

Analytical solutions for co- and counter-current imbibition of sorbing, dispersive solutes in immiscible two-phase flow

Karen Sophie Schmid · Sebastian Geiger · Kenneth Stuart Sorbie

Received: 18 February 2011 / Accepted: 24 January 2012
© Springer Science+Business Media B.V. 2012

Abstract We derive a set of analytical solutions for the transport of adsorbing solutes in an immiscible, incompressible two-phase system. This work extends recent results for the analytical description for the movement of inert tracers due to capillary and viscous forces and dispersion to the case of adsorbing solutes. We thereby obtain the first known analytical expression for the description of the effect of adsorption, dispersion, capillary forces and viscous forces on solute movement in two-phase flow. For the purely advective transport, we combine a known exact solution for the description of flow with the method of characteristics for the advective transport equations to obtain solutions that describe both co- and spontaneous counter-current imbibition and advective transport in one dimension. We show that for both cases, the solute front can be located graphically by a modified Welge tangent. For the dispersion, we derive approximate analytical solutions by the method of singular perturbation expansion. The solutions reveal that the amount of spreading depends on the flow regime and that adsorption diminishes the spreading behavior of the solute. We give some illustrative examples and compare the analytical solutions with numerical results.

Keywords Analytical solutions · Two-phase flow · Mixing · Transport · Adsorption · Dispersion · Spontaneous imbibition · Perturbation expansion · Welge tangent

1 Introduction

In many reservoir engineering and environmental applications, the unsteady flow of the two phases and at the same time miscible displacement within each phase occur. For example, if water is pumped into a reservoir to recover oil, the ionic composition of the connate water is often different from that of the injected brine. The changing ionic composition can enhance recovery [2, 29, 65], or the mixing of the two different brines leads to the precipitation of minerals and formation of scale [41, 58] that hinder production. For the purpose of enhanced oil recovery and the bioremediation of contaminant non-aqueous phase liquids, chemical floods are designed where understanding the brine composition is crucial, since the interfacial activity, phase behavior and mobility control of the chemical flood depend as much on the concentration of the chemicals as they depend on the composition and mixing behavior of the ionic environment itself [37]. Another example is carbon sequestration. In this case, CO₂ occurs as a component dissolved in the water phase, and the mixing with the brine triggers a number of aqueous reactions which trap the CO₂ in the minerals [63]. In all these cases, a proper understanding of miscible displacement and dispersive mixing is fundamental to properly assess the amount of reactive solutes involved in chemical reactions (e.g. [12, 17–19, 21]).

K. S. Schmid (✉) · S. Geiger · K. S. Sorbie
Institute of Petroleum Engineering, Heriot-Watt University,
Edinburgh, EH14 4AS, UK
e-mail: karen.schmid@pet.hw.ac.uk

S. Geiger
e-mail: sebastian.geiger@pet.hw.ac.uk

K. S. Sorbie
e-mail: ken.sorbie@pet.hw.ac.uk

Contrary to the significant body of literature on mixing and spatial heterogeneity (for a recent review, see [19]), investigations for two-phase systems so far focus on the spreading of the phases themselves only [14, 38, 50, 51] and omit transport which can be explained by the complexity of the governing equations where both capillary, viscous and dispersive terms are coupled in a highly non-linear way.

Clearly, for gaining a full understanding of all the mechanisms and effects involved, numerical simulations are important, and in recent years, there has been a substantial progress in the development of numerical methods (e.g. [7, 24, 30, 31, 40, 55]). But analytical solutions are needed as a possible benchmark tool. Also, analytical solutions often act as ‘building blocks’ for numerical methods themselves (e.g. [7, 39]).

For the growth of the dispersive zone, the adsorption behavior of a solute plays a particularly important role since it affects the way, how the dispersive zone grows. Adsorption leads to a retardation of a component behind the fluid front of the carrying phase, and as a consequence, the fluid field which determines the component’s dispersive behavior is different from the one of an inert component.

In this paper, we therefore extend an earlier work [56] where an analytical description for the movement of inert solutes in two-phase flow was given, in three ways: (1) We solve the case of pure advection, i.e. if dispersion can be ignored and if the tracers are not inert but rather interact with the rock through adsorption. We show that for specific cases, the solution can be represented by a modified Welge tangent even in the presence of capillarity. These are the first known expressions for the description of the movement of solutes due to capillarity, viscous forces and adsorption. (2) We show that for the viscous limit, i.e. the case of negligible capillarity, the solutions given in [32] are approached. (3) We derive closed form analytical expressions for hydrodynamic dispersion and show analytically how the growth rate of the dispersive zone depends on the adsorption behavior of the solute. These solutions are the first known analytical expressions for hydrodynamic dispersion, capillarity and adsorption in two-phase flow. For all the extensions (1)–(3), we additionally show that our earlier solutions for the inert case are recovered as a special case.

The remainder of this paper is structured as follows: First, we introduce the mathematical model and basic notation and give a short overview over existing solutions for immiscible two-phase flow without transport. Then, we solve the advection problem exactly by two different methods: Based on a known integral solution for two-phase flow, we first combine a vari-

able transformation with the physical notion that for the dispersion-free limit, the solutes can be written as functions of their carrying fluid only; second, we use the method of characteristics. We show that if the boundary and initial conditions of the flow problem satisfy the McWhorter and Sunada problem [45], the solution to the transport equation can be represented by a modified Welge tangent [60]. Subsequently, we use a perturbation expansion to derive analytical expressions for hydrodynamic dispersion for the case where the dispersion coefficient is small compared to the characteristic length of the system. Based on these equations, we are able to obtain an analytical expression for the growth rate of the dispersive mixing zone. Then, we compare the obtained solutions against numerical references solution for the cases of co- and counter-current imbibition and for the capillary-free limit, the Buckley–Leverett problem [9] and finish with some conclusions.

2 Mathematical model

We consider immiscible, incompressible, isothermal two-phase flow through a homogeneous, horizontal, one-dimensional porous medium where the fluid phases additionally transport components. Material balance for the two phases leads to the equations [4]

$$\phi \frac{\partial S_w}{\partial t} = - \frac{\partial}{\partial x} (q_w), \tag{1}$$

and

$$S_n + S_w = 1, \tag{2}$$

where S_w is the wetting phase saturation, S_n the non-wetting phase saturation and ϕ is porosity which is assumed to be constant throughout the whole domain. Furthermore, we assume that the volume flux of the wetting phase and the non-wetting phase, q_w and q_{nw} , can be described by the multiphase extension of Darcy’s equation [48] which describes the volume flux due to a gradient in the phase pressures p_w and p_{nw} ,

$$\begin{aligned} q_w &= -K \frac{k_w}{\mu_w} \frac{\partial}{\partial x} p_w, \\ q_{nw} &= -K \frac{k_{nw}}{\mu_{nw}} \frac{\partial}{\partial x} p_{nw}. \end{aligned} \tag{3}$$

Here, K is the absolute permeability, μ_w is the viscosity of the wetting phase and μ_{nw} that of the non-wetting phase and $k_{nw} = k_{nw}(S_w)$ and $k_w = k_w(S_w)$ are the relative permeability of the non-wetting and wetting fluid, respectively, that describe the impairment of the one fluid phase by the other. The two-phase pressures p_w

and p_{nw} are related through the capillary pressure $p_c = p_{nw} - p_w$. Combining the definition of capillary pressure with Eqs. 1 and 2, one can rewrite q_w as an expression of the total volume flux $q_t = q_{nw} + q_w$ which yields

$$q_w = f(S_w)q_t - D \frac{\partial S_w}{\partial x}. \tag{4}$$

Here, D can be thought of as a capillary dispersion coefficient for the fluid phases, and together with f , it describes the capillary hydraulic properties of the fluid-porous medium system and is defined through

$$f(S_w) = \left(1 + \frac{k_{nw}\mu_w}{k_w\mu_{nw}} \right)^{-1},$$

$$D(S_w) = -K \cdot \frac{k_{nw} f dP_c}{\mu_{nw} dS_w}. \tag{5}$$

In the following, we assume that (a) the only chemical interaction between the components and the porous medium is through adsorption and otherwise they do not alter the porous medium, (b) the components do not change the flow parameters, (c) they do not partition into the other phase, (d) the solute mass flux due to hydrodynamic dispersion within a phase is described by a Fickian model and (e) density effects can be ignored. Then the n continuity equations for the n different components can be written as [1, 27]

$$\phi \frac{\partial (S_w C_j)}{\partial t} + \frac{\partial}{\partial t} \cdot [(1 - \phi)\rho_t A_{s,j}] =$$

$$-\frac{\partial}{\partial x} (q_w \cdot C_j) + \frac{\partial}{\partial x} \cdot \left(\phi S_w D_{H,w} \frac{\partial C_j}{\partial x} \right), \quad j = 1, \dots, n \tag{6}$$

and

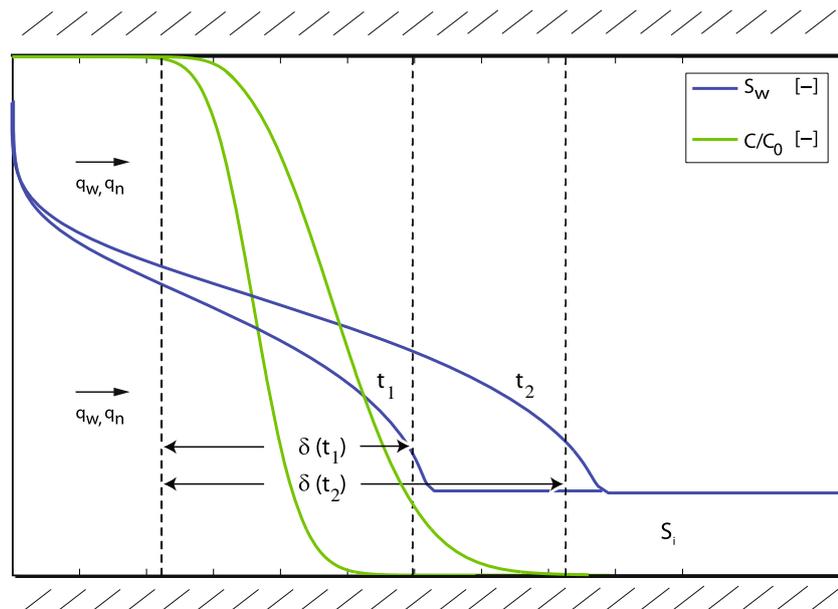
$$\phi \frac{\partial (S_n \chi_k)}{\partial t} + \frac{\partial}{\partial t} \cdot [(1 - \phi)\rho_t B_{s,k}] =$$

$$-\frac{\partial}{\partial x} (q_n \cdot \chi_k) + \frac{\partial}{\partial x} \cdot \left(\phi S_n D_{H,n} \frac{\partial \chi_k}{\partial x} \right), \quad k = 1, \dots, m, \tag{7}$$

where we denoted the adsorption per unit mass of rock of component C_j and χ_k by $A_{s,j}$ and $B_{s,k}$, respectively, and the rock density by ρ_t .

As stated above, the components are assumed to not change the flow field. If chemical flooding with surfactants, polymers, foams etc. is considered, the constitutive relationships depend on both saturation and component concentration. For this case, analytical solutions can be derived, if both capillarity and hydrodynamic dispersion are ignored. This leads to a system of hyperbolic conservation laws, and the method of characteristics or the method of chromatography can be used to derive analytical solutions (e.g. [32, 33, 36, 53, 54, 57]). As explained in the introduction, our primary interest is the mixing of the adsorbing but otherwise inert components (Fig. 1). We hence assume the capillary hydraulic properties to be functions of saturation only. For the solutes in the water phase, Eq. 6 assumes that the volume fraction of the components is small compared to that of the wetting phase which for most practical applications, like different ion compositions, is an excellent approximation [53]. The solutes in the non-wetting phase can consume any arbitrary fraction of the non-wetting phase volume [39]. $D_{H,\gamma}$ is the

Fig. 1 Schematic representation of one-dimensional, uni-directional displacement of a non-wetting phase by a wetting phase with an initial wetting saturation S_i . Behind the wetting front, a mixing zone between the ‘old’ composition of the wetting phase and the ‘new’ one of length $\delta(t)$ develops. Note that the solute front always trails the saturation front if $S_{wr} > 0$, see Fig. 3



hydrodynamic dispersion coefficient and for the one-dimensional case becomes [4]

$$D_{H,\gamma} = \alpha_{l,\gamma} \frac{q_\gamma}{\phi} + D_{\text{mol}}, \quad \gamma \in \{\text{n}, \text{w}\} \tag{8}$$

where $\alpha_{l,\gamma}$ is the coefficient of hydrodynamic dispersion and accounts for effects of the flow field and D_{mol} is the effective molecular diffusion coefficient. In the analysis that follows, we will assume $j = 1$, but the entire analysis immediately carries over to the case where more than one component is present. Similarly, we mainly will focus on the case where the non-wetting phase has a homogeneous composition, i.e. $k = 1$, and is completely described by the restriction Eq. 2. Again, the analysis that follows can easily be extended to multiple solutes $\chi_j, j = 1, \dots, m$. To simplify notation, we will write D_H instead of $D_{H,w}$. We set

$$\Gamma := \frac{(1 - \phi)}{\phi} \rho_r A_s. \tag{9}$$

For thermodynamic equilibrium, the isotherm is a function of C only, i.e. $\Gamma = \Gamma(C)$ [5], and for small C can be approximated by a linear isotherm [5]

$$\Gamma = \Gamma(C) = \left(\frac{d\Gamma}{dC} \right) \cdot C =: D_s \cdot C. \tag{10}$$

D_s can be thought of as a ‘retardation’ term. Both the conservation equation for the fluid phase and the solutes are of parabolic type, and consequently, the resulting solutions are smooth. Therefore, we can expand Eq. 6 to arrive at

$$\phi(S_w + D_s) \frac{\partial C}{\partial t} = -q_w \frac{\partial C}{\partial x} + \frac{\partial}{\partial x} \cdot \left(\phi S_w D_H \frac{\partial C}{\partial x} \right). \tag{11}$$

We denote the Peclet number of phase γ by $Pe_\gamma = q_\gamma \cdot L / (\phi D_{\text{mol}})$, $\gamma \in \{\text{n}, \text{w}\}$, where L is the length characteristic for hydrodynamic dispersion. For advection dominated problems with a Peclet number $Pe_\gamma > 10$, molecular diffusion becomes negligible compared to mechanical dispersion [4] and thus is ignored in the following. The transport of a component thus consist of an advective part which according to Eq. 4 has a viscous and a capillary component and a dispersive one.

We derive an analytical solution for the transport Eq. 6 that fully considers linear adsorption, capillary effects and hydrodynamic dispersion. Thus, all the physical mechanisms that account for solute transport and mixing in a homogeneous two-phase system are taken into account. The solution is obtained from two main ideas. First, we note that for cases where S_w and q_w in the conservation equation for C (Eq. 6) are known either from analytical or numerical solutions, the problem of solving the conservation equation for

S_w (Eq. 1), together with equations for $q_w, f(S_w)$ and $D(S_w)$ (Eqs. 4, 5 and 6), reduces to solving one advection–dispersion–reaction equation (ADRE) for the concentration C . S_w and q_w are fully determined by Eqs. 1 together with Eqs. 4 and 5 and are not affected by the adsorption of the solute. The highly non-linear term due to capillary forces in Eq. 4 poses a main mathematical difficulty for deriving analytical solutions, and thus, only few exact solutions are known (see [56] for an overview). We choose the ones derived in [45] since they allow for both general capillary hydraulic properties and the consideration of co- and counter-current flow. Also, it can be shown that their solution given for counter-current flow situation is equivalent to the common situation of spontaneous, counter-current imbibition [56]. Thus, our solutions contain the common situation where a sorbing solute is transported during spontaneous, counter-current imbibition. The only time when we make specific use of the special form of these solutions, however, is for the explicit determination of the saturation level at which the solute advective front breaks through and in the examples given in Section 5. The nonlinear expressions derived for the characteristics and the hydrodynamic dispersion and reaction are valid for any flow and saturation field known either from numerical solutions like streamline simulations [7, 16, 35] or analytical considerations.

Although this significantly reduces the complexity of the problem, the ADRE Eq. 11 has still time- and space-dependent coefficients, and no analytical solutions are known. Secondly therefore, to derive a solution for it, we use the same approximation as in [56]: We separate the two physical transport mechanisms in Eq. 6, i.e. the advective motion due to viscous and capillary forces, and dispersive mixing. The advective part is solved for exactly by two different approaches: First, we use the physical notion that if dispersion can be ignored, i.e. $D_H = 0$ in Eq. 6, C is a function of S_w only, and an explicit expression for the location of the solute front can be derived. Secondly, we use the method of characteristics. Both approaches yield the same result. We show that if q_w and S_w are described by the McWhorter and Sunada problem, the location of the solute front can be determined graphically by a modified Welge tangent [60]. To the best of our knowledge, this is the first analytical solution that accounts for adsorption and capillary effects on tracer transport.

Next the effect of hydrodynamic dispersion is superimposed on the advective motion via a singular perturbation expansion around the advective front of the solute. Singular perturbation techniques have been used previously for describing dispersion in unsteady flow fields of a single phase [15, 20, 26, 49, 61, 62]

and only recently were extended to the description of dispersion of inert tracers in two-phase flow [56]. We show that if the dispersion is small compared to a characteristic length of the system, very good agreement between our analytical approximation and a numerical reference solution is achieved. While we are mainly concerned with the combined effects of adsorption, capillary, viscous and dispersive processes and adsorption in this paper, the equations derived for the characteristics and the hydrodynamic dispersion are valid for any given flow field, and for illustration, we also combine them with the solution for the capillary-free limit, the Buckley–Leverett problem [9]. To the best of our knowledge, this is the first analytical solution that fully describes the complex dependence of the effective dispersion on adsorption and the simultaneous and unsteady flow of the two phases. From these analytical expressions, we finally obtain equations for the growth rate of the dispersive zone both for the case where capillary pressure is considered and for the viscous limit.

3 Solution of the advective problem

We first consider the dispersion-free limit of Eq. 11, i.e. the case $D_H = 0$. We will show that if an initial wetting phase is present, the solute front travels behind the fluid displacement front and breaks through at a certain saturation value S_w^* . We will show that the retardation is due to the combination of the initial wetting saturation that acts as a storage for the solute and the adsorption, i.e. that adsorption alone cannot explain the retardation of solutes.

Two possibilities exist for deriving an analytical solution. The first one uses the physical notion that C is carried by the respective fluid phase, and thus, we can write $C = C(S_w)$. This together with a variable transformation leads to a simple ordinary differential equation (ODE) for C . From this, we obtain an explicit expression for the saturation value S_w^* at which the advective front occurs that can be represented graphically by a modified Welge tangent [60]. We can obtain the same result for the location of the jump, if we employ the method of characteristics for solving Eq. 11. This has two advantages: First, it gives a mathematically rigorous justification for the physical notion that for the dispersion-free limit, C must be a function of S_w . Second, we obtain analytical expressions for the characteristic coordinates. They will prove to be central for the derivation of the dispersion approximation. Furthermore, if the solute is inert, i.e. we have $\mathcal{D}_s = 0$, the

obtained solutions reduce to the ones derived in [56] for the advective case.

3.1 Preliminaries

For the solute, we consider the boundary and initial conditions

$$\begin{aligned} C(x = 0, t) &= C_0, \\ C(\infty, t) &= C_i, \\ C(x, 0) &= C_i, \end{aligned} \tag{12}$$

and for q_w and S_w , we use the initial and boundary conditions

$$q_0 = q_w(x = 0, t) = At^{-1/2}, \tag{13a}$$

$$S_w(x = 0, t) = S_0, \tag{13b}$$

$$S_w(\infty, t) = S_i, \tag{13c}$$

$$S_w(x, 0) = S_i, \tag{13d}$$

where the parameter A is a constant that cannot be chosen freely but depends on the capillary hydraulic properties according to [45]

$$A^2 = \frac{\phi}{2(1 - f_i R)^2} \int_{S_i}^{S_0} \frac{(S_w - S_i) D(S_w)}{(F - f_n)(S_w)} dS_w, \tag{14}$$

where $f_n = (f - f_i)R \cdot (1 - f_i R)^{-1}$ is the normalized fractional flow function, $f_i = f(S_{wi})$, and $R = q_t/q_0$. For unidirectional displacement, $q_t = q_0$ and consequently $R = 1$, and for counter-current flow, $q_t = R = 0$. The maximally possible value for S_0 is $1 - S_{nr}$, where S_{nr} is the residual saturation of the non-wetting phase. We introduce the modified fractional flow function [44, 52]

$$F(x, t) = \frac{q_w/q_0 - f_i R}{1 - f_i R}, \tag{15}$$

F has the physical meaning of the ratio of the net wetting phase flux at (x, t) to the net influx of a wetting phase. In contrast to the classical fractional flow function f , F fully incorporates the influence of capillary pressure and is given by the non-linear equation [45]

$$\begin{aligned} F(S_w) &= 1 - \left(\int_{S_w}^{S_0} \frac{(\beta - S_w) D(\beta)}{F(\beta) - f_n(\beta)} d\beta \right) \\ &\quad \cdot \left(\int_{S_i}^{S_0} \frac{(\gamma - S_i) D(\gamma)}{F(\gamma) - f_n(\gamma)} d\gamma \right)^{-1}. \end{aligned} \tag{16}$$

Before we proceed to transform the conservation Eq. 6 for C into an equivalent integrable ODE, a remark on the fixed flow rate q_0 is in order. Both for the case of co- and counter-current flow, the situation of an inflow rate that declines with $t^{-1/2}$ over time occurs in many practical settings. For the case of co-current imbibition (Fig. 2), the flow rate q_0 as specified above corresponds to a pressure drawdown at the inlet according to Darcy's Eq. 3. Possible boundary conditions for that scenario are, for example, setting $p = p_w$ at $x = 0$ or $p = p_{res} < p_w$ at $x = \infty$.

For the counter-current case, however (Fig. 2), it has been overlooked until recently [56] that the constant A in Eq. 14 is exactly such that $q_0 = q_w(x = 0, t)$ is determined by the saturation gradients and the resulting gradient in capillary pressure only, i.e. there is no imposed forced inflow rate at the left boundary [56]. The situation is that of spontaneous, counter-current imbibition and A measures the material's ability to spontaneously imbibe the wetting phase [56]. Spontaneous, counter-current imbibition is of outstanding interest since it constitutes one of the main production mechanisms in water-wet and mixed wet fractured reservoirs [47] where the wetting phase drawn from the high permeability fracture into the oil-rich low permeability rock matrix by capillary action. Note also that the total amount of fluid injected/imbibed can be expressed as $Q_w(t) = \int_0^t q_0(\tau) d\tau = 2At^{1/2}$. Thus, although the rate q_0 tends towards infinity for early times, $Q_w(t)$ satisfies $Q_w(t = 0) = 0$. Finally, we point out that boundary conditions with S_0 and C_0 facilitate the solution. Physical boundary conditions at $x = 0$ fix fluxes for the fluid phases and components, resulting in mixed 1–2 type boundary conditions.

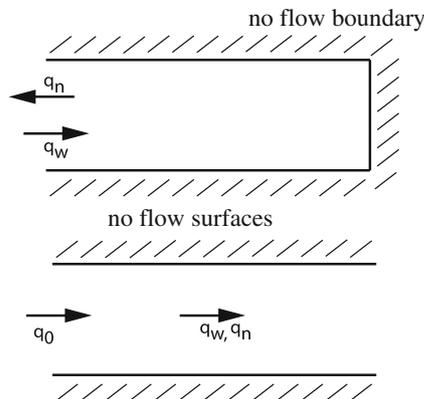


Fig. 2 Situation of counter-current imbibition (top) and co-current imbibition (bottom)

Altogether, for the counter-current case, the initial and boundary conditions reduce to

$$q_w(x, t) = -q_n(x, t), \tag{17a}$$

$$S_w(x = 0, t) = S_0, \tag{17b}$$

$$S_w(\infty, t) = S_i, \tag{17c}$$

$$S_w(x, 0) = S_i. \tag{17d}$$

3.2 Solution as a Welge tangent

We introduce the similarity variable

$$\lambda = xt^{-1/2}. \tag{18}$$

Since the saturation profile $S_w(x, t)$ is a monotone function of (x, t) , we have $S_w = S_w(\lambda)$, or $\lambda = \lambda(S_w)$, respectively. Employing the definition of F , Eq. 15, and using that $q_0 = At^{-1/2}$, the conservation equation for S_w , Eq. 1, can be expressed as

$$-\phi \frac{\partial S_w}{\partial t} = At^{-1/2}(1 - f_i R) \frac{\partial F}{\partial x}. \tag{19}$$

Then, the similarity variable λ allows Eq. 19 to be written as an ODE [45]

$$\lambda(S_w) = \frac{2A(1 - f_i R)}{\phi} \frac{dF}{dS_w}. \tag{20}$$

Since F is defined in terms of q_w and q_w depends on S_w , the ODE Eq. 20 is subject to

$$F = \begin{cases} 1 & \text{for } S_w = S_0 \\ 0 & \text{for } S_w = S_i. \end{cases} \tag{21}$$

The conservation Eq. 11 for C can be rewritten as an ODE in the same manner

$$\frac{dC}{dS_w} \left[-\lambda + \frac{2A(F(1 - f_i R) + f_i R)}{\phi(S_w + \mathcal{D}_s)} \right] = 0 \tag{22}$$

subject to

$$C = \begin{cases} C_0 & \text{for } S_w = S_0 \\ C_i & \text{for } S_w = S_i. \end{cases} \tag{23}$$

Equation 22 describes the transport of the jump from the initial concentration C_i to the injected concentration C_0 depending on the saturation and has the simple solution

$$C(S_w) = \begin{cases} C_0 & \text{for } S_w < S_w^* \\ C_i & \text{for } S_w > S_w^*. \end{cases} \tag{24}$$

Since the jump C occurs at S_w^* , the value of S_w^* must occur where the expression in the bracket of the ODE

Eq. 22 becomes zero. This yields a non-linear expression for S_w^*

$$\frac{F(S_w^*)}{\mathcal{D}_s + S_w^*} + \frac{f_i R}{(1 - f_i R)S_w^*} = \frac{dF}{dS_w} \Big|_{S_w^*}, \tag{25}$$

respectively, for $S_{wi} = S_{wr}$ and $f_w(S_{wi}) = f_i = 0$:

$$\frac{F(S_w^*)}{\mathcal{D}_s + S_w^*} = \frac{dF}{dS_w} \Big|_{S_w^*}. \tag{26}$$

All the functions and parameters in Eqs. 25 and 26 are known explicitly, and the solution can easily be obtained by prescribing S_0 , determining F from Eq. 16 and then solving the non-linear Eq. 25. Any capillary hydraulic properties can be used. For arbitrary functions, the integrals of the exact solution need to be solved numerically. Determining S_w^* can also be performed graphically by drawing a straight line from $(0, \frac{f_i R}{(1 - f_i R)})$ tangent to the fractional flow curve F , see Fig. 3. Note that if initially a wetting phase is present, which is the case for most realistic geological formations and reservoirs, the component front gets retarded even if $\mathcal{D}_s = 0$ and does not travel along with the phase front. This is intuitively obvious, since if the connate wetting phase has a composition different from the injected one, the ‘new’ composition needs to fill the ‘old’ phase first and thus breaks through behind the wetting front (Fig. 1).

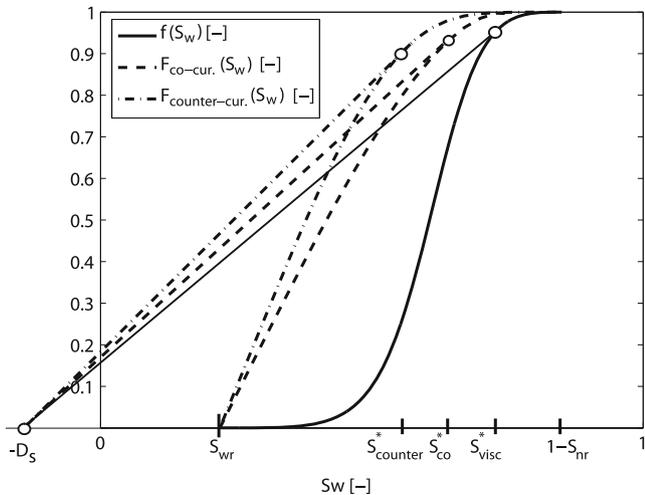


Fig. 3 Fractional flow functions for purely viscous, co-current and counter-current (spontaneous imbibition) flow for different inlet saturations S_0 . For the viscous and the counter-current case, $S_0 = 1 - S_{nr}$, and for the cocurrent case, $S_0 < 1 - S_{nr}$. The straight lines give the saturation values for the respective cases at which the component that adsorbs with rate \mathcal{D}_s jumps from its initial value to the injected concentration for the dispersion-free limit

Spontaneous counter-current imbibition Spontaneous counter-current imbibition occurs when the wetting fluid spontaneously imbibe into the porous medium thus replacing the non-wetting phase which flows out into the opposite direction, i.e. in our notation $q_w = -q_o$, see Fig. 2, and hence $R = f_n = 0$. As outlined above, for the case of counter-current flow, the boundary condition $q_0 = A \cdot t^{-1/2}$ does not represent a forced inflow rate, but describes spontaneous imbibition, where A is a measure of the material’s ability to imbibe the wetting fluid [56].

In the foregoing analysis, R was not set to a specific value, and therefore, the respective expressions for A and F can be obtained immediately from setting $R = 0$, and the semi-analytical solution for C directly follows from Eq. 24 for the thus modified expressions for A and F with

$$\frac{F(S_w^*)}{(S_w^* + \mathcal{D}_s)} = \frac{dF}{dS_w} \Big|_{(S_w^*)}. \tag{27}$$

For partly water-wet fractured reservoirs, spontaneous, counter-current imbibition represents a key recovery mechanism since there, the water imbibe from the fracture into the matrix thus replacing the oil that could not be produced through flooding and thus through viscous effects [6, 47]. Equations 24–26 therefore contain the important situation where a sorbing solute is transported by spontaneous, counter-current imbibition.

As stated initially, we mainly focus on solutes in the wetting phase and merely note that for the case where $S_0 < 1$, the saturation of the non-wetting phase at the left boundary is non-zero and we can prescribe the following initial and boundary conditions for solutes in the non-wetting phase:

$$\begin{aligned} \chi(x = 0, t) &= \chi_0, \\ \chi(\infty, t) &= \chi_i, \\ \chi(x, 0) &= \chi_i, \end{aligned} \tag{28}$$

which immediately gives

$$\chi(S_n) = \begin{cases} \chi_0 & \text{for } S_n < S_n^* \\ \chi_i & \text{for } S_n > S_n^* \end{cases}, \tag{29}$$

where S_n^* satisfies

$$S_n^* = 1 - S_w^{**}, \tag{30}$$

and

$$\frac{dF}{dS_w} \Big|_{(S_w^{**})} = \frac{F(S_w^{**})}{(1 - S_w^{**} + \tilde{\mathcal{D}}_s)} - \frac{R(1 - f_i)}{(1 - f_i R)(1 - S_w^{**} + \tilde{\mathcal{D}}_s)}, \tag{31}$$

where we use

$$\tilde{\Gamma} := \left(\frac{1-\phi}{\phi}\right)\rho_r B_s, \quad \text{and} \quad \tilde{\Gamma}(\chi) = \tilde{D}_s \cdot \chi. \quad (32)$$

3.3 Method of characteristics

Next, we derive the location of the jump in C at S_w^* by the method of characteristics and show that the so derived value for S_w^* agrees with the one given in Eq. 25. The method of characteristics is more technical and lengthy than the intuitive approach taken above, where we simply assumed that C is carried along with the saturation and wrote C as a function of S_w only. However, it has two advantages: First, it yields a rigorous mathematical justification for the analytical solution given in Eqs. 24–26. Second, it results in the introduction of characteristic coordinates τ and θ that will prove to be useful when we solve for dispersion in Section 4.

The equation for characteristics for the Eq. 11 is

$$q_w dt - (\phi S_w + \phi D_s) dx = 0. \quad (33)$$

Equation 33 has an analytical solution in the sense that there exists a function $\eta(x, t)$ such that

$$-d\eta = q_w dt - (\phi S_w + \phi D_s) dx, \quad (34)$$

$$\frac{\partial \eta}{\partial t} = -q_w, \quad \text{and} \quad \frac{\partial \eta}{\partial x} = (\phi S_w + \phi D_s)$$

if and only if

$$\frac{\partial (\phi S_w + \phi D_s)}{\partial t} = \frac{\partial (\phi S_w)}{\partial t} \stackrel{!}{=} -\frac{\partial q_w}{\partial x}. \quad (35)$$

The above is simply the continuity equation for the wetting phase, and thus, η as specified above exists. The characteristic can be determined from Eq. 34. From the second equation of Eq. 34, it follows

$$\eta(x, t) = \int_0^x (\phi S_w(\xi, t) + \phi D_s) d\xi + \tilde{c}(t). \quad (36)$$

The function $\tilde{c}(t)$ must be determined from the first equation in Eq. 34. It follows

$$\begin{aligned} \frac{\partial \eta}{\partial t} &= \frac{\partial}{\partial t} \int_0^x (\phi S_w(\xi, t) + \phi D_s) d\xi + \frac{d\tilde{c}(t)}{dt} \\ &= \int_0^x \frac{\partial}{\partial t} (\phi S_w(\xi, t) + \phi D_s) d\xi + \frac{d\tilde{c}}{dt} = -q_w \\ &= \int_0^x -\frac{\partial q_w}{\partial x} \Big|_{\xi} d\xi + \frac{d\tilde{c}}{dt}. \end{aligned} \quad (37)$$

Altogether, we arrive at

$$\begin{aligned} \eta(x, t) &= \int_0^x (\phi S_w(\xi, t) + \phi D_s) d\xi \\ &\quad - \int_0^t q_w(0, \alpha) d\alpha. \end{aligned} \quad (38)$$

In the following it will be useful to transform the first integral on the right-hand side of η onto the (S_w, t) coordinate system, i.e. to use the fact that $x = x(S_w, t)$. By substitution, we thus get

$$\begin{aligned} \eta(S_w, t) &= \int_{S_0}^{S_w} (\phi S_w(\xi, t) + \phi D_s) \frac{\partial x}{\partial S_w} \Big|_{\xi} d\xi \\ &\quad - \int_0^t q_w(0, \alpha) d\alpha. \end{aligned} \quad (39)$$

We set

$$\begin{aligned} \theta(S_w, t) &:= \int_{S_0}^{S_w} (\phi S_w(\xi, t) + \phi D_s) \frac{\partial x}{\partial S_w} \Big|_{\xi} d\xi, \quad \text{and} \\ \tau(t) &:= \int_0^t q_w(0, \alpha) d\alpha. \end{aligned} \quad (40)$$

The characteristic coordinates given in Eq. 39 are valid for arbitrary initial and boundary conditions, and any q_w, S_w and S_n that satisfy Eqs. 1 and 2. To derive an explicit expression for the value S_w at which the solute front occurs in the case where capillary effects are fully considered, we now capitalize on the features of the solution derived in [45].

By construction, θ and τ are the coordinates along which Eq. 6 reduces to the simple form

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial \theta} = 0. \quad (41)$$

If C is given by the function $H(x)$ at time $t = 0$, then the above PDE has the simple solution

$$C(\theta, \tau) = H(\theta - \tau) \quad (42)$$

and an initial solute front travels along the curve which satisfies $\theta \stackrel{!}{=} \tau$, i.e. S_w^* is such that $\eta \stackrel{!}{=} 0$. If the physically motivated approach of assuming $C = C(S_w)$ is valid, then the saturation S_w^* is again given by Eqs. 25 and 26, respectively, which follows in the same manner as in [56].

Before we derive the dispersion approximation, we discuss some features of the solution for the advective case.

3.4 Buckley–Leverett limit

It is interesting to note the similarity of Eq. 24 together with Eq. 26 with the solution obtained for the unidirectional two-phase, multicomponent viscous case,

sometimes referred to as extended Buckley–Leverett problem. The extended Buckley–Leverett problem also satisfies Eq. 24, where for $S_i = S_{wr}$ the constant S_w^* is given in [32, 53]:

$$\frac{f(S_w^*)}{(S_w^* + D_s)} = \frac{dF}{dS_w}|_{(S_w^*)}, \tag{43}$$

i.e. we have the very same structure with the only difference that the fractional flow function $f(S_w)$ neglects capillary forces where $F(S_w)$ can be viewed as a ‘modified’ fractional flow function that incorporates both viscous and capillary effects. Equation 43 can also be obtained from the method of chromatography, see [54].

In cases where the imposed injection is large, capillary effects can be neglected and the Buckley–Leverett, i.e. the viscous, limit is approached. For our setting, this is reached by making the parameter A large. It can be shown analytically [11] that $\lim_{S_0 \rightarrow S_m} A(S_0) = A_{cr}$, where S_m is the maximal achievable value and

$$A_{cr} = \left[\frac{\phi}{2(1 - f_i)^2} \int_{S_i}^{S_m} \frac{(S_w - S_i)D}{F - f_n} dS_w \right]^{1/2} < \infty. \tag{44}$$

If the Welge tangent saturation [60] is denoted by S_b , the fractional flow function F for the limiting case becomes [45, 46]:

$$F(S_w) = \begin{cases} f_n(S_w) & \text{for } S_w \geq S_b \\ f_n(S_b) \left(\frac{S_w - S_i}{S_b - S_i} \right) & \text{for } S_w \leq S_b, \end{cases} \tag{45}$$

where f_n is the normalized fractional flow function

$$f_n = \frac{(f - f_i)R}{1 - f_i R} \tag{46}$$

This gives Eq. 43 since the component front occurs after the wetting front, and thus, $S_w^* \geq S_b$.

4 Dispersion approximation

The analytical solution derived above is valid if hydrodynamic dispersion can be ignored. We will now derive an approximate analytical solution for the ADRE. The solution is constructed in the same way the solution to the linear ADE would be constructed, with the only difference that the parameters depend on the solution for the saturation profile. This introduces a strong time and space dependency of the coefficients, for which no exact analytical solutions for dispersion are known, and we will give an approximate analytical solution through an asymptotic expansion. Although we will focus on the case where the non-wetting phase is homogeneous

and consists of one component only, the same analytical procedure can be used for analysing the effect of hydrodynamic dispersion in the non-wetting phase. To this end, we first normalize the ADRE by introducing $c := C/C_0$, $\bar{x} := x/L_0$, $\bar{t} = t/T_0$ and $\bar{q}_w = q_w/V_0$, where L_0 , T_0 and V_0 are a characteristic length, time and velocity, respectively, such that $\mathcal{O}(T_0) = \mathcal{O}(L_0) = \mathcal{O}(V_0)$ [61]:

$$(\phi S_w + \phi D_s) \frac{\partial c}{\partial \bar{t}} = -\bar{q}_w v \frac{\partial c}{\partial \bar{x}} + \varepsilon v \frac{\partial}{\partial \bar{x}} \left(S_w \bar{q}_w \frac{\partial c}{\partial \bar{x}} \right), \tag{47}$$

with

$$\varepsilon := \frac{\alpha L}{L_0} \quad \text{and} \quad v := \frac{V_0 T_0}{L_0}.$$

For the case where dispersion needs to be taken into account, the only known analytical solutions for the ADRE are valid for the single-phase case with a constant flow field and constant D_H [10].

We therefore employ a different approach: singular perturbation expansion. Singular perturbation techniques have been used before for treating the effect of non-uniform flow fields on dispersion of inert and adsorbing tracers in saturated and unsaturated single-phase flow through porous media [15, 20, 26, 49, 61, 62]. We recently extended them to the case of inter tracers in two-phase flow [56]. Its fundamental idea is that for small ε , dispersion can be thought of as a perturbation to the advection equation. For $\varepsilon \neq 0$, the mathematical character of Eq. 47 fundamentally changes from a hyperbolic PDE to a parabolic one, and thus, the perturbation is of singular nature. The solution (Eq. 24) to the advection problem (Eq. 11) is viewed as an ‘outer solution’ to the ADRE that is a good approximation away from a boundary layer. The boundary layer is characterized as the zone where dispersive effects are strong and thus will be located around the advective front. By ‘magnifying’ this zone through appropriate coordinate transformations and by using the notion that around the front, q_w and S_w can be approximated by their values at the front, the PDE (Eq. 11) reduces to the well-known heat equation. Then inner and outer solution are matched and a uniformly valid, closed form analytical solution is obtained.

Obviously, the idea of finding an approximate solution through a perturbation expansion does not only apply to hydrodynamic dispersion, but to any situation where a sharp front described by a hyperbolic PDE is smeared out by some parabolic terms. Consequently, earlier attempts to account for solute dispersion and capillary effects used a perturbation expansion both around the jump in C and around the Buckley–Leverett shock in S_w [3, 5, 64].

However, this approach is unsatisfactory for two reasons. First, the perturbation expansion for the capillary part is only an approximation and leads to a loss of some of the information on the flow field. Second, to be able to use a perturbation approach, the flow must develop a discontinuity which can serve as the outer solution. While for the co-current situation the outer solution would be the Buckley–Leverett solution, it is not clear what can serve as outer solution for the counter-current case. There, one has $q_t = 0$, and the conservation equation for S_w Eq. 1 only comprises parabolic terms according to Eq. 4 for q_w . Indeed, none of the earlier attempts account for the situation of spontaneous, counter-current imbibition despite its tremendous practical importance for fractured reservoirs [47], but rather give an approximate solution for the co-current case only.

To the best of our knowledge, the solutions we present here therefore for the first time describe the situation where all the physical mechanisms—co- and counter-current imbibition, viscous effects and dispersion—that account for the transport of a sorbing solute and mixing in a homogeneous two-phase system are taken into account.

Dispersive effects are strong around the jump in C which travels along the characteristic coordinates $(\bar{\theta}, \bar{\tau})$, where the overbar denotes normalized variables. Thus, to obtain an inner solution, it makes sense to first transform Eq. 47 onto the $(\bar{\theta}, \bar{\tau})$ coordinate system. Through usage of the Leibnitz rule and the product rule, we obtain

$$\frac{\partial c}{\partial \bar{\tau}} + \frac{\partial c}{\partial \bar{\theta}} = \frac{\varepsilon}{\bar{q}_{w0}} \left[\frac{1}{(S_w + D_s)(\partial \bar{x} / \partial S_w)} \frac{\partial}{\partial S_w} \left((S_w + D_s) S_w \bar{q}_w \right) \frac{\partial c}{\partial \bar{\theta}} + (\phi(S_w + D_s) S_w \bar{q}_w) \frac{\partial^2 c}{\partial \bar{\theta}^2} \right]. \tag{48}$$

Note that if $\varepsilon = 0$ in Eq. 48, we obtain the normalized version of the hyperbolic advection Eq. 41.

To magnify the region around the solute front, we introduce the coordinate transformation

$$\xi = \frac{\bar{\theta} - \bar{\tau}}{\varepsilon^m}. \tag{49}$$

The exponent m determines the ‘thickness’ of the boundary layer and can be determined either from physical or mathematical reasoning. Physically, it needs to be such that within the boundary layer, dispersive changes are of same order of magnitude as temporal changes. Mathematically, it follows from the principle that it must be possible to match the inner solution ‘around’ the boundary region with the outer one close

to the boundary region. Formally, this leads to Van Dyke’s principle of least degeneracy [34, 59], which yields the same boundary-layer thickness as the one obtained from the physical approach. Transforming Eq. 48 onto the $(\bar{\tau}, \xi)$ coordinate system yields

$$\frac{\partial c}{\partial \bar{\tau}} = \frac{1}{\bar{q}_{w0} \varepsilon^{2m-1}} \left[\frac{\varepsilon^m}{(S_w + D_s)(\frac{\partial \bar{x}}{\partial S_w})} \frac{\partial}{\partial S_w} \left((S_w + D_s) S_w \bar{q}_w \right) \times \frac{\partial c}{\partial \xi} + (\phi(S_w + D_s) S_w \bar{q}_w) \frac{\partial^2 c}{\partial \xi^2} \right]. \tag{50}$$

The order of temporal change of the left-hand side of Eq. 50 needs to be the same as the one of the right hand side which leads to $m = 1/2$. This is the same value for m as for the case without adsorption as expected since adsorption does not affect the flow field [56]. The PDE (Eq. 50) was derived through a number of coordinate transformation and thus is equivalent to Eq. 6.

We now seek an approximate analytical solution for Eq. 47 through an asymptotic expansion

$$C(\bar{\tau}, \xi) \sim C_0(\bar{\tau}, \xi) + \varepsilon^{(1/2)} C_1(\bar{\tau}, \xi) + \mathcal{O}(\varepsilon). \tag{51}$$

Inserting this in Eq. 50 with $m = 1/2$ and only retaining terms of zeroth order in ε leads to

$$\frac{\partial c}{\partial \bar{\tau}} = \frac{1}{\bar{q}_{w0}} \left(\phi S_w (S_w + D_s) \bar{q}_w \right) \frac{\partial^2 c}{\partial \xi^2}. \tag{52}$$

This is the well-known diffusion equation, and for the case where the coefficients on the right-hand side are functions of $\bar{\tau}$ only, many analytical solutions are known [10, 13]. To arrive at that form of the diffusion equation, we use the heuristic notion that S_w and \bar{q}_w will undergo small changes around the solute front and thus can be approximated by their values at the front. Formally, this corresponds to a Taylor expansion around the solute front that is truncated after the first term and thus gives the same order $\mathcal{O}(\varepsilon^{1/2})$ as the perturbation expansion. Altogether, we arrive at

$$\frac{\partial c}{\partial \bar{\tau}} = \frac{1}{\bar{q}_{w0}^*} \left(\phi(S_w^* + D_s) S_w^* \bar{q}_w^* \right) \frac{\partial^2 c}{\partial \xi^2}, \tag{53}$$

where $()^*$ denotes that the value is taken at the solute front. The consequences and limitations of this approximation are discussed below. To be complete, the diffusion Eq. 53 needs to be supplemented with initial and boundary conditions. They follow from the inner and outer solution and for the case of the step profile coinciding with Eq. 12. The diffusion Eq. 53 together

with Eq. 12 written in the (x, t) -coordinate system has the solution [10, 15]

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \left(\frac{\int_0^x (\phi S_w(\xi, t) + \phi \mathcal{D}_s) d\xi - \int_0^t q_w(0, \delta) d\delta}{2\alpha_l^{1/2} \left[\int_0^{\tau(t)} \phi (S_w^* + \mathcal{D}_s) S_w^* \left(\frac{q_w(S_w^*)}{q_w(S_0)} \right) dt \right]^{1/2}} \right) \tag{54}$$

By construction, the solution given in Eq. 54 is valid for the region around the boundary layer, whereas the solution given through Eq. 24 is valid away from the boundary layer.

For the initial- and boundary conditions as specified in Eq. 12, the uniformly valid composite solution for the zeroth-order approximation coincides with Eq. 54. This is obtained as follows: To acquire a zeroth-order approximation that is uniformly valid throughout the whole region, we need to construct the composite solution which is given by [34, 59]

$$c^{\text{comp}}(\bar{\theta}, \bar{\tau}) = c^{\text{in}}(\bar{\theta}, \bar{\tau}) + c^{\text{out}}(\bar{\theta}, \bar{\tau}) - c^{\text{match}}(\bar{\theta}, \bar{\tau}), \tag{55}$$

where the superscripts comp, in, out and match denote the composite, the inner, the outer and the matched solution, respectively. The inner solution $c^{\text{in}}(\bar{\theta}, \bar{\tau})$ has been derived above and is given in Eq. 54 in the (x, t) coordinate system. The outer solution $c^{\text{out}}(\bar{\theta}, \bar{\tau})$ is the solution to the hyperbolic PDE and is given by a step profile, Eq. 42. The matched solution $c^{\text{match}}(\bar{\theta}, \bar{\tau})$ is the function that overlaps with $c^{\text{out}}(\bar{\theta}, \bar{\tau})$ in the boundary layer and with $c^{\text{in}}(\bar{\theta}, \bar{\tau})$ away from it [34, 59]. Given the functional form of $c^{\text{out}}(\bar{\theta}, \bar{\tau})$ and $c^{\text{in}}(\bar{\theta}, \bar{\tau})$, we therefore obtain that $c^{\text{match}}(\bar{\theta}, \bar{\tau})$ must be the step function, i.e. $c^{\text{match}}(\bar{\theta}, \bar{\tau}) = H(\bar{\theta} - \bar{\tau})$. Altogether, from Eq. 55, we obtain that $c^{\text{comp}}(\bar{\theta}, \bar{\tau}) = c^{\text{in}}(\bar{\theta}, \bar{\tau})$, and thus, the solution uniformly valid throughout the whole region $c^{\text{comp}}(\bar{\theta}, \bar{\tau})$ is given by Eq. 54 in the (x, t) coordinate system.

If the solute is non-adsorbing, i.e. $\mathcal{D}_s = 0$, the solution given in [56] is recovered as a special case. As in the purely advective case, for the derivation of the first Eq. 54, no features of the solution derived in [45] were used. Consequently, this expression is valid for the initial and boundary conditions given in Eq. 12 and any q_w, S_w and S_n that satisfy Eqs. 1 and 2. The respective expressions can stem from either analytical solutions or could be combined with numerical calculations from, e.g. streamline simulations [7, 16, 35]. In case boundary and initial conditions other than Eq. 12 are used, the matching function and the composite solution need to be modified accordingly.

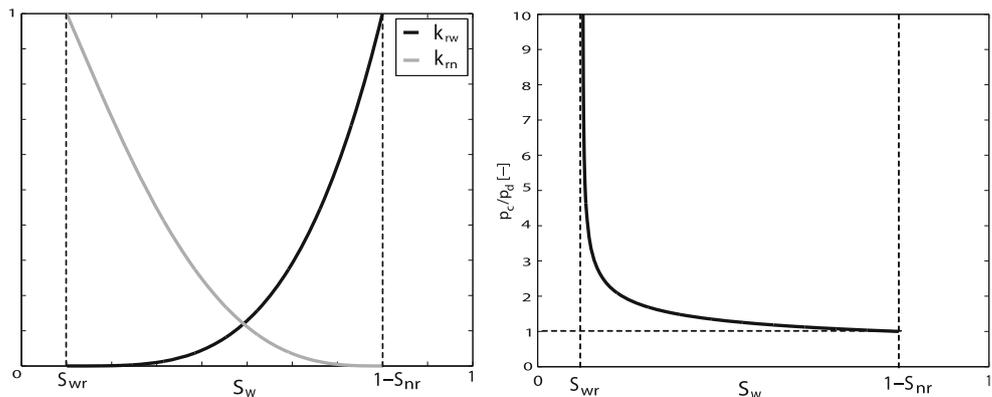
From Eq. 54, we can obtain an expression for the growth of the dispersive zone (Fig. 1), δ . Dispersion only plays a role around the solute front, i.e. where $x = x(S_w^*, t)$, and thus, δ can be described by the rate of change around that front. This gives

$$\delta(t) = - \left(\frac{\partial C / C_0}{\partial x} \right)_{x=x(S_w^*, t)}^{-1}. \tag{56}$$

5 Applications

In this section, we give some examples where we compare our analytical expressions to some numerical solutions. Furthermore, we discuss the difference between the growth rate $\delta(t)$ of the dispersive zone (Fig. 1) for the cases with and without capillary pressure and with adsorption. We have shown earlier that for the case of spontaneous imbibition, the order of the growth rate, and thus the rate of dispersive mixing, is smaller than that for the viscous case by a factor (1/2) [56]. If adsorption is taken into account, we show that $\delta(t)$ grows even slower. For the numerical simulations, we use the Complex System Modeling Platform (CSMP++), a C++ library for multiphase flow in heterogeneous media,

Fig. 4 Example for the Brooks–Corey parametrization: residual saturations S_{wr} and S_{nr} and corresponding relative permeability functions (left) and capillary pressure function for $\lambda_{BC} = 3$ (right)



which is widely used to model single- and multi-phase flow in fractured porous media (e.g. [22–25, 42, 43]).

The functions $D(S_w)$, $f(S_w)$ and $P_c(S_w)$ represent the capillary and hydraulic properties of the fluid–medium interaction and are either determined from experimental measurements or described analytically, see Fig. 4. Several models exist to algebraically describe them. In the foregoing analysis, no assumptions for the functions D , f and P_c were used other than what is known from the underlying physics, and thus, any description for them can be used in our context. One common model employed in both hydrological applications and the petroleum literature [28] uses the effective wetting saturation

$$S_e = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}, \quad 0 \leq S_e \leq 1, \quad (57)$$

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \left(\frac{\int_0^x (\phi S_w + \phi \mathcal{D}_s)(\xi, t) d\xi - 2At^{1/2}}{2\alpha_l^{1/2} (\phi S_w^* (\mathcal{D}_s + S_w^*))^{1/2} (2At^{1/2} (F(S_w^*) (1 - f_i R) + f_i R))^{1/2}} \right)$$

$$\delta(t) = 2 \left[\left(\frac{\pi \alpha_l}{\phi} \right) \cdot \left(\frac{S_w^*}{S_w^* + \mathcal{D}_s} \right) 2q_w^* t \right]^{1/2}$$

$$= 2 \left[\left(\frac{\pi \alpha_l}{\phi} \right) \cdot \left(\frac{S_w^*}{S_w^* + \mathcal{D}_s} \right) 2A \sqrt{t} (F(S_w^*) (1 - f_i R) + f_i R) \right]^{1/2} \quad (59)$$

Figure 5 shows the comparison between numerical solutions and the analytical solution for the cocurrent flow and transport of solutes derived in this paper for times $t = 0.7, 1.5, 2.5$ days and the parameter set given in Table 2. Figure 6 shows the comparison for the case of counter-current imbibition for times $t = 0.7, 1.7, 17$ days and the parameter set given in Table 1. The perturbation expansion assumes $\varepsilon^{1/2} \ll 1$, $\varepsilon = \alpha_L/L_0$. The characteristic length of the system L_0 is the distance between the wetting front and the point where the concentrations start to break through. This is different from the perturbation expansions derived for the saturated and under-saturated single-phase case, where the characteristic length is the distance traveled by the solute front [15, 20, 26, 49, 61, 62]. Figure 7 shows the comparison for spontaneous imbibition and the parameter set given in Table 1 for times $t = 2, 17, 34$ days. In this case, the connate wetting saturation is smaller than the ones in the previous two examples, and $\mathcal{D}_s = 0$, and consequently the retardation between the wetting front and the point where the solutes start to break through is smaller. At time $t = 2$ days, the distance traveled by the solute front is already longer than for $t = 0.7$ days for the case shown in Fig. 6. However, the perturbation expansion for the

where S_{nr} is the residual saturation of the non-wetting phase. Then the Brooks–Corey model [8] uses the relations

$$k_{rw}(S_e) = S_e^{(2+3\lambda_{BC})/\lambda_{BC}}, \quad (58a)$$

$$k_{rn}(S_e) = (1 - S_e)^2 (1 - S_e^{(2+3\lambda_{BC})/\lambda_{BC}}), \quad (58b)$$

$$P_c(S_e)/p_d = S_e^{-1/\lambda_{BC}}, \quad P_c \geq p_d. \quad (58c)$$

In the Brooks–Corey model, p_d is the entry pressure for the non-wetting fluid and λ_{BC} is the Brooks–Corey parameter, $\lambda_{BC} \in [0.2, 3.0]$, see Fig. 4. In the following examples, we restrict ourselves to this model, see Fig. 4, but as already mentioned above, any choice for k_{rw} , k_{rn} and P_c is applicable.

Co-current and counter-current imbibition For the McWhorter and Sunada problem, Eqs. 54 and 56 become

case shown in Fig. 7 overestimates the dispersion for this time and predicts that the components disperse ahead of the solute front. This is physically impossible

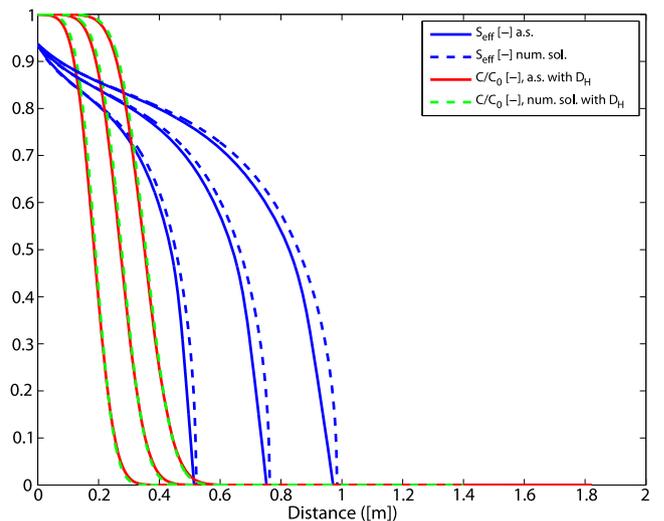


Fig. 5 Dispersion approximation for cocurrent flow and transport. Parameter set given in Table 2 with $\mathcal{D}_s = 0.5 \text{ m}^3_{\text{fluid}}/\text{m}^3_{\text{pv}}$ at times $t = 0.7$ days, 1.5 days, 2.5 days and corresponding $\varepsilon = 0.12, 0.056, 0.03$

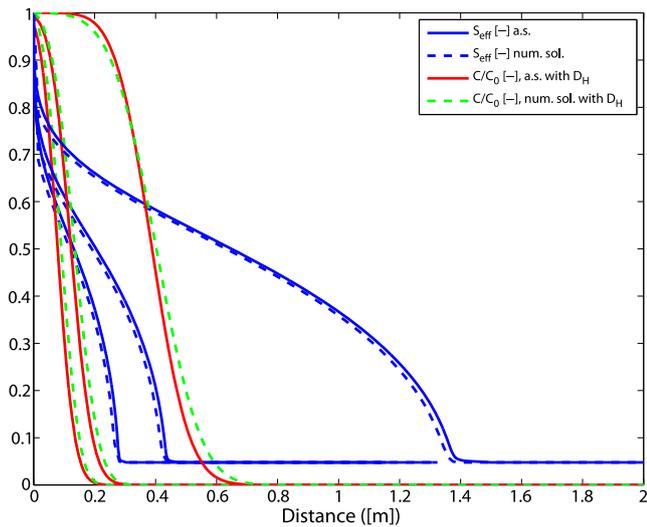


Fig. 6 Dispersion approximation for spontaneous, counter-current imbibition and transport. Parameter set given in Table 1 with $\mathcal{D}_s = 0.3 \text{ m}_{\text{fluid}}^3/\text{m}_{\text{pv}}^3$ at times $t = 0.7, 1.7, 17$ days and corresponding $\varepsilon = 0.64, 0.25, 0.044$

since there $q_w = 0$ and shows that the characteristic length for the two-phase system is not the distance traveled by the solute front but rather the distance between the wetting front and the point where the solutes start to break through. For later times, this distance increases, yielding declining values for ε and a good agreement between the numerical and the analytical solution is achieved.

Adsorbing components get retarded and hence, according to Eq. 26, ‘see’ a flow field different from the one for the inert solutes. Consequently, although the order over time for the growth of the dispersive zone stays the same, the slope will not. Adsorption results in a slightly higher S_w^* and thus a slightly higher flow rate. However, at the same time, $\delta(t)$ according to Eq. 59 is diminished by a factor $(S_w^*/(S_w^* + \mathcal{D}_s))$ which is a

Table 1 Parameter sets for counter-current, spontaneous imbibition as shown in Figs. 6 and 7

Parameter	Unit	Set I (Fig. 6)	Set II (Fig. 7)
S_i	[-]	0.25	0.11
S_0	[-]	0.85	0.85
S_{wr}	[-]	0.22	0.1
S_{nr}	[-]	0.15	0.15
λ_{BC}	[-]	3.0	3.0
p_d	[Pa]	1.5×10^3	1.5×10^3
α_L	[m]	0.02	0.02
ϕ	[-]	0.25	0.25
μ_w	[Pa s]	1.0×10^{-3}	1.0×10^{-3}
μ_n	[Pa s]	0.5×10^{-3}	0.5×10^{-3}
\mathcal{D}_s	$[\text{m}_f^3/\text{m}_{pv}^3]$	0.3	0

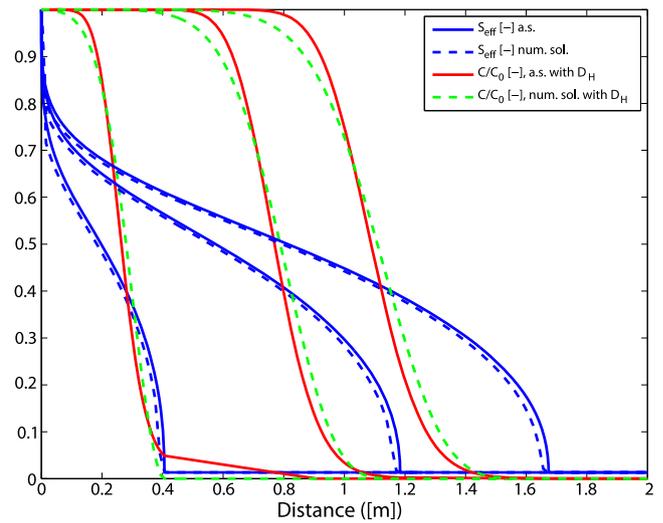


Fig. 7 Dispersion approximation for spontaneous imbibition and parameter set II (Table 1) with $\alpha_L = 0.02 \text{ m}$ at times $t = 2, 17, 34$ days. At time $t = 2$ days, the distance between the solute and the wetting front is zero, which yields $\varepsilon_1 = \infty$ and thus the condition $\varepsilon \ll 1$ is violated. Consequently, the dispersion is overestimated and dispersion of the components ahead of the solute front is wrongly predicted. For $t_2 = 17$ and $t_3 = 34$ days, $\varepsilon_2 = 0.43$ and $\varepsilon_3 = 0.2$, and the comparisons show good agreement

stronger effect than the increase in q_w , and altogether, adsorption results in $\delta(t)$ growing more slowly compared to the inert case (Fig. 8).

Buckley–Leverett problem For the Buckley–Leverett problem with constant inflow rate q_I and boundary

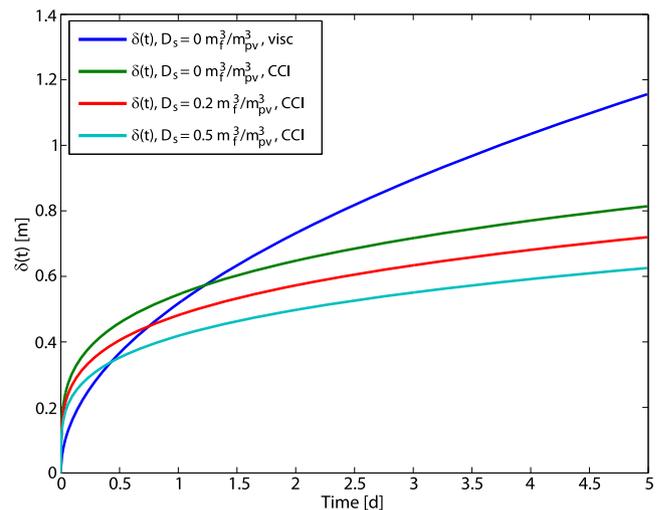


Fig. 8 Comparison of growth of dispersive zones for spontaneous, counter-current imbibition, different adsorption rates \mathcal{D}_s and the parameter set I given in Table 1 and for the viscous limit for the parameter set given in Table 2 with $\mathcal{D}_s = 0$

conditions for S_w and C as specified in Eqs. 13 and 12, respectively, Eq. 54 becomes

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \left(\frac{\int_0^x \phi(S_w + D_s) d\xi - q_t \cdot t}{2(S_w^*(S_w^* + D_s))^{1/2} [\phi \alpha_L q_t f_w(S_w^*) \cdot t]^{1/2}} \right),$$

$$\delta(t) = 2 \left[\left(\frac{\pi \alpha_l}{\phi} \right) \cdot \left(\frac{S_w^*}{S_w^* + D_s} \right) \cdot q_t f_w(S_w^*) t \right]^{1/2}. \quad (60)$$

We note that for the Buckley–Leverett problem, the dispersive zone grows with order $\mathcal{O}(t^{1/2})$ compared to order $\mathcal{O}(t^{1/4})$ for the cocurrent McWhorter–Sunada problem. This is due to the specific inflow conditions of the former, and not due to capillary forces. To evaluate the influence of capillary forces on $\delta(t)$, we have to consider the Buckley–Leverett problem with inflow condition $q_t = \tilde{A}t^{-1/2}$ for some positive constant \tilde{A} . This leads to $\delta(t)$ as in Eq. 59 with \tilde{A} substituting A and $f(S_w)$ substituting $F(S_w)$ for the co-current case, i.e. $R = 1$. Hence, for the case $\tilde{A} = A$, the difference in growth over time for the problem with and without capillarity is quantified through the difference between F and f at their respective values for S_w^* , where the same boundary and initial conditions for S_w have been chosen.

For the counter-current case, the boundary condition $q_0 = At^{1/2}$ agrees with the one obtained from Eq. 4 for $q_t = 0$ and thus is redundant. Consequently, there $\delta(t)$ as specified in Eq. 59 describes the growth rate for the standard situation of both laboratory setting of

Table 2 Parameter set for cocurrent case and viscous limit (Buckley–Leverett problem) as shown in Figs. 5 and 9

Parameter	Unit	Cocurrent case (Fig. 5)	Buckley–Leverett (Fig. 9)
S_i	[–]	0.22	0.85
S_0	[–]	0.81	0.78
S_{wr}	[–]	0.22	0.22
S_{nr}	[–]	0.15	0.15
p_d	[Pa]	1.5×10^3	–
λ_{BC}	[–]	3.0	3.0
α_L	[m]	0.01	0.00488
q_t	[m/s]	–	2.1×10^{-7}
ϕ	[–]	0.25	0.25
μ_w	[Pa s]	1.0×10^{-3}	1.0×10^{-3}
μ_n	[Pa s]	1.0×10^{-3}	0.5×10^{-3}
D_s	[m ³ /m ³ _{pv}]	0.5	0.3

spontaneous imbibition and the situation in the field where spontaneous, counter-current imbibition is the dominant process (e.g. for the exchange between high- and low-permeability regions). In this case, the growth rate, and thus the rate of dispersive mixing, is smaller than that for the viscous case by a factor (1/2) (Fig. 8). Consequently, for cases where the transport of components is considered whose *mixing* triggers reactions (e.g. wettability changes due to surface reactions), the amount or reactants available is much smaller than for viscous dominated processes.

Figure 9 shows the comparison between numerical solutions and the analytical solution for times $t = 5, 8, 14$ days and the parameter set given in Table 2. The characteristic lengths are such that the condition $\varepsilon^{1/2} \ll 1$ is satisfied, and an excellent agreement between the numerical solution and the analytical one of this paper is achieved.

6 Summary and conclusions

We extended our earlier work on the analytical description of the movement of inert tracers in two phases to the case of adsorbing solutes. Thus, the first known set of semi-analytical solutions for solute transport in immiscible two-phase systems that describe all physical mechanisms, i.e. advection due to adsorption, co- and counter-current imbibition and viscous forces and the movement due to the time- and space-dependent hydrodynamic dispersion, has been obtained.

The analytical solutions for the advective part were obtained by a heuristic argument and by the method of characteristics. The effect of time- and space-dependent dispersion was solved for by a singular perturbation technique. If the dispersion coefficient is

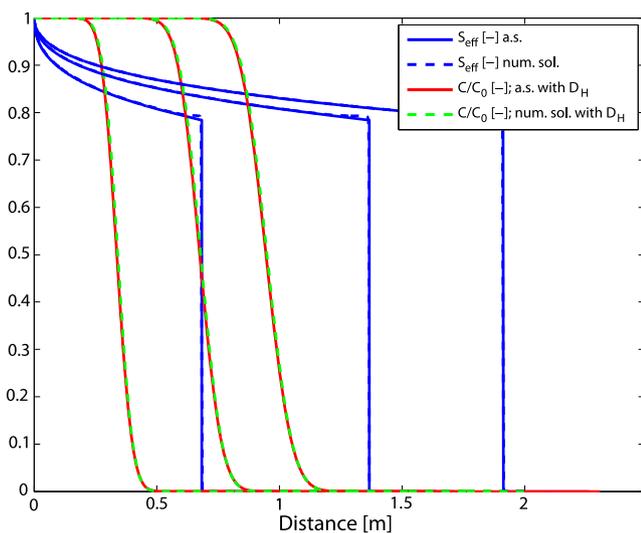


Fig. 9 Dispersion approximation for viscous limit and transport. Parameter set given in Table 2 with $D_s = 0.3 \text{ m}_{\text{fluid}}^3/\text{m}_{\text{pv}}^3$ at times $t = 5, 8, 14$ days and corresponding $\varepsilon = 0.09, 0.02, 0.009$

small compared to the distance between the wetting front and the point where the solutes break through, the analytical approximations are in excellent agreement with numerical solutions for the cases of cocurrent flow, counter-current spontaneous imbibition and the Buckley–Leverett problem.

The presented solutions can serve as a tool for the verification of new numerical methods. The closed-form analytical expressions for $C(x, t)$ (Eq. 54) can be employed in connection with any solution for q_w and S_w . Thus, they also could act as building block for numerical schemes when numerical approximations for the flow and saturation field are used.

The solutions allow the following insights:

- For the dispersion-free limit, the solution with capillarity can be represented as a Welge-tangent to the capillary fractional flow function F (Fig. 3).
- The solutions also contain the important case of solute transport during spontaneous, counter-current imbibition (Eqs. 24 together with Eqs. 27 and 59 for $R = 0$). The constant A (Eq. 14) is then a measure for the medium's ability to imbibe.
- The amount of dispersive mixing depends on the flow regime (Fig. 8). The growth rate $\delta(t)$ of the dispersive zone for the viscous dominated regime grows with $t^{1/2}$, and for imbibition with $t^{1/4}$ (Eqs. 59 and 60). Consequently, the amount of mixing, and thus if reactive solutes are considered, the amount of reactants, is far smaller for spontaneous, counter-current imbibition than for the viscous case.
- The dispersive zone of adsorbing components grows slower than that of inert ones (Fig. 8) (Eqs. 59 and 60). The dependence of temporal order of $\delta(t)$ on the flow regime, however, is not affected by adsorption.

Acknowledgements We thank the following for the financial support for this work: The Exxon-Mobil Research Alliance 'Fundamental Controls of Flow in Carbonates' (FC)² and the Edinburgh Collaborative of Subsurface Science and Engineering, a joint research institute of the Edinburgh Research Partnership in Engineering and Mathematics. We also thank the anonymous reviewers whose comments have helped to greatly improve this paper.

References

1. Acs, G., Doreschall, S., Farkas, E.: General purpose compositional model. *SPE J.* **25**(4), 543–553 (1985)
2. Austad, T., Standnes, D.C.: Spontaneous imbibition of water into oil-wet carbonates. *J. Pet. Sci. Eng.* **39**(3–4), 363–376 (2003)
3. Barenblatt, G., Entov, V., Ryzhik, V.: *Theory of Fluid Flows Through Natural Rocks*, vol. 3. Springer, New York (1990)
4. Bear, J.: *Dynamics of Fluids in Porous Media*. Dover, New York (1972)
5. Bedrikovetsky, P.: *Mathematical Theory of Oil and Gas Recovery: with Applications to Ex-USSR Oil and Gas Fields*, vol. 4. Kluwer Academic, Dordrecht (1993)
6. Behbahani, H.S., Di Donato, G., Blunt, M.J.: Simulation of counter-current imbibition in water-wet fractured reservoirs. *J. Pet. Sci. Eng.* **50**(1), 21–39 (2006)
7. Blunt, M.J., Liu, K., Thiele, M.R.: A generalized streamline method to predict reservoir flow. *Pet. Geosci.* **2**(3), 259 (1996)
8. Brooks, R.H., Corey, A.T.: *Hydraulic properties of porous media*. Hydrological Paper 3, Colorado State University, CO, USA (1964)
9. Buckley, S.E., Leverett, M.C.: Mechanisms of fluid displacement in sands. *Trans. Am. Inst. Min. Metall. Pet. Eng. AIME* **146**, 107–116 (1942)
10. Carslaw, H.S., Jaeger, J.C.: *Conduction of Heat in Solids*. Oxford University Press, Oxford (1959)
11. Chen, Z.X., Bodvarsson, G.S., Witherspoon, P.A., McWhorter, D.B., Sunada, D.K.: Comment on 'Exact integral solutions for two-phase flow' by David B. McWhorter and Daniel K. Sunada. Author's reply. *Water Resour. Res.* **28**(5), 1477–1479 (1992)
12. Cirpka, O.A.: Choice of dispersion coefficients in reactive transport calculations on smoothed fields. *J. Contam. Hydrol.* **58**(3–4), 261–282 (2002)
13. Crank, J.: *The Mathematics of Diffusion*. Oxford University Press, USA (1979)
14. Cvetkovic, V., Dagan, G.: Reactive transport and immiscible flow in geological media. II. applications. *Proc. Math. Phys. Eng. Sci.* **452**(1945), 303–328 (1996)
15. Dagan, G.: Perturbation solutions of the dispersion equation in porous mediums. *Water Resour. Res.* **7**, 135–142 (1971)
16. Datta-Gupta, A., King, M.J.: A semianalytic approach to tracer flow modeling in heterogeneous permeable media. *Adv. Water Resour.* **18**(1), 9–24 (1995)
17. De Simoni, M., Carrera, J., Sanchez-Vila, X., Guadagnini, A.: A procedure for the solution of multicomponent reactive transport problems. *Water Resour. Res.* **41**(11) (2005). doi:[10.1029/2005WR004056](https://doi.org/10.1029/2005WR004056)
18. De Simoni, M., Sanchez-Vila, X., Carrera, J., Saaltink, M.W.: A mixing ratios-based formulation for multicomponent reactive transport. *Water Resour. Res.* **43**(7) (2007). doi:[10.1029/2006WR005256](https://doi.org/10.1029/2006WR005256)
19. Dentz, M., Le Borgne, T., Englert, A., Bijeljic, B.: Mixing, spreading and reaction in heterogeneous media: a brief review. *J. Contam. Hydrol.* **120–121**, 1–17 (2011). doi:[10.1016/j.jconhyd.2010.05.002](https://doi.org/10.1016/j.jconhyd.2010.05.002)
20. Eldor, M., Dagan, G.: Solutions of hydrodynamic dispersion in porous media. *Water Resour. Res.* **8**, 1316–1331 (1972)
21. Emmanuel, S., Berkowitz, B.: Mixing-induced precipitation and porosity evolution in porous media. *Adv. Water Resour.* **28**(4), 337–344 (2005)
22. Geiger, S., Driesner, T., Heinrich, C., Matthäi, S.: Multiphase thermohaline convection in the Earth's crust: I. A new finite element–finite volume solution technique combined with a new equation of state for NaCl–H₂O. *Transp. Porous Media* **63**(3), 399–434 (2006)
23. Geiger, S., Matthäi, S.K., Niessner, J., Helmig, R.: Black-oil simulations for three-component—three-phase flow in fractured porous media. *SPE J.* **14**, 338–354 (2009)
24. Geiger, S., Roberts, S., Matthäi, S.K., Zoppou, C., Burri, A.: Combining finite element and finite volume methods for efficient multiphase flow simulations in highly heterogeneous and structurally complex geologic media. *Geofluids* **4**(4), 284–299 (2004)

25. Geiger S., Emmanuel, S.: Non-Fourier thermal transport in fractured geological media. *Water Resour. Res.* (2010). doi:[10.1029/2009WR008671](https://doi.org/10.1029/2009WR008671), 2010
26. Gelhar, L.W., Collins, M.A.: General analysis of longitudinal dispersion in nonuniform flow. *Water Resour. Res.* **7**, 1511–1521 (1971)
27. Gerritsen, M.G., Durlafsky, L.J.: Modelling fluid flow in oil reservoirs. *Annu. Rev. Fluid Mech.* **37**(1), 211–238 (2005)
28. Helmig, R.: *Multiphase Flow and Transport Processes in the Subsurface*. Springer, New York (1997)
29. Hiorth, A., Cathles, L.M., Madland, M.V.: The impact of pore water chemistry on carbonate surface charge and oil wettability. *Transp. Porous Media* (2010). doi:[10.1007/s11242-010-9543-6](https://doi.org/10.1007/s11242-010-9543-6)
30. Hoteit, H., Firoozabadi, A.: Multicomponent fluid flow by discontinuous Galerkin and mixed methods in unfractured and fractured media. *Water Resour. Res.* **41**(11) (2005). doi:[10.1029/2005WR004339](https://doi.org/10.1029/2005WR004339)
31. Huber, R., Helmig, R.: Multiphase flow in heterogeneous porous media: a classical finite element method versus an implicit pressure-explicit saturation-based mixed finite element-finite volume approach. *Int. J. Numer. Methods Fluids* **29**(8), 899–920 (1999)
32. Johansen, T., Winther, R.: The solution of the Riemann problem for a hyperbolic system of conservation laws modeling polymer flooding. *SIAM J. Math. Anal.* **19**(3), 541–566 (1988)
33. Juanes, R., Blunt, M.J.: Analytical solutions to multiphase first-contact miscible models with viscous fingering. *Transp. Porous Media* **64**(3), 339–373 (2006)
34. Kevorkian, J., Cole, J.D.: *Perturbation Methods in Applied Mathematics*. Springer, New York (1981)
35. King, M.J., Datta-Gupta, A.: Streamline simulation: a current perspective. In *Situ* **22**(1), 91 (1998)
36. LaForce, T., Johns, R.: Analytical solutions for surfactant-enhanced remediation of nonaqueous phase liquids. *Water Resour. Res.* **41**(10), W10,420 (2005). doi:[10.1029/2004WR003862](https://doi.org/10.1029/2004WR003862)
37. Lake, L.W., Helfferich, F.: Cation exchange in chemical flooding: part 2—the effect of dispersion, cation exchange, and polymer/surfactant adsorption on chemical flood environment. *SPE J.* **6769**, 435–444 (1977)
38. Langlo, P., Espedal, M.S.: Macrodispersion for two-phase, immiscible flow in porous media. *Adv. Water Resour.* **17**(5), 297–316 (1994)
39. Lie, K., Juanes, R.: A front-tracking method for the simulation of three-phase flow in porous media. *Comput. Geosci* **9**(1), 29–59 (2005)
40. Lunati, I., Jenny, P.: Multiscale finite-volume method for compressible multiphase flow in porous media. *J. Comput. Phys.* **216**(2), 616–636 (2006)
41. Mackay, E.: Predicting in situ sulphate scale deposition and the impact on produced ion concentrations. *Chem. Eng. Res. Bull.* **81**(3), 326–332 (2003)
42. Matthäi, S., Nick, H., Pain, C., Neuweiler, I.: Simulation of solute transport through fractured rock: a higher-order accurate finite-element finite-volume method permitting large time steps. *Transp. Porous Media* **83**(2), 1–30 (2009)
43. Matthäi, S.K., Geiger, S., Roberts, S.G., Paluszny, A., Belayneh, M., Burri, A., Mezentsev, A., Lu, H., Coumou, D., Driesner, T., et al.: *Numerical Simulation of Multi-phase Fluid Flow in Structurally Complex Reservoirs*. Geological Society London Special Publications, vol. 292(1), p. 405. Geological Society London, London (2007)
44. McWhorter, D.B.: *Infiltration affected by flow of air*. Hydrological Paper 49, Colorado State University, CO, USA (1971)
45. McWhorter, D.B., Sunada, D.K.: Exact integral solutions for two-phase flow. *Water Resour. Res.* **26**(3), 399–413 (1990)
46. McWhorter, D.B., Sunada, D.K.: Exact integral solutions for two-phase flow: reply. *Water Resour. Res.* **28**(5), 1479 (1992)
47. Morrow, N.R., Mason, G.: Recovery of oil by spontaneous imbibition. *Curr. Opin. Colloid Interface Sci.* **6**(4), 321–337 (2001). doi:[10.1016/S1359-0294\(01\)00100-5](https://doi.org/10.1016/S1359-0294(01)00100-5)
48. Muskat, M.: *Physical Principles of Oil Production*. McGraw-Hill, New York (1949)
49. Nachabe, M.H., Islas, A.L., Illangasekare, T.H.: Analytical solutions for water flow and solute transport in the unsaturated zone. *Ground Water* **33**, 304–310 (1995)
50. Neuweiler, I., Attinger, S., Kinzelbach, W., King, P.: Large scale mixing for immiscible displacement in heterogeneous porous media. *Transp. Porous Media* **51**(3), 287–314 (2003)
51. Panfilow, M., Floriat, S.: Nonlinear two-phase mixing in heterogeneous porous media. *Transp. Porous Media* **57**(3), 347–375 (2004)
52. Philip, J.R.: On solving the unsaturated flow equation: 1. The flux-concentration relation. *Soil Sci.* **116**(5), 328 (1973)
53. Pope, G.: The application of fractional flow theory to enhanced oil recovery. *SPE J.* **20**(3), 191–205 (1980)
54. Pope, G.A.: Cation exchange in chemical flooding: part 1—basic theory without dispersion. *SPE* **6771**, 418–434 (1978)
55. Reichenberger, V., Jakobs, H., Bastian, P., Helmig, R.: A mixed-dimensional finite volume method for two-phase flow in fractured porous media. *Adv. Water Resour.* **29**(7), 1020–1036 (2006)
56. Schmid, K.S., Geiger, S., Sorbie, K.: Semianalytical solutions for co- and countercurrent imbibition and dispersion of solutes in immiscible two-phase flow. *Water Resour. Res.* **47**(2), 1–16 (2011). doi:[10.1029/2010WR009686](https://doi.org/10.1029/2010WR009686)
57. Seto, C.J., Orr, F.M.: Analytical solutions for multicomponent, two-phase flow in porous media with double contact discontinuities. *Transp. Porous Media* **78**(2), 161–183 (2009)
58. Sorbie, K.S., Mackay, E.J.: Mixing of injected, connate and aquifer brines in waterflooding and its relevance to oilfield scaling. *J. Pet. Sci. Eng.* **27**(1–2), 85–106 (2000)
59. Van Dyke, M.: *Perturbation Methods in Fluid Mechanics/Annotated Edition*. The Parabolic, Stanford (1975)
60. Welge, H.: A simplified method for computing oil recovery by gas or water drive. *Trans. AIME* **195**, 91–98 (1952)
61. Wilson, J.L., Gelhar, L.W.: *Dispersive mixing in a partially saturated porous medium*. Tech. rep., Ralph M. Parsons Lab. for Water Resour. and Hydrodyn., Mass. Inst. of Technol., Cambridge (1974)
62. Wilson, J.L., Gelhar, L.W.: Analysis of longitudinal dispersion in unsaturated flow 1. The analytical method. *Water Resour. Res.* **17**(1), 122–130 (1981)
63. Xu, T., Sonnenthal, E., Spycher, N., Pruess, K.: TOUGHREACT—a simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO₂ geological sequestration. *Comput. Geosci.* **32**(2), 145–165 (2006)
64. Zazovskii, A.F.: Structure of discontinuities in problems of oil displacement by reactants that influence the phase equilibrium. *Fluid Dyn.* **20**(5), 765–774 (1985)
65. Zhang, Y., Morrow, N.R.: Waterflood performance by injection of brine with different salinity for reservoir cores. *SPE J.* **109849**, 1–12 (2007)