solutes, the dispersion tensor for a non-conservative solute may be smaller or larger at a given time, depending on whether solute mass is created or removed, respectively. Note that  $\hat{r}^s$  is not necessarily a constant and in general it may depend on the solute mass fraction, temperature, and medium properties. It may be modelled by (non-)linear equilibrium isotherms or kinetic relationships. This term will be positive when there is desorption taking place and negative when adsorption of solutes occur. Obviously to model adsorption or matrix diffusion, an additional mass balance equation (for the concentration of adsorbed solute or for the concentration of solute in stagnant pores) is needed.

The modification of dispersion tensor given by (56) is distinct from the effect of retardation coefficient (associated with an equilibrium isotherm) which reduces both dispersion coefficient and flow velocity. For example, consider an experiment wherein the movement of a pulse of a conservative solute is compared with that of a non-conservative solute. In the case of a linear isotherm and Fickian dispersion, where retardation factor will be a constant, the shape of solute profiles for conservative and non-conservative solutes will be identical and the only difference would be a shift of the time axis. With the modification introduced here, however, the effective dispersion coefficient for the non-conservative solute will be smaller in front of the pulse, because adsorption takes place (negative  $\hat{r}^s$ ), and will be larger behind the pulse where desorption occurs (positive  $\hat{r}^s$ ). This means that the concentration profile of an adsorbing solute, as compared to that of a conservative solute, will be steeper in front of the pulse and will show a tailing behind the pulse.

### 5.3. INCOMPRESSIBLE FLUIDS

Next, consider a situation where inertial terms are important but the flow may be assumed to be incompressible and the solute is conservative (i.e.,  $\nabla \cdot \mathbf{v} = 0$  and  $\hat{r}^s = 0$ ). If one also assumes that the last term in the right-hand side of (49) is negligible (being of second order), then the following equation is obtained:

$$(n\rho\omega^s\mathbf{R} + \nabla\mathbf{v}) \cdot \mathbf{J} = -n\rho\omega^s \frac{\partial\mu_*^s}{\partial\omega^s} \nabla\omega^s - \frac{\partial\mathbf{J}}{\partial t} - \mathbf{v} \cdot \nabla\mathbf{J}, \quad (57)$$

which is equivalent to Equation (15) obtained by Tompson (1988). If we additionally assume that the fluid velocity is constant, the second term inside the parenthesis on the left hand side disappears, and the resulting equation may be rearranged to

$$\mathbf{J} = -n\rho\mathbf{D} \cdot \nabla\omega^s - \mathbf{A} \cdot \frac{\partial\mathbf{J}}{\partial t} - \mathbf{A} \cdot (\mathbf{v} \cdot \nabla\mathbf{J}), \quad (58)$$

where  $\mathbf{A}$ , defined by (55), is the three-dimensional counterpart of  $A$  introduced by Scheidegger. This relationship is a generalized form of Equation (8), which is implied by Scheidegger's theory. It also generalizes Equation (22) proposed by Strack.

## 6. Discussion and Conclusions

The equation of motion of a solute in a porous medium is employed to derive a generalized non-Fickian dispersion equation (Equation (49)). It is shown that various relationships proposed in the literature can be obtained from this general equation under simplifying assumptions. It is shown that if all inertial terms are neglected, then for a conservative solute, the Fickian dispersion equation is applicable.

If the solute is nonconservative, still the Fickian dispersion equation may be employed, but the dispersion tensor must be scaled by a quantity related to the

rate of mass exchange for the solute. For example, in a medium with a micropore-macropore structure (with aggregates), the solute may diffuse into the aggregates in the early stage of spreading of the solute. This would be a sink for the macropore fluid and, according to Equation (56), in the early stage, the dispersion tensor for the macropore fluid would be smaller than when there are no micropores. At a later stage (for example after the passage of a front), if the solute starts to diffuse out of the micropores, then the dispersion tensor would become larger than when there are no micropores present. This would result in greater dispersion and a tailing of the front (see also the example in the previous section).

It must be noted that memory effects discussed by some authors in the case of aggregated porous media (with macropore-micropore structure) is quite different from the kind of memory considered here. For example, Raats (1981) considers dispersion in a structured porous medium using the one-dimensional form of classical advection-dispersion equation (Equation (1) and (2)), supplemented with a kinetic relationship for  $\hat{r}$  and a mass balance equation for solutes in the micropore. Then, employing the Duhamel's theorem and by application of Laplace transform, Raats derives four different approximate forms of the combined equation. None of the approximate forms, however, produce a telegraph equation. Therefore, the feature of a finite speed of propagation of a front is not found in his theory.

For cases that the inertial terms cannot be neglected, a differential equation for the dispersive flux  $\mathbf{J}$  is obtained. This equation contains spatial and temporal derivatives of  $\mathbf{J}$  and is called transient non-Fickian equation. The non-Fickian effects stem from the inertial terms in the equation of motion of a solute. It is shown that the relationships proposed by Tompson (1988), Scheidegger (1958), and Strack (1992) are special cases of the equation derived here. It is shown that the non-Fickian terms give rise to some kind of memory effect in the dispersion process. The memory effect (or the non-Fickian behavior) is characterized by a tensor which is related to the dispersion tensor and the chemical potential of the fluid (Equation (55)). Also, it is found that scale-dependency is dispersivities, implied by nonlocal dispersion theories obtained from stochastic approaches (e.g., Cushman and Ginn 1993; Neuman, 1993), is also included in transient non-Fickian dispersion theories. True that inertial effects are not believed to be of importance in commonly-encountered transport problems, but, the fact that Equations (8) or (58) result in a scale-dependent dispersion tensor is of practical significance in the case of heterogeneous media.

In this development, no assumptions were made about the solid velocity. Therefore, the equations derived here are valid for deformable as well as rigid porous media. The assumption of low concentration of solute may be relaxed if necessary. That, however, may lead to some modifications to the results (see Hassanizadeh and Leijnse, 1995). The derivation presented here illustrates the fact that basic laws of physics can be used to provide the necessary foundations to our theories and to reduce empiricism in our conceptual descriptions of porous media processes.

## Acknowledgement

The author would like to gratefully acknowledge discussions with Professor C. J. van Duijn of the Centre for Mathematics and Computer Sciences (CWI) in Amsterdam. Comments by A. F. B. Tompson and anonymous referees, which led to the improvement of the article, are gratefully appreciated.

## References

- Dagan, G.: 1989, *Flow and Transport in Porous Media*, Springer-Verlag, Berlin.
- De Josselin de Jong, G.: 1958, Longitudinal and transverse diffusion in granular deposits, *Trans. Amer. Geophys. Union*, **39**, 67–74.
- Glass, D. E. Özisik, M. N., and McRae, D. S.: 1987, Hyperbolic heat conduction with radiation in an absorbing and emitting medium, *Numer. Heat Transfer* **12**, 321–333.
- Hassanizadeh, S. M.: 1986a, Derivation of basic equations of mass transport in porous media, Part 1. Macroscopic balance laws, *Adv. Water Resour.* **9**, 196–206.
- Hassanizadeh, S. M.: 1986b, Derivation of basic equations of mass transport in porous media, Part 2. Generalized Darcy's and Fick's laws, *Adv. Water Resour.* **9**, 207–222.
- Hassanizadeh, S. M. and Leijnse, A.: 1995, A Non-linear theory of high-concentration-gradient dispersion in porous media, *Adv. Water Resour.* **18**, 203–215.
- Maas, C.: 1994, On convolutional processes and dispersive groundwater flow, PhD Thesis, Faculty of Civil Engineering, Delft University of Technology, Delft, The Netherlands, 1994.
- Matheron, G. and De Marsily, G.: 1980, Is transport in porous media always diffusive? A counter example, *Water Resour. Res.* **16**, 901–917.
- Raats, P. A. C.: 1981, Transport in structured porous media, in A. Verruijt and F. Borends (eds), *Proceedings of Euromech 143*, pp. 221–226.
- Scheidegger, A. E.: 1958, Typical solutions of the differential equations of statistical theories of flow through porous media, *Trans. Amer. Geophys. Union* **39**, 929–932.
- Scheidegger, A. E.: 1960, *The Physics of Flow Through Porous Media*, Univ. of Toronto Press, Toronto.
- Strack, O. D. L.: 1992, A mathematical model for dispersion with a moving front in groundwater, *Water Resour. Res.* **28**, 2973–2980.
- Tompson, A. F. B.: 1988, On a new functional form for the dispersive flux in porous media, *Water Resour. Res.* **24**, 1939–1947.
- Tompson, A. F. B. and Gray, W. G.: 1986, A second-order approach for the modeling of dispersive transport in porous media, 1. Theoretical development, *Water Resour. Res.* **22**, 591–599.