

## Semianalytical solutions for cocurrent and countercurrent imbibition and dispersion of solutes in immiscible two-phase flow

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[1] We derive a set of semianalytical solutions for the movement of solutes in immiscible two-phase flow. Our solutions are new in two ways: First, we fully account for the effects of capillary and viscous forces on the transport for arbitrary capillary-hydraulic properties. Second, we fully take hydrodynamic dispersion for the variable two-phase flow field into account. The understanding of immiscible two-phase flow and the simultaneous miscible displacement and mixing of components within a phase is important for many applications, including the location of nonaqueous phase liquids in the subsurface, the design of contaminant cleanup procedures, the sequestration of carbon dioxide, and enhanced oil-recovery techniques. For purely advective transport we combine a known exact solution for the description of immiscible two-phase flow with the method of characteristics for the advective transport equations to obtain solutions that describe cocurrent flow and countercurrent spontaneous 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 advective-dispersive solute transport, we derive approximate analytical solutions by the method of singular perturbation expansion. On the basis of this, we obtain analytical expressions for the growth of the dispersive zone for the case with and without the influence of capillary pressure. We show that for the case of spontaneous countercurrent imbibition the order of magnitude of the growth rate is far smaller than that for the viscous limit. We give some illustrative examples and compare the analytical expressions with numerical reference solutions.

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### 1. Introduction

[2] The movement of solutes within two-phase systems is important in many environmental and engineering applications because in almost all cases each fluid phase consists of different components rather than just one. Consequently, both the unsteady flow of the two phases and miscible displacement within each phase occur at the same time. Displacement processes of this kind take place, for example, if water is pumped into a geological formation or aquifer contaminated with nonaqueous phase liquids (NAPL) and the ionic composition of the connate water is different from that of the injected water. In this scenario, both for the purpose of bioremediation and the cleanup of NAPL and enhanced oil recovery, surfactants and polymers are dissolved in the injected aqueous phase to mobilize the NAPL [West and Harwell, 1992; Khan *et al.*, 1996; Sorbie, 1991]. Here the appropriate design of an efficient chemical flood crucially depends upon the brine composition 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 [Lake and Helfferich, 1977]. Similarly, for the design of aquifer remediation schemes, a vital step is to identify the location and distribution of the NAPL. To this end, tracer tests can be performed where a range of both partitioning and nonpartitioning solutes are injected into the subsurface and recovered down gradient at the extraction wells [Datta-Gupta *et al.*, 2002]. Another example is carbon sequestration. In recent years, a growing awareness of the hazardous consequences of anthropogenic greenhouse gases has been seen, and one helpful mitigation method seems to be the sequestration of carbon dioxide in the subsurface, i.e., the reaction of carbon dioxide molecules (CO<sub>2</sub>) with mineral grains [Javadpour, 2009; Xu *et al.*, 2006]. In this case, CO<sub>2</sub> is dissolved in the water phase, and the mixing with the brine triggers a number of aqueous reactions that lead to the CO<sub>2</sub> being trapped by the minerals. If water is pumped into a hydrocarbon reservoir in order to produce oil, the two aqueous solutions mix while replacing the oil, and the otherwise inert brine components react. In many reservoirs, this leads to the precipitation of minerals, such as barium sulfate (BaSO<sub>4</sub>), and formation of scale [Sorbie and Mackay, 2000; Mackay, 2003] that can hinder production. In other scenarios, different ionic compositions have been shown to enhance oil recovery if the injected brine has a salinity

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different from that of the connate brine [Zhang and Morrow, 2007; Austad and Standnes, 2003; Hiorth et al., 2010], and a good understanding of the transport of the different compositions within the two phases due to the interplay of dispersion and viscous and capillary forces builds the fundament for appropriate upscaling of transport and for determining its field efficiency [Stoll et al., 2008; Stephen et al., 2001]. In all of 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 [see, e.g., Emmanuel and Berkowitz, 2005; De Simoni et al., 2005, 2007; Cirpka, 2002; Dentz et al., 2011]. Although the effects of dispersion and even spatial heterogeneity on miscible displacement and mixing for single-phase flow are increasingly well understood and a significant body of literature exists [see, e.g., Werth et al., 2006; Rahman et al., 2005; Bolster et al., 2010; Paster and Dagan, 2008; Willingham et al., 2008], investigations for two-phase systems so far only focus on the spreading of the phases themselves [Neuweiler et al., 2003; Cvetkovic and Dagan, 1996; Langlo and Espedal, 1994; Panfilow and Floriat, 2004]. This is surprising given the practical importance of simultaneous flow and transport in two-phase systems, but it can be explained with the complexity of the governing equations where capillary, viscous, and dispersive terms are coupled in a highly nonlinear way.

[3] Clearly, for gaining a full understanding of all the mechanisms and effects involved, numerical simulations are important, and in recent years, there has been substantial progress in the development of numerical methods [see, e.g., Blunt et al., 1996; Geiger et al., 2004; Huber and Helmig, 1999; Reichenberger et al., 2006; Hoteit and Firoozabadi, 2005; Lunati and Jenny, 2006]. However, the development of numerical models requires verification and validation as to which new analytical solutions contribute an important part. Also, analytical solutions allow a deeper insight into the structure of a problem and, thus, as to which parameters control processes and often act as a building block for numerical methods [e.g., Lie and Juanes, 2005; Blunt et al., 1996]. Finally, constitutive relationships, such as relative permeabilities, are normally gained from core flood experiments where numerical simulations are matched with flow rates. However, interpretation of experimental data would be faster and more reliable if the forward problem was solved analytically [Juanes, 2003]. Our solutions provide the framework for the common situation of two-phase core floods, where both flow rates and breakthrough curves of tracers are available and where all physical mechanisms, i.e., viscous and capillary forces and hydrodynamic dispersion, are considered.

[4] The outline of this paper is as follows: In section 2, we introduce the mathematical model and basic notation and give a short overview of existing solutions for immiscible two-phase flow without transport. In section 3, we solve the advection problem exactly by two different methods: On the basis of a known integral solution for two-phase flow, we first combine a variable transformation with the physical notion for which in 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

[McWhorter and Sunada, 1990], the solution to the transport equation can be represented by a modified Welge tangent [Welge, 1952]. In section 4, 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. On the basis of these equations, we are able to obtain an analytical expression for the growth rate of the dispersive mixing zone. These solutions are the first known analytical expressions for hydrodynamic dispersions in two-phase flow. In section 4, we compare the obtained solutions against the numerical reference solution for the cases of cocurrent and countercurrent imbibition and for the capillary-free limit, the Buckley-Leverett problem [Buckley and Leverett, 1942], and then finish with some conclusions.

## 2. Preliminaries

### 2.1. Problem Formulation and Assumptions

[5] 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 [Bear, 1972]

$$\varphi \frac{\partial S_w}{\partial t} = -\frac{\partial}{\partial x}(q_w) \quad (1)$$

$$S_n + S_w = 1, \quad (2)$$

where  $S_w$  is the wetting phase saturation,  $S_n$  is the nonwetting phase saturation, and  $\varphi$  is the porosity, which is assumed to be constant throughout the whole domain. Furthermore, we assume that the volume flux of the wetting and the nonwetting phases,  $q_w$  and  $q_{nw}$ , can be described by the multiphase extension of Darcy's equation [Muskat, 1949], which describes the volume flux because of a gradient in the phase pressures  $p_w$  and  $p_{nw}$ :

$$\begin{aligned} q_w &= -K \frac{k_w}{\mu_w} \nabla p_w, \\ q_{nw} &= -K \frac{k_{nw}}{\mu_{nw}} \nabla p_{nw}. \end{aligned} \quad (3)$$

[6] Here  $K$  is the absolute permeability,  $\mu_w$  is the viscosity of the wetting phase,  $\mu_{nw}$  is the viscosity of the nonwetting phase, and  $k_{nw} = k_{nw}(S_w)$  and  $k_w = k_w(S_w)$  are the relative permeability of the nonwetting and wetting fluids, respectively, which 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 equations (1) and (2), one can rewrite  $q_w$  as an expression of the total volume flux  $q_t = q_{nw} + q_w$ , which yields

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

[7] 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

$$f(S_w) = \left(1 + \frac{k_{nw}\mu_w}{k_w\mu_{nw}}\right)^{-1}, \quad (5)$$

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

[8] We consider components  $C_j, j = 1, \dots, n$  and  $\chi_k, k = 1, \dots, m$  that are transported in the wetting phase and the nonwetting phase, respectively. In the following, we assume that (1) they do not alter the porous medium (e.g., through chemical reactions), (2) they do not change the flow parameters, (3) they do not partition into the other phase, (4) the solute mass flux due to hydrodynamic dispersion within a phase is described by a Fickian model, and (5) density effects can be ignored. The continuity equation can then be written as [Acs et al., 1985; Gerritsen and Durlofsky, 2005]

$$\varphi \frac{\partial(S_w C_j)}{\partial t} = -\frac{\partial}{\partial x}(q_w \cdot C_j) + \frac{\partial}{\partial x}\left(\varphi S_w D_{H,\gamma} \frac{\partial C_j}{\partial x}\right) \quad (6)$$

$$\varphi \frac{\partial(S_n \chi_k)}{\partial t} = -\frac{\partial}{\partial x}(q_n \cdot \chi_k) + \frac{\partial}{\partial x}\left(\varphi S_n D_{H,\gamma} \frac{\partial \chi_k}{\partial x}\right). \quad (7)$$

[9] As stated, 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 can be used to derive analytical solutions [e.g., Pope, 1980; Johansen and Winther, 1988; Juanes and Blunt, 2006; LaForce and Johns, 2005; Seto and Orr, 2009]. As explained in section 1, our primary interest is the mixing of the inert components (Figure 1). We hence assume that the capillary-hydraulic properties are functions of saturation only.

[10] For the solutes in the water phase, equation (6) assumes that the volume fraction of the components is small compared to that of the wetting phase, which, for most practical applications, such as different ion-compositions, is an excellent approximation [Pope, 1980]. The solutes in the nonwetting phase can consume any arbitrary fraction of the nonwetting phase volume [Lie and Juanes, 2005]. The  $D_H$  is the hydrodynamic dispersion coefficient and for the one-dimensional case becomes [Bear, 1972]

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

where  $\alpha_{l,\gamma}$  is the coefficient of hydrodynamic dispersion and accounts for effects of the flow field and  $D_{\text{mol}}$  is the effective molecular diffusion coefficient. In the analysis that follows, we will assume that  $j = 1$ , 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 nonwetting phase has a homogeneous composition, i.e.  $k = 1$ , and is completely described by the restriction (2). Again, the analysis that follows can easily be extended to multiple solutes  $\chi_k, k = 1, \dots, m$ . To simplify notation, we will write  $D_H$  instead of  $D_{H,w}$ .

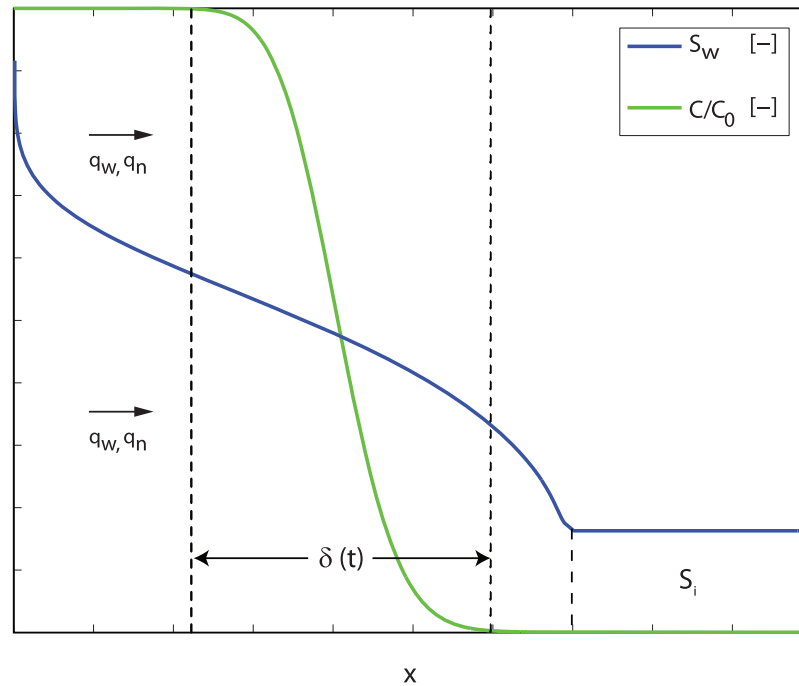
[11] Both the conservation equation for the fluid phase and the solutes are of parabolic type and, consequently, the resulting solutions are smooth. Therefore, we can expand equation (6) to arrive at

$$\varphi S_w \frac{\partial C}{\partial t} = -q_w \frac{\partial}{\partial x}(C) + \frac{\partial}{\partial x}\left(\varphi S_w D_H \frac{\partial C}{\partial x}\right). \quad (9)$$

[12] We denote the Peclet number of phase  $\gamma$  by  $Pe_\gamma = q_\gamma \cdot L / (\varphi D_{\text{mol}})$ ,  $\gamma \in \{n, w\}$ , 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 [Bear, 1972] and thus is ignored in the following. The transport of a component thus consists of an advective part, which, according to equation (4), has a viscous and a capillary component and a dispersive component.

[13] We derive an analytical solution for the transport equation (6) that fully considers both 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  $q_w$  are known in equation (9) either from analytical or numerical solutions, the problem of solving equations (1)–(6) reduces to solving an advection-dispersion equation (ADE). The  $S_w$  and  $q_w$  are fully determined by equations (1) together with equations (4) and (5). The highly nonlinear term because of capillary forces in equation (4) poses a main mathematical difficulty for deriving analytical solutions and, thus, only few exact solutions are known. We will capitalize on the one derived by McWhorter and Sunada [1990] for reasons explained below. Although this significantly reduces the complexity of the problem, the ADE (equation (9)) still has time- and space-dependent coefficients, and no analytical solutions are known. Second, to derive a solution for it, we use a general analytical approximation that separates the two physical transport mechanisms in equation (6), i.e., the advective motion because of 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.,  $D_{H,\gamma} = 0$  in equation (6),  $C$  is a function of  $S_w$  only, and an explicit expression for the location of the solute front can be derived. Second, we use the method of characteristics. Both approaches yield the same result, which furthermore gives the mathematically rigorous justification that for the dispersion-free limit,  $C$  is a function of  $S_w$  only. 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 [Welge, 1952]. To the best of our knowledge, this is the first analytical solution that accounts for capillary effects on tracer transport.

[14] 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 [Gelhar and Collins, 1971; Dagan, 1971; Eldor and Dagan, 1972; Nachabe et al., 1995; Wilson and Gelhar, 1981, 1974]. We show that if the dispersion is



**Figure 1.** Schematic representation of one-dimensional, unidirectional displacement of a nonwetting 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 Figure 3).

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 capillary, viscous, and dispersive processes in this paper, the equations derived for the characteristics and the hydrodynamic dispersion are valid for any given flow field. For illustration, we also combine them with the solution for the capillary-free limit, i.e., the Buckley-Leverett problem [Buckley and Leverett, 1942], which is the classical solution for the case where external driving forces become large and capillary effects become negligible. To the best of our knowledge, this is the first analytical solution that fully describes the complex dependence of the hydrodynamic dispersion on 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.

## 2.2. Semianalytical Solutions for Immiscible Two-Phase Flow

[15] Since the derivatives in the conservation equation for the solutes can be written out because of the product rule, for known  $q_w$  and  $S_w$ , the problem of solving for simultaneous flow and transport, and thus the whole set of conservation equations, reduces to solving one advection-dispersion equation for highly nonlinear, but known, coefficients. Hence, we first give a short overview over analytical solutions for  $q_w$  and  $S_w$  that satisfy equations (1)–(5). The strong nonlinearity of the capillary drive in equation (4) makes the determination of exact solutions difficult, and only a few analytical solutions are known. Two approaches

exist: either closed-form solutions are determined at the cost of restricting the capillary-hydraulic properties  $k_{rw}(S_w)$ ,  $k_{rn}(S_w)$ , and  $P_c(S_w)$  to very particular nonlinearities, or more general nonlinearities are chosen and the resulting exact analytical expressions are mostly nonlinear expressions that generally need to be solved numerically. Examples for the first approach are the solution given by [Fokas and Yortsos, 1982; Chen, 1988; van Duijn and de Neef, 1998; Philip, 1960; Kashchiev and Firoozabadi, 2002]. For all these solutions, the specific form of the nonlinearities excludes the adequate study of flow for different porous media and often also the possibility to study both cocurrent and countercurrent flows. Examples for the second approach can be found by Chen *et al.* [1995], McWhorter and Sunada [1990], and van Duijn and Peletier [1992]. We choose the ones derived by McWhorter and Sunada [1990] since they allow for both general capillary-hydraulic properties and the consideration of cocurrent and countercurrent flows. The only time 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 are valid for any flow and saturation field known, either from numerical solutions such as streamline simulations [Blunt *et al.*, 1996; King and Datta-Gupta, 1998; Datta-Gupta and King, 1995] or analytical considerations.

## 3. Solution of the Advective Problem

[16] We first consider the dispersion-free limit of equation (9), 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 certain saturation value  $S_w^*$ . We will show that the retardation is because of the initial wetting saturation, which acts as a storage for the solute. Two possibilities exist for deriving an analytical solution and the determination of  $S_w^*$ . The first one uses the physical notion that  $C$  is carried by the respective fluid phase and we can therefore 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, which can be represented graphically by a modified Welge tangent [Welge, 1952]. We can obtain the same result for the location of the shock front if we employ the method of characteristics for solving equation (9). 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.

[17] For the solute, we consider the boundary and initial conditions

$$\begin{aligned} C(x = 0, t) &= C_0, \\ C(\infty, t) &= C_i, \\ C(x, 0) &= C_i, \end{aligned} \tag{10}$$

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

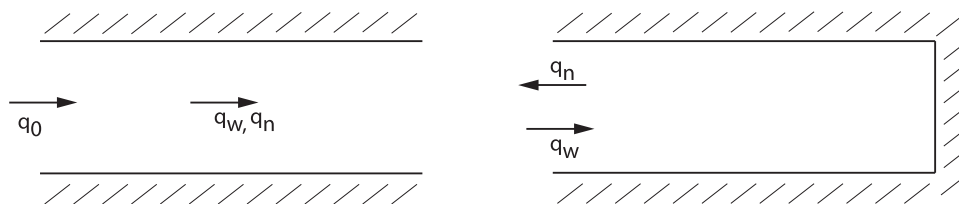
$$q_0 = q_w(x = 0, t) = At^{-1/2}, \tag{11a}$$

$$S_w(x = 0, t) = S_0, \tag{11b}$$

$$S_w(\infty, t) = S_i \tag{11c}$$

$$S_w(x, 0) = S_i, \tag{11d}$$

where the parameter  $A$  is a constant that depends on  $S_i$  and  $S_0$  as specified by the analytical expression given in Appendix A. This represents cocurrent flow (see Figure 2). The maximal possible value for  $S_0$  is  $1 - S_{nr}$ , where  $S_{nr}$  is the residual saturation of the nonwetting phase. The conditions given in equation (11) are as specified by McWhorter and Sunada [1990] and are the ones that they used for their investigations. However, for the case of countercurrent flow (Figure 2), these conditions are equivalent to spontaneous imbibition, where



**Figure 2.** Situation of cocurrent imbibition where the displacement is (left) unidirectional and (right) countercurrent imbibition.

$$q_w(x, t) = -q_n(x, t), \tag{12a}$$

$$S_w(x = 0, t) = S_0, \tag{12b}$$

$$S_w(\infty, t) = S_i, \tag{12c}$$

$$S_w(x, 0) = S_i, \tag{12d}$$

i.e., there is no forced inflow rate at the left boundary as is the case for the cocurrent setting, and the flow within the system is totally determined by the saturation gradients and the resulting gradient in capillary pressure (see Appendix A). We set  $f_i = f(S_{wi})$  and we introduce the modified fractional flow function [Philip, 1973; McWhorter, 1971]

$$F(x, t) = \frac{q_w/q_0 - f_i R}{1 - f_i R}, \tag{13}$$

where  $q_0 = q_w(x = 0, t)$  and  $R = q_n/q_0$ . Contrary to the classical fractional flow function  $f(S_w)$ ,  $F$  fully incorporates the influence of capillary pressure and will be helpful for the following derivations. For one-dimensional injection,  $q_n = q_0$  and thus  $R = 1$ , and for countercurrent flow,  $q_n = 0$ . The physical meaning of  $F$  is therefore the ratio of the net wetting phase flux at  $(x, t)$  to the net influx of a wetting phase. We introduce the variable transformation

$$\lambda = xt^{-1/2}. \tag{14}$$

[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, and one obtains the ODE [McWhorter and Sunada, 1990]

$$\lambda(S_w) = \frac{2A(1 - f_i R)}{\varphi} \frac{dF}{dS_w} \tag{15}$$

subject to

$$F = \begin{cases} 1 & \text{for } S_w = S_0, \\ 0 & \text{for } S_w = S_i. \end{cases} \tag{16}$$

[19] For transformation of equation (16), the continuity equation (9) becomes

$$\frac{dC}{dS_w} \left[ -\lambda + \frac{2A(F(1 - f_i R) + f_i R)}{\phi S_w} \right] = 0. \tag{17}$$

[20] The ODE given in equation (17) needs to be supplemented with boundary conditions. By using  $C = C(S_w)$ , the boundary and initial conditions for  $C$  given in (10) can be rewritten as

$$C = \begin{cases} C_0 & \text{for } S_w = S_0, \\ C_i & \text{for } S_w = S_i. \end{cases} \quad (18)$$

[21] The solution to equation (17) is a step profile, where  $C$  jumps from its initial concentration  $C_0$  to the injected one  $C_i$  at some saturation  $S_w^*$  where the concentrations break through, i.e.,  $C$  satisfies

$$C(S_w) = \begin{cases} C_0 & \text{for } S_w < S_w^*, \\ C_i & \text{for } S_w > S_w^*. \end{cases} \quad (19)$$

[22] From the ODE (17), it is apparent that  $S_w^*$  must be such that the bracket becomes zero. From (15), it directly follows that  $S_w^*$  needs to satisfy

$$\frac{F(S_w^*)}{S_w^*} + \frac{f_i R}{(1 - f_i R)S_w^*} = \frac{dF}{dS_w} \Big|_{(S_w^*)}, \quad (20)$$

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

$$\frac{F(S_w^*)}{S_w^*} = \frac{dF}{dS_w} \Big|_{(S_w^*)}. \quad (21)$$

[23] All the functions and parameters in equations (20) and (21) are known explicitly from the equations given in Appendix A, and the solution easily can be obtained by prescribing  $S_0$ , determining  $F$  from (A2b), and then solving the nonlinear equation (20). Any capillary-hydraulic properties can be used. For arbitrary functions, the integrals of the exact solution need to be solved numerically. The derivative of a function (in our case the fractional flow function) at a certain point can always be visualized as a tangent to that function at that point. If equation (21) is multiplied with  $S_w^*$ , the equation reads like the standard formulation of the straight line with its slope being  $dF/dS_w$ . Determining  $S_w^*$  can therefore 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 Figure 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 and does not travel along with the phase front. This is intuitively obvious because, if the connate wetting phase has a composition different from the injected wetting phase, the “new” composition needs to fill the “old” phase first (Figure 1).

[24] 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 nonwetting phase at the left boundary is nonzero, and we can prescribe the following initial and boundary conditions for solutes in the nonwetting phase:

$$\begin{aligned} \chi(x = 0, t) &= \chi_0, \\ \chi(\infty, t) &= \chi_i, \\ \chi(x, 0) &= \chi_i, \end{aligned} \quad (22)$$

which immediately gives

$$\chi(S_n) = \begin{cases} \chi_0 & \text{for } S_n < S_n^*, \\ \chi_i & \text{for } S_n > S_n^*, \end{cases} \quad (23)$$

where  $S_n^*$  satisfies

$$S_n^* = 1 - S_w^{**}, \quad (24)$$

and

$$\frac{dF}{dS_w} \Big|_{(S_w^{**})} = \frac{F(S_w^{**})}{(1 - S_w^{**})} - \frac{R(1 - f_i)}{(1 - f_i R)(1 - S_w^{**})}. \quad (25)$$

[25] Equation (25) is the counterpart of equation (20).

[26] Next, we derive the location of  $S_w^*$  by the method of characteristics. The equation for characteristics for the conservation equation (9) is

$$q_w dt - (\varphi \cdot S_w) dx = 0. \quad (26)$$

[27] Equation (26) has an analytical solution in the sense that there exists a function  $\eta(x, t)$  such that

$$\begin{aligned} -d\eta &= q_w dt - (\varphi \cdot S_w) dx, \\ \frac{\partial \eta}{\partial t} &= -q_w, \quad \frac{\partial \eta}{\partial x} = (\varphi S_w), \end{aligned} \quad (27)$$

if and only if

$$\frac{\partial(\varphi S_w)}{\partial t} \stackrel{!}{=} -\frac{\partial q_w}{\partial x}. \quad (28)$$

[28] This is simply the continuity equation for the wetting phase and, thus,  $\eta$  as specified above exists. The characteristic can be determined from equation (27). From the second equation of (27), it follows that

$$\eta(x, t) = \int_0^x (\varphi \cdot S_w(\xi, t)) d\xi + \tilde{c}(t). \quad (29)$$

[29] The function  $\tilde{c}(t)$  must be determined from the first equation in (27). It follows that

$$\frac{\partial \eta}{\partial t} = -q_w = \int_0^x -\frac{\partial q_w}{\partial x} \Big|_{\xi} d\xi + \frac{d\tilde{c}}{dt}. \quad (30)$$

[30] Altogether, we arrive at

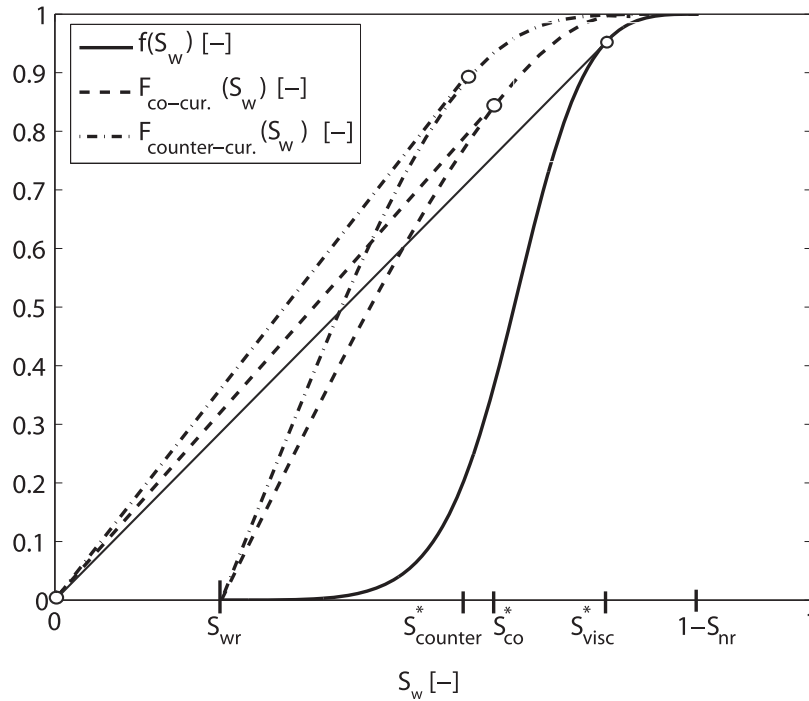
$$\eta(x, t) = \int_0^x [\varphi S_w(\xi, t)] d\xi - \int_0^t q_w(0, \alpha) d\alpha. \quad (31)$$

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

$$\eta(S_w, t) = \int_{S_0}^{S_w} (\varphi \xi) \frac{\partial x}{\partial S_w} \Big|_{\xi} d\xi - \int_0^t q_w(0, \alpha) d\alpha. \quad (32)$$

[32] We set

$$\begin{aligned} \theta(S_w, t) &:= \int_{S_0}^{S_w} (\varphi \xi) \frac{\partial x}{\partial S_w} \Big|_{\xi} d\xi, \\ \tau(t) &:= \int_0^t q_w(0, \alpha) d\alpha. \end{aligned} \quad (33)$$



**Figure 3.** Fractional flow functions for purely viscous, cocurrent, and countercurrent (spontaneous imbibition) flow for different inlet saturations  $S_0$  and for  $S_i = S_{wr}$ . For the viscous and the countercurrent 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 jumps from its initial value to the injected concentration for the dispersion-free limit.

[33] The characteristic coordinates given in equation (32) are valid for arbitrary initial and boundary conditions, and any  $q_w$ ,  $S_w$ , and  $S_n$  that satisfy equations (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 by *McWhorter and Sunada* [1990].

[34] By construction,  $\theta$  and  $\tau$  are the coordinates along which equation (6) reduces to the simple form

$$\frac{\partial C}{\partial \tau} + \frac{\partial C}{\partial \theta} = 0. \tag{34}$$

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

$$C(\theta, \tau) = H(\theta - \tau) \tag{35}$$

and an initial solute front travels along the curve that satisfies  $\theta = \tau$ , i.e.,  $S_w^*$  is such that  $\eta = 0$ , and the saturation  $S_w^*$ , which satisfies this condition, is again given by equations (20) and (21), respectively (see Appendix B). Before we derive the dispersion approximation, we discuss some features of the solution for the advective case.

### 3.1. Buckley-Leverett Limit for the Case of Unidirectional Displacement

[36] It is interesting to note the similarity of equations (19) together with (21) with the solution obtained for the two-phase, multicomponent viscous case, sometimes referred to as the extended Buckley-Leverett problem. The

extended Buckley-Leverett problem also satisfies equation (21), where, for  $S_i = S_{wr}$ , the constant  $S_w^*$  is given by *Pope* [1980] and *Johansen and Winther* [1988]:

$$\frac{f(S_w^*)}{S_w^*} = \frac{df}{dS_w} |_{(S_w^*)}, \tag{36}$$

i.e., we have the very same structure with the only difference being 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.

[37] In cases where the imposed injection is large, capillary effects can be neglected and the Buckley-Leverett, i.e., viscous, limit is approached. For our setting, this is reached by making the parameter  $A$  large. It can be shown analytically [*Chen et al.*, 1992] that  $\lim_{S_0 \rightarrow S_m} A(S_0) = A_{cr}$ , where  $S_m$  is the maximal achievable value and

$$A_{cr} = \left[ \frac{\phi}{2(1-f_i)^2} \int_{S_i}^{S_m} \frac{(S_w - S_i)D}{F - f_n} dS_w \right]^{1/2} < \infty. \tag{37}$$

[38] If the Welge tangent saturation [*Welge*, 1952] is denoted by  $S_b$ , for the limiting case, the fractional flow function  $F$  becomes [*McWhorter and Sunada*, 1990, 1992]

$$F(S_w) = \begin{cases} f_n(S_w) & \text{for } S_w \geq S_b, \\ f_n(S_b) \left( \frac{S_w - S_i}{S_b - S_i} \right) & \text{for } S_w \leq S_b, \end{cases} \tag{38}$$

where  $f_n$  is the normalized fractional flow function

$$f_n = \frac{(f - f_i)R}{1 - f_i R}. \quad (39)$$

[39] This gives equation (36), since the component front occurs after the wetting front, and thus  $S_w^* \geq S_b$ .

### 3.2. Countercurrent Imbibition

[40] Countercurrent imbibition occurs when the wetting fluid spontaneously imbibes into the porous medium, thus replacing the nonwetting phase, which flows out into the opposite direction, i.e., in our notation  $q_w = -q_o$  (see Figure 2) and hence  $R = f_n = 0$ . We can show that the inflow condition  $q_0 = A \cdot t^{-1/2}$  is automatically satisfied for saturation values as specified in equation (12) (see Appendix A). For partly water-wet fractured reservoirs, spontaneous, countercurrent imbibition represents a key recovery mechanism since there the water imbibes from the fracture into the matrix, thus replacing the oil that could not be produced through flooding and thus through viscous effects [Behbahani *et al.*, 2006]. 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  $R = 0$  (see Appendix A) and the semianalytical solution for  $C$  directly follows from equation (19) for the modified expressions for  $A$  and  $F$  with

$$\frac{F(S_w^*)}{S_w^*} = \frac{dF}{dS_w} |_{(S_w^*)}. \quad (40)$$

### 4. Dispersion Approximation

[41] The analytical solution derived above is valid if hydrodynamic dispersion can be ignored; we will now derive an approximate analytical solution for the ADE. The solution is constructed in the same way the solution to the linear ADE would be constructed, with the only difference being 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 nonwetting phase is homogeneous and consists of one component only, the same analytical procedure can be used for analyzing the effect of hydrodynamic dispersion in the nonwetting phase. To this end, we first normalize the ADE 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  $\mathbf{O}(T_0) = \mathbf{O}(L_0) = \mathbf{O}(V_0)$  [Wilson and Gelhar, 1974]:

$$(\varphi S_w) \frac{\partial c}{\partial \bar{t}} = -\bar{q}_w \nu \frac{\partial c}{\partial \bar{x}} + \varepsilon \nu \frac{\partial}{\partial \bar{x}} \left( S_w \bar{q}_w \frac{\partial c}{\partial \bar{x}} \right), \quad (41)$$

with

$$\varepsilon := \frac{\alpha_L}{L_0} \quad \text{and} \quad \nu := \frac{V_0 T_0}{L_0}.$$

[42] For the case where dispersion needs to be taken into account, the only known analytical solutions for the ADE

are valid for the single-phase case with a constant flow field where the fact that  $D_H$  is constant is heavily exploited to derive a solution [Carslaw and Jaeger, 1959]. We therefore employ a different approach: singular-perturbation expansion. Singular-perturbation techniques have been used in many areas of applied mathematics and fluid mechanics [Kevorkian and Cole, 1981; Van Dyke, 1975] and have been used before for treating the effect of nonuniform flow fields on dispersion of inert and adsorbing tracers in saturated and unsaturated single-phase flow through porous media [Gelhar and Collins, 1971; Dagan, 1971; Eldor and Dagan, 1972; Nachabe *et al.*, 1995; Wilson and Gelhar, 1981, 1974]. Its fundamental idea is that, for small  $\varepsilon$ , dispersion can be thought of as a perturbation to the advection equation. For  $\varepsilon \neq 0$ , the mathematical character of equation (41) fundamentally changes from a hyperbolic PDE to a parabolic PDE, and thus the perturbation is of singular nature. The solution (19) to the advection problem (9) is viewed as an outer solution to the ADE 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 (9) reduces to the well-known heat equation. The inner and outer solutions are matched and a uniformly valid, closed-form analytical solution is obtained. Formally, equation (6) is the same as for the unsaturated single-phase case, where  $\varphi S_w$  corresponds to the soil-moisture content and no restriction for a second phase is present. Thus, formally the dispersion approximation for equation (6) can be derived in the same manner as the one employed by Wilson and Gelhar [1981, 1974], and we will only give a rough outline. However, the characteristic length  $L_0$  for the two-phase case is the distance between the wetting front and the point where the solutes start to break through. This is different from the single-phase case, where  $L_0$  is the total distance traveled by the solute front [Gelhar and Collins, 1971; Dagan, 1971; Eldor and Dagan, 1972; Nachabe *et al.*, 1995; Wilson and Gelhar, 1981, 1974].

[43] Through extensive use of Leibnitz' rule and the product rule, the PDE (41) can first be transformed from the  $(\bar{x}, \bar{t})$  coordinate system onto the  $(S_w, \bar{t})$  coordinate system and from there onto the  $(\bar{\tau}, \bar{\theta})$  coordinate system, where the overbar denotes the normalized version of a variable, which yields

$$\begin{aligned} \frac{\partial c}{\partial \bar{\tau}} + \frac{\partial c}{\partial \bar{\theta}} &= \frac{\varepsilon}{\bar{q}_{w0}} \left[ \frac{1}{S_w (\partial \bar{x} / \partial S_w)} \frac{\partial}{\partial S_w} (S_w^2 \bar{q}_w) \frac{\partial c}{\partial \bar{\theta}} \right. \\ &\left. + (\phi(S_w)^2 \bar{q}_w) \frac{\partial^2 c}{\partial \bar{\theta}^2} \right]. \end{aligned} \quad (42)$$

[44] Note that if  $\varepsilon = 0$  in equation (42), we obtain the normalized version of the hyperbolic advection equation (34).

[45] Next, the region around the solute front is magnified through the coordinate transformation of equation  $(\bar{\tau}, \bar{\theta})$  onto  $(\xi, \bar{\theta})$ , where

$$\xi = \frac{\bar{\theta} - \bar{\tau}}{\varepsilon^m}. \quad (43)$$



[46] 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 the 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 [Van Dyke, 1975; Kevorkian and Cole, 1981], which yields the same boundary-layer thickness as the one obtained from the physical approach. Transforming equation (42) onto the  $(\bar{\tau}, \xi)$ -coordinate system leads to  $m = 1/2$ , which is the same thickness as for the single phase case with nonuniform flow and with streamlines nontangential to the solute front [Dagan, 1971]. We now seek an approximate analytical solution for equation (41) through an asymptotic expansion

$$C(\bar{\tau}, \xi) \sim C_0(\bar{\tau}, \xi) + \varepsilon^{(1/2)} C_1(\bar{\tau}, \xi) + O(\varepsilon). \quad (44)$$

[47] Inserting this and only retaining terms of zeroth order in  $\varepsilon$  leads to

$$\frac{\partial c}{\partial \bar{\tau}} = \frac{1}{\bar{q}_{w0}} (\phi S_w^2 \bar{q}_w) \frac{\partial^2 c}{\partial \xi^2}. \quad (45)$$

[48] 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 [Crank, 1979; Carslaw and Jaeger, 1959]. 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  $O(\varepsilon^{1/2})$  as the perturbation expansion. Altogether, we arrive at

$$\frac{\partial c}{\partial \bar{\tau}} = \frac{1}{\bar{q}_{w0}} (\phi S_w^* \bar{q}_w^*) \frac{\partial^2 c}{\partial \xi^2}, \quad (46)$$

where the  $( )^*$  denote that the value is taken at the solute front. The consequences and limitations of this approximation are discussed below. To be complete, the diffusion equation (46) needs to be supplemented with initial and boundary conditions. They follow from the inner and outer solutions, and, for the case of the step profile, coincide with equation (10). The diffusion equation (46) together with (10) has the solution [Dagan, 1971; Carslaw and Jaeger, 1959]

$$c(\bar{\theta}, \bar{\tau}) = \frac{1}{2} \operatorname{erfc} \left( \frac{\bar{\theta} - \bar{\tau}}{2\varepsilon^{(1/2)} \left[ \int_0^{\bar{\tau}} \frac{\phi(S_w^*)^2 \bar{q}_w^*}{\bar{q}_{w0}} \right]^{(1/2)}} \right). \quad (47)$$

[49] By construction, the solution given in equation (47) is valid for the region around the boundary layer, whereas the solution given through equation (19) is valid away from the boundary layer. For the initial and boundary conditions as specified in (10), the uniformly valid composite solution for the zeroth-order approximation coincides with equation (47), and we can rewrite equation (47) in the  $(x, t)$  coordinate system as

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \left( \frac{\int_0^x \phi S_w(\xi, t) d\xi - \int_0^t q_w(0, \delta) d\delta}{2\alpha_l^{1/2} \left[ \int_0^{\tau(t)} \phi(S_w^*)^2 \left( \frac{q_w(S_w^*)}{q_w(S_0)} \right) dt \right]^{1/2}} \right). \quad (48)$$

[50] As in the purely advective case, for the derivation of equation (48), no features of the solution derived by McWhorter and Sunada [1990] were used. Consequently, this expression is valid for the initial and boundary conditions given in equation (10) and any  $q_w, S_w,$  and  $S_n$  that satisfy equations (1) and (2). The respective expressions can stem from either analytical solutions or could be combined with numerical calculations from, e.g., streamline simulations [Blunt et al., 1996; King and Datta-Gupta, 1998; Datta-Gupta and King, 1995]. In case boundary and initial conditions other than equation (10) are used, the matching function and the composite solution need to be modified accordingly.

[51] From equation (48), we can obtain an expression for the growth of the dispersive zone  $\delta$  (Figure 1). Dispersion only plays a role around the solute front, i.e., where  $x = x(S_w^*, t)$ , and thus  $\delta$ , can be described by the rate of change around that front. This gives

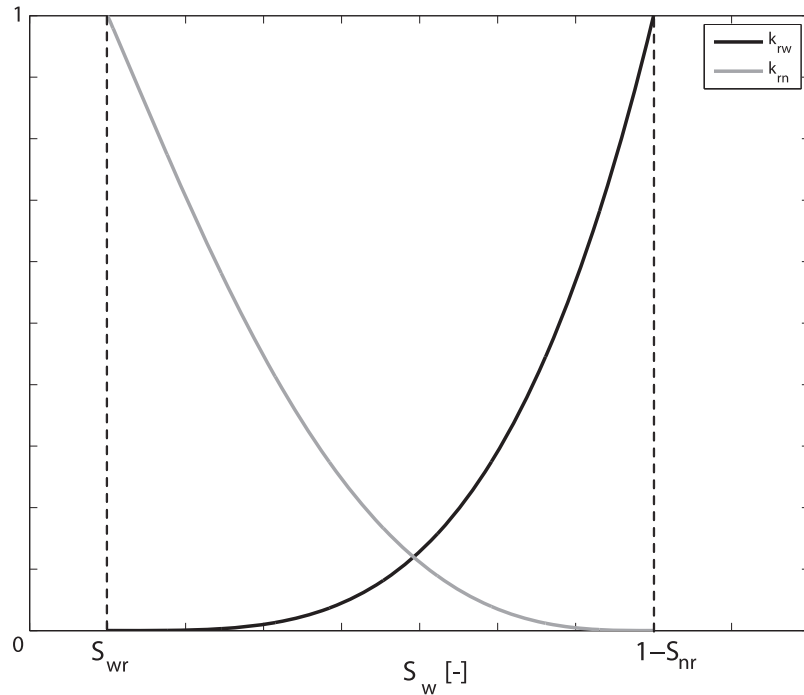
$$\delta(t) = - \left( \frac{\partial C / C_0}{\partial x} \right)_{x=x(S_w^*, t)}^{-1}. \quad (49)$$

### 5. Discussion of Validity and Illustrative Examples

[52] In this section, we give some examples and compare our analytical expressions to some numerical solutions. For the perturbation expansion to be valid,  $\varepsilon^{1/2} = (\alpha_L / L_0)^{1/2} \ll 1$  needs to be satisfied. We show that, for the two-phase case,  $L_0$  is the distance between the wetting front and the point where the solutes start to break through. This is different from the single-phase case, where  $L_0$  is the total distance traveled by the solute front. Furthermore, we discuss the difference between the growth rate  $\delta(t)$  of the dispersive zone (Figure 1) for the cases with and without capillary pressure. We can show 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, i.e., the Buckley-Leverett case, by a factor of  $(1/2)$ .

[53] For the numerical simulations, we use the complex system modeling platform (CSMP++), a C++ library for multiphase-flow in heterogeneous media, a software package widely used to model single-phase and multiphase flow in fractured porous media [see, e.g., Geiger et al., 2006, 2004, 2009; Geiger, 2010; Matthäi et al., 2007, 2009].

[54] 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 Figures 4 and 5). 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 of the most common models employed in both hydrological applications and the petroleum literature, the Brooks-Corey model, uses the effective wetting saturation



**Figure 4.** Residual saturations  $S_{wr}$  and  $S_{nr}$  and corresponding relative permeability functions.

$$S_e = \frac{S_w - S_{wr}}{1 - S_{wr} - S_{nr}}, \quad 0 \leq S_e \leq 1, \quad (50)$$

where  $S_{nr}$  is the residual saturation of the nonwetting phase. The Brooks-Corey model [Brooks and Corey, 1964] then uses the relations

$$k_{rw}(S_e) = S_e^{(2+3\lambda_{BC})/\lambda_{BC}}, \quad (51a)$$

$$k_{rn}(S_e) = (1 - S_e)^2(1 - S_e^{(2+3\lambda_{BC})/\lambda_{BC}}), \quad (51b)$$

$$P_c(S_e)/p_d = S_e^{-1/\lambda_{BC}}, \quad P_c \geq p_d. \quad (51c)$$

[55] Here  $p_d$  is the entry pressure for the nonwetting fluid and  $\lambda_{BC}$  is the Brooks-Corey parameter, with  $\lambda_{BC} \in [0.2, 3.0]$  (see Figures 4 and 5). In the following examples, we restrict ourselves to the Brooks-Corey model, but as already mentioned above, any choice for  $k_{rw}$ ,  $k_{rn}$  and  $P_c$  is applicable.

**5.1. Cocurrent and Countercurrent Imbibition**

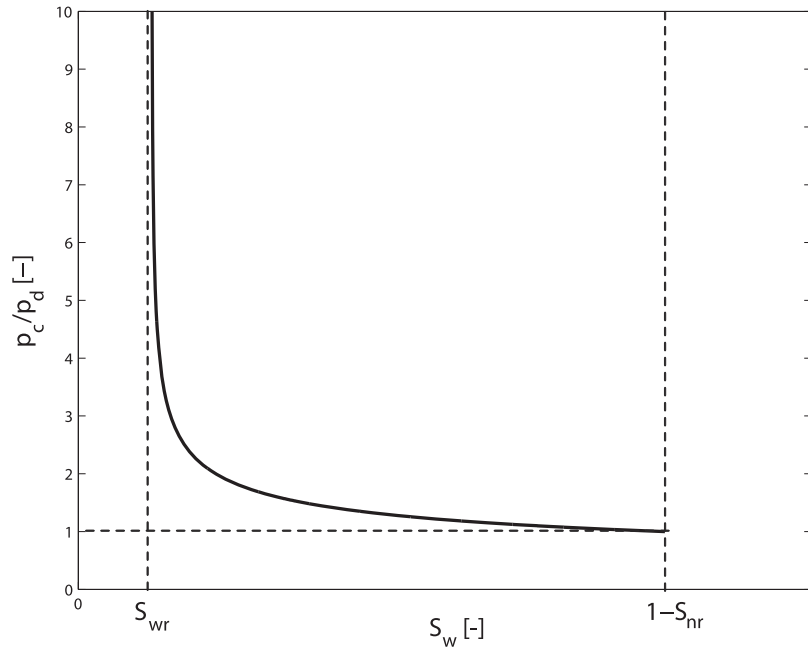
[56] For the McWhorter and Sunada problem, equations (48) and (49) become

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

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

$$= 2 \left[ \frac{\pi\alpha_l}{\phi} 2A\sqrt{t} (F(S_w^*) (1 - f_i R) + f_i R) \right]^{1/2}. \quad (52)$$

[57] Figure 6 shows the comparison between numerical solutions and the analytical solution for the cocurrent flow and transport of solutes derived in this paper for times  $t = 0.7d, 1.5d, 2.5d$  and the parameter set given in Table 1. Figure 7 shows the comparison for the case of countercurrent imbibition for times  $t = 0.7d, 1.7d, 17d$  and the parameter set given in Table 2. 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 single-phase case, where the characteristic length is the distance traveled by the solute front [Gelhar and Collins, 1971; Dagan, 1971; Eldor and Dagan, 1972; Nachabe et al., 1995; Wilson and Gelhar, 1981, 1974]. Figure 8 shows the comparison for spontaneous imbibition and the parameter set given in Table 3 for times  $t = 2d, 17d, 34d$ . In this case, the connate wetting saturation is smaller than the ones in the previous two examples, and consequently the retardation between the wetting front and the point where the solutes start to break through is smaller. At time  $t = 2d$ , the distance traveled by the solute front is already longer than for  $t = 0.7d$  for the case shown in Figure 7. However, the perturbation expansion for the case shown in Figure 8 overestimates the dispersion for this time, and predicts that the components disperse ahead of the solute front. This is physically impossible since  $q_w = 0$  there 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  $\varepsilon$  and a good agreement between the numerical and the analytical solution is achieved.



**Figure 5.** Capillary pressure function for the Brooks-Corey parametrization for  $\lambda_{BC} = 3$ .

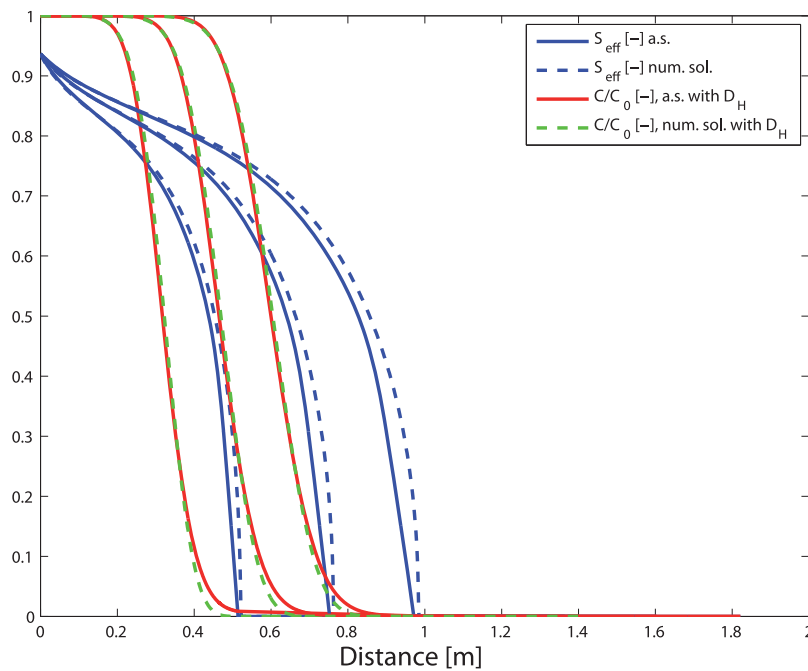
**5.2. Buckley-Leverett Problem**

[58] For the Buckley-Leverett problem with constant inflow rate  $q_t$ , and boundary conditions for  $S_w$  and  $C$  as specified in (11) and (10), respectively, equation (48) becomes

$$C(x, t) = \frac{C_0}{2} \operatorname{erfc} \left( \frac{\int_0^x \phi S_w d\xi - q_t \cdot t}{2S_w^* [\phi \alpha_L q_t f_w(S_w^*) \cdot t]^{1/2}} \right), \tag{53}$$

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

[59] We note that for the Buckley-Leverett problem, the dispersive zone grows with order  $\mathbf{O}(t^{1/2})$  compared to order  $\mathbf{O}(t^{1/4})$  for the McWhorter-Sunada problem. This is because of the specific inflow conditions of the former, and not because of capillary forces. To evaluate the influence of capillary forces on  $\delta(t)$ , we have to consider the Buckley-Leverett problem with the inflow condition  $q_t = \tilde{A} t^{-1/2}$  for some positive constant  $\tilde{A}$ . This leads to  $\delta(t)$  as in equation (52) with  $\tilde{A}$  substituting for  $A$  and  $f(S_w)$  substituting for  $F(S_w)$  for the cocurrent case, i.e.,  $R = 1$ . Hence, for the case



**Figure 6.** Dispersion approximation for cocurrent imbibition with  $\alpha_L = 0.01$  m at times  $t = 0.7, 1.5,$  and  $2.5$  days and the parameters given in (1) and the corresponding  $\varepsilon = 0.4, 0.3, 0.14$ .

**Table 1.** Parameter Set for Cocurrent Flow Shown in Figure 6

Parameter	Units	Value
$S_i$		0.22
$S_0$		0.81
$S_{wr}$		0.22
$S_{nr}$		0.15
$\lambda_{BC}$		3.0
$p_d$	Pa	$1.5 \times 10^3$
$\alpha_L$	m	0.01
$\phi$		0.25
$\mu_w$	Pa s	$1.0 \times 10^{-3}$
$\mu_n$	Pa s	$0.5 \times 10^{-3}$

$\tilde{A} = A$ , 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.

[60] As we have seen above, the boundary condition  $q_0 = At^{1/2}$  for the countercurrent case agrees with the one obtained from equation (4) for  $q_t = 0$  and thus is redundant. Consequently, for the countercurrent case,  $\delta(t)$  as specified in equation (52) describes the growth rate for the standard situation of both a laboratory setting of spontaneous imbibition and the situation in the field where spontaneous, countercurrent 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 of  $(1/2)$ . Consequently, for cases where the transport of components is considered, the mixing of which triggers reactions, the amount of reactants available is much smaller than for viscous-dominated processes.

[61] Figure 9 shows the comparison between numerical solutions and the analytical solution for times  $t = 5d, 8d,$

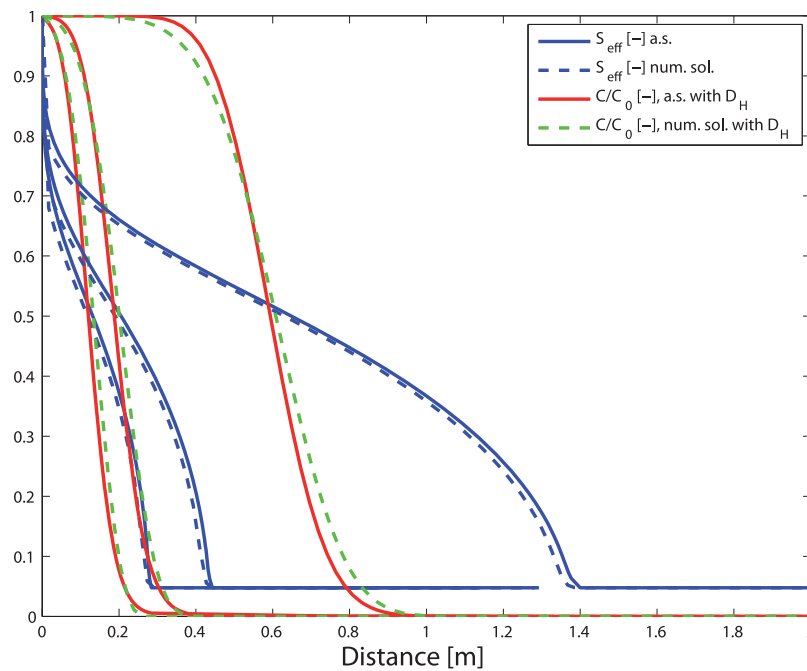
**Table 2.** Parameter Set for Countercurrent, Spontaneous Imbibition Shown in Figure 7

Parameter	Units	Value
$S_i$		0.25
$S_0$		0.85
$S_{wr}$		0.22
$S_{nr}$		0.15
$\lambda_{BC}$		3.0
$p_d$	Pa	$1.5 \times 10^3$
$\alpha_L$	m	0.02
$\phi$		0.25
$\mu_w$	Pa s	$1.0 \times 10^{-3}$
$\mu_n$	Pa s	$0.5 \times 10^{-3}$

$14d$  and the parameter set given in Table 4. 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 solution of this paper is achieved.

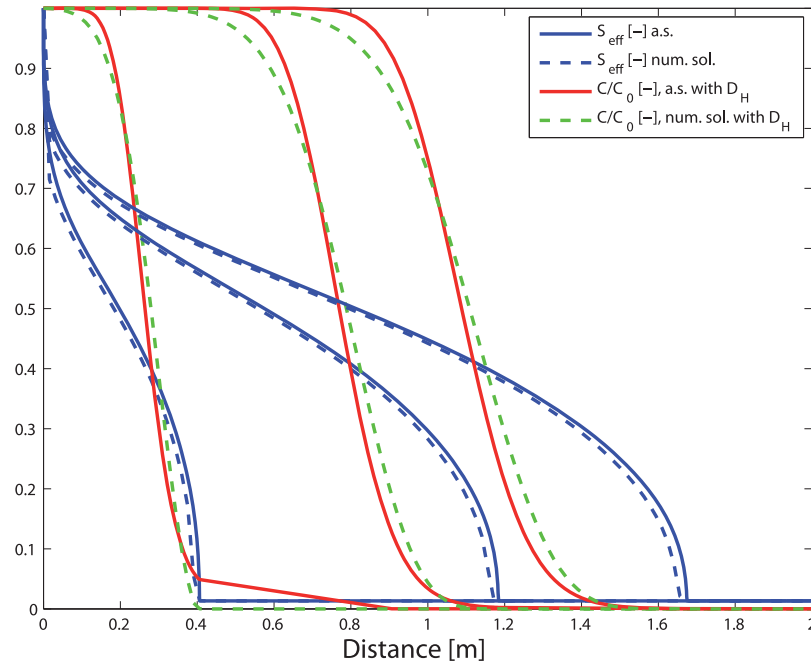
## 6. Summary and Conclusions

[62] The first known set of semianalytical solutions for solute transport in immiscible two-phase, one-dimensional systems that describe all physical mechanisms, i.e., advection because of capillary and viscous forces and the movement because of the time- and space-dependent hydrodynamic dispersion, have been derived. These new solutions can be used both as a tool for the verification of new numerical methods and as a building block for numerical algorithms, e.g., streamline simulations. Furthermore, our solutions describe the standard situation of core-flood experiments where both flow rates and tracer data are available and thus can be employed for an improved method of determining constitutive relationships, such as relative permeabilities and capillary pressure curves, from given measurements. The exact solution for the advective part



**Figure 7.** Dispersion approximation for spontaneous imbibition and the parameter set in Table 2 with  $\alpha_L = 0.02$  m at times  $t = 0.7, 1.7,$  and  $17$  days and the corresponding  $\varepsilon = 0.4, 0.3, 0.1$ .





**Figure 8.** Dispersion approximation for spontaneous imbibition and the parameter set in Table 3 with  $\alpha_L = 0.02$  m at times  $t = 2, 17,$  and  $34$  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 a dispersion of the components ahead of the solute front is wrongly predicted. For  $t_2 = 17$  days and  $t_3 = 34$  days,  $\varepsilon_2 = 0.43$  and  $\varepsilon_3 = 0.2$ , and the comparisons show good agreement.

was obtained by first combining a known integral solution for immiscible two-phase flow with a coordinate transformation and the physical notion that, for pure advection, the solutes are a function of saturation distribution only. By the method of characteristics, we then showed that for the dispersion-free limit and certain boundary conditions, the solution can be represented graphically by a modified Welge tangent. The effect of time- and space-dependent dispersion was solved for by a singular-perturbation technique. The approximate solutions obtained can be used in connection with any flow and saturation field known either from numerical or analytical techniques. They provided the basis for analytical expressions for the growth of dispersive zones. The order of magnitude of the growth rate for the case of spontaneous, countercurrent imbibition is smaller than that for viscous-dominated processes by a factor of  $(1/2)$ . Consequently, the amount of mixing and thus, if reactive solutes are considered, the amount of reactants are

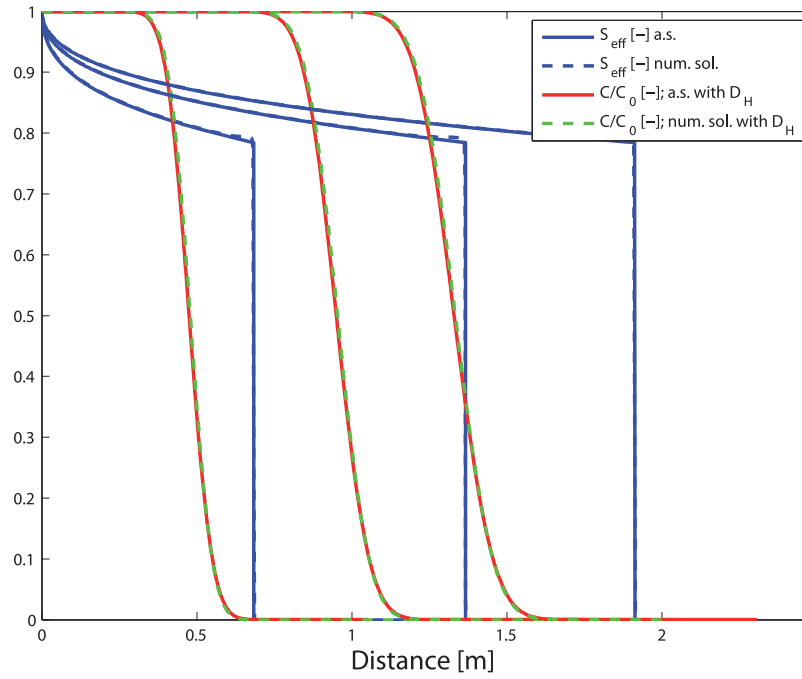
**Table 3.** Parameter set for Countercurrent, Spontaneous Imbibition Shown in Figure 8

Parameter	Units	Value
$S_i$		0.11
$S_0$		0.85
$S_{wr}$		0.1
$S_{mr}$		0.15
$\lambda_{BC}$		3.0
$p_d$	Pa	$1.5 \times 10^3$
$\alpha_L$	m	0.02
$\phi$		0.25
$\mu_w$	Pa s	$1.0 \times 10^{-3}$
$\mu_n$	Pa s	$0.5 \times 10^{-3}$

far smaller than for the viscous case. If the dispersion coefficient is 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, countercurrent spontaneous imbibition, and the case of the capillary-free limit, i.e., the Buckley-Leverett problem.

## Appendix A

[63] The main work of this paper builds upon the solutions derived by *McWhorter and Sunada* [1990] to obtain analytical expressions for transport of solutes in two-phase flow. Therefore, for convenience, we repeat them here, and furthermore show that the inflow boundary condition for the countercurrent case, i.e.,  $R = 0$ , becomes redundant and the situation is that of spontaneous, countercurrent imbibition. *McWhorter and Sunada* [1990] derive exact integral solutions for two-phase flow without transport for horizontal, unsteady displacement that can either be cocurrent or countercurrent. They fully consider the influence of the capillary drive for arbitrary capillary-hydraulic properties. The authors consider the situation in which, at the left boundary, an inflow rate proportional to  $t^{-1/2}$  is present. The proportionality factor  $A$  depends on the capillary-hydraulic properties, and the saturation at the inlet. Their solutions are derived through a self-similarity transformation. The obtained saturation profile for the wetting front is monotonically decreasing, and any arbitrary, but fixed, saturation level is propagated into the medium with time dependence  $t^{1/2}$ . They also show that, for the case where the inflow rate becomes large and capillary forces become negligible, their solutions



**Figure 9.** Dispersion approximation for the viscous limit (Buckley-Leverett problem) for  $\alpha_L = 0.00488$  m at times  $t = 5, 8,$  and  $14$  days and the parameters given in Table 4 and the corresponding  $\varepsilon = 0.51, 0.06, 0.02$ .

approximate the classical Buckley-Leverett solution [Buckley and Leverett, 1942]. The exact solution for equations (1) together with (11) is [McWhorter and Sunada, 1990]

$$x(S_w, t) = \frac{2A(1 - f_i R)}{\phi} F'(S_w) t^{1/2}, \quad (A1)$$

where  $A, F(S_w),$  and  $F'(S_w) = dF(S_w)/dS_w$  satisfy the equations

$$A = \left( -\frac{D}{(1 - f_i R)(F - f_n)} \right) \frac{dS_w}{d\lambda} \quad (A2a)$$

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

$$F(S_w) = 1 - \left( \int_{S_w}^{S_0} \frac{(\beta - S_w)D(\beta)}{F(\beta) - f_n(\beta)} d\beta \right) \left( \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{F(\gamma) - f_n(\gamma)} d\gamma \right)^{-1}, \quad (A2b)$$

**Table 4.** Parameter Set for the Viscous Limit (Buckley-Leverett Problem) Shown in Figure 9

Parameter	Units	Value
$S_i$		0.22
$S_0$		0.85
$S_{wr}$		0.22
$S_{nr}$		0.15
$\lambda_{BC}$		3.0
$\alpha_L$	m	0.00488
$q_t$	m/s	$2.1 \times 10^{-7}$
$\phi$		0.25
$\mu_w$	Pa s	$1.0 \times 10^{-3}$
$\mu_n$	Pa s	$0.5 \times 10^{-3}$

$$F'(S_w) = \left( \int_{S_w}^{S_0} \frac{D(\beta)}{F(\beta) - f_n(\beta)} d\beta \right) \left( \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{F(\gamma) - f_n(\gamma)} d\gamma \right)^{-1}, \quad (A2c)$$

$$F''(S_w) = -\frac{\phi}{2A^2(1 - f_i R)^2} \frac{D}{F - f_n}. \quad (A2d)$$

[64] For the case of countercurrent flow,  $q_t = 0$  and thus the analytical solution directly follows from setting  $R = 0$  in the expressions given above. For this case, McWhorter and Sunada worked with the boundary conditions as given in (11) as well. The physical interpretation of this equation is that, aside from prescribing a saturation level at the inlet, additionally a certain inflow rate is imposed. The situation for countercurrent flow that is far more common in the subsurface, however, is the one where a wetting fluid spontaneously imbibes into a porous medium because of the saturation gradients and the resulting gradients in capillary pressure only. We show that, for  $R = 0$ , the condition for  $q_0$  becomes redundant, and the situation is that of spontaneous countercurrent imbibition. This follows from  $f_n = 0, F(S_0) = 1,$  and

$$q_0 = q_w(x = 0, t) \stackrel{A}{=} \left( -KD(S_0) \frac{dS_w}{d\lambda} \Big|_{\lambda=0} \right) t^{-1/2} \quad (A3a)$$

$$= At^{-1/2}. \quad (A3b)$$

**Appendix B**

[65] The values for the saturation  $S_w^*$  at which the advective front travels as determined by our physically motivated approach and by the method of characteristics agree. For determining  $S_w^*$  from the method of characteristics, we have

$$\eta \stackrel{!}{=} 0 \Leftrightarrow \int_{S_0}^{S_w} \varphi \xi \frac{\partial x}{\partial \xi} d\xi \stackrel{!}{=} \int_0^t q_w(0, \tau) d\tau, \quad (\text{B1})$$

where, for  $q_w = (0, t) = At^{-1/2}$ , the right-hand side becomes  $\tau(t) = 2At^{1/2}$ . The left-hand side becomes

$$\begin{aligned} \int_{S_0}^{S_w} \phi \xi \frac{\partial x}{\partial \xi} d\xi &\stackrel{(\text{A1})}{=} t^{1/2} \int_{S_0}^{S_w} \phi \xi \frac{2A(1-f_i R)}{\phi} F''(\xi) d\xi \\ &\stackrel{(\text{A2d})}{=} t^{1/2} \int_{S_0}^{S_w} \phi \xi \frac{2A(1-f_i R)}{\phi} \left[ -\frac{\phi}{2A^2(1-f_i R)^2 F - f_n} \frac{D}{D} \right] d\xi \\ &= \int_{S_0}^{S_w} \phi \xi \frac{-D(\xi)}{A(1-f_i R)(F(\xi) - f_n)} d\xi. \end{aligned} \quad (\text{B2})$$

[66] Taking the expression for the right-hand side  $\tau$  and the left-hand side  $\theta$ , we thus obtain that  $S_w$  needs to be such that

$$\frac{2A^2(1-f_i R)}{\varphi} \stackrel{!}{=} \int_{S_w}^{S_0} \beta \frac{D(\beta)}{(F(\beta) - f_n)} d\beta. \quad (\text{B3})$$

[67] The left-hand side of (B3) contains the constant  $A$  as determined by the analytical solution derived by McWhorter and Sunada (see Appendix A). Successively inserting explicit expressions for  $A$ ,  $F$ , and  $F'$  as given in Appendix A shows that equation (B3) is satisfied. In detail, these steps are as follows:

$$\begin{aligned} \frac{2A^2(1-f_i R)}{\phi} &\stackrel{(\text{A2a})}{=} \frac{1}{(1-f_i R)} \int_{S_i}^{S_0} \frac{(\xi - S_i)D(\xi)}{(F - f_n)} d\xi \\ &\stackrel{(\text{A2b})}{=} \frac{1}{(1-f_i R)} \left[ F(S_w) \cdot \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{F(\gamma) - f_n} d\gamma + \int_{S_w}^{S_0} \frac{(\beta - S_w)D(\beta)}{(F(\beta) - f_n)} d\beta \right] \\ &\stackrel{(20)}{=} \frac{1}{(1-f_i R)} \left[ \left( S_w F'(S_w) \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{(F(\gamma) - f_n)} d\gamma \right) + \int_{S_w}^{S_0} \frac{(\beta - S_w)D(\beta)}{(F(\beta) - f_n)} d\beta - \frac{1}{(1-f_i R)} f_i R \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{(F(\gamma) - f_n)} d\gamma \right] \\ &\stackrel{(\text{A2c})}{=} \frac{1}{(1-f_i R)} \left[ \int_{S_w}^{S_0} \frac{S_w D}{F - f_n} d\gamma + \int_{S_w}^{S_0} \frac{(\beta - S_w)D}{(F - f_n)} d\beta - \frac{1}{(1-f_i R)} f_i R \int_{S_i}^{S_0} \frac{(\gamma - S_i)D(\gamma)}{(F(\gamma) - f_n)} d\gamma \right] \\ &= \frac{1}{(1-f_i R)} \left[ \int_{S_w}^{S_0} \frac{\beta D}{(F - f_n)} d\gamma - \frac{f_i R}{(1-f_i R)} \int_{S_i}^{S_0} \frac{(\gamma - S_i)D}{(F - f_n)} d\gamma \right]. \end{aligned} \quad (\text{B4})$$

[68] Thus, for the case  $S_{wi} = S_{wr}$ ,  $f_i = 0$ , equation (B1) is satisfied if  $S_w$  satisfies (21), which yields the mathematical rigorous justification for the assumption  $C = C(S_w)$  for the advective case made initially. Since the assumption  $C = C(S_w)$  stays valid for  $f_i \neq 0$ , we obtain (20).

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## References

- Acs, G., S. Doreschall, and E. Farkas (1985), General purpose compositional model, *SPE J.*, 25(4), 543–553.
- Austad, T., and D. C. Standnes (2003), Spontaneous imbibition of water into oil-wet carbonates, *J. Pet. Sci. Eng.*, 39(3–4), 363–376.
- Bear, J. (1972), *Dynamics of Fluids in Porous Media*, Dover, New York, N.Y.
- Behbahani, H. S., G. Di Donato, and M. J. Blunt (2006), Simulation of counter-current imbibition in water-wet fractured reservoirs, *J. Pet. Sci. Eng.*, 50(1), 21–39.
- Blunt, M. J., K. Liu, and M. R. Thiele (1996), A generalized streamline method to predict reservoir flow, *Pet. Geosci.*, 20(3), 259.
- Bolster, D., F. J. Valdés-Parada, T. LeBorgne, M. Dentz, and J. Carrera (2010), Mixing in confined stratified aquifers, *J. Contam. Hydrol.*, 120–121, 198–212.
- Brooks, R. H., and A. T. Corey (1964) Hydraulic properties of porous media, *Hydrol. Pap. 3*, Colo. State Univ., Fort Collins.
- Buckley, S. E., and M. C. Leverett (1942), Mechanisms of fluid displacement in sands, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 146, 107–116.
- Carslaw, H. S., and J. C. Jaeger (1959), *Conduction of Heat in Solids*, Oxford Univ. Press, Oxford, U. K.
- Chen, Z. X. (1988), Some invariant solutions to two-phase fluid displacement problems including capillary effect, *SPE Reservoir Eng.*, 30(2), 691–700.
- Chen, Z. X., G. S. Bodvarsson, P. A. Witherspoon, D. B. McWhorter, and D. K. Sunada (1992), Comment on ‘Exact Integral Solutions For Two-Phase Flow’ by David B McWhorter and Daniel K Sunada, *Water Resour. Res.*, 28(5), 1477–1479.
- Chen, Z. X., G. S. Bodvarsson, P. A. Witherspoon, and Y. C. Yortsos (1995), An integral equation formulation for the unconfined flow of groundwater with variable inlet conditions, *Transp. Porous Media*, 18(1), 15–36.
- Cirpka, O. A. (2002), Choice of dispersion coefficients in reactive transport calculations on smoothed fields, *J. Contam. Hydrol.*, 58(3–4), 261–282.
- Crank, J., (1979), *The Mathematics of Diffusion*, Oxford Univ. Press, New York.
- Cvetkovic, V., and G. Dagan (1996), Reactive transport and immiscible flow in geological media. ii. Applications, *Proc. Math. Phys. Eng. Sci.*, 452(1945), 303–328.
- Dagan, G. (1971), Perturbation solutions of the dispersion equation in porous mediums, *Water Resour. Res.*, 7, 135–142.
- Datta-Gupta, A., and M. J. King (1995), A semianalytic approach to tracer flow modeling in heterogeneous permeable media, *Adv. Water Resour.*, 180(1)9–24.
- Datta-Gupta, A., S. Yoon, D. W. Vasco, and G. A. Pope (2002), Inverse modeling of partitioning interwell tracer tests: A streamline approach, *Water Resour. Res.*, 38(6), 1079, doi:10.1029/2001WR000597.
- De Simoni, M., J. Carrera, X. Sanchez-Vila, and A. Guadagnini (2005), A procedure for the solution of multicomponent reactive transport problems, *Water Resour. Res.*, 41(11), W11410, doi:10.1029/2005WR004056.
- De Simoni, M., X. Sanchez-Vila, J. Carrera, and M. W. Saaltink (2007), A mixing ratios-based formulation for multicomponent reactive transport, *Water Resour. Res.*, 43(7), W07419, doi:10.1029/2006WR005256.
- Dentz, M., T. Le Borgne, A. Englert, and B. Bijeljic (2011), Mixing, spreading and reaction in heterogeneous media: A brief review, *J. Contam. Hydrol.*, 120–121, 1–17, doi:10.1016/j.jconhyd.2010.05.002.
- Eldor, M., and G. Dagan (1972), Solutions of hydrodynamic dispersion in porous media, *Water Resour. Res.*, 8, 1316–1331.
- Emmanuel, S., and B. Berkowitz (2005), Mixing-induced precipitation and porosity evolution in porous media, *Adv. Water Resour.*, 28(4), 337–344.
- Fokas, A. S., and Y. C. Yortsos (1982), On the exactly solvable equation  $s_t = [(\beta s + \gamma)^{-2} s_x]_x + \alpha(\beta s + \gamma)^{-2} s_x$  occurring in two-phase flow in porous media, *SIAM J. Appl. Math.*, 42(2)318–332, doi:10.1137/0142025.
- Geiger, S., and S. Emmanuel (2010), Non-Fourier thermal transport in fractured geological media, *Water Resour. Res.*, 46, W07504, doi:10.1029/2009WR008671.
- Geiger, S., S. Roberts, S. K. Matthäi, C. Zoppou, and A. Burri (2004), Combining finite element and finite volume methods for efficient multiphase flow simulations in highly heterogeneous and structurally complex geologic media, *Geofluids*, 40(4), 284–299.
- Geiger, S., T. Driesner, S. K. Matthäi, and C. A. Heinrich (2006), Multiphase thermohaline convection in the Earth’s crust: I. A novel finite element-finite volume solution technique combined with a new equation of state for NaCl-H<sub>2</sub>O, *Transp. Porous Media*, 63.
- Geiger, S., S. K. Matthäi, J. Niessner, and R. Helmig (2009), Black-oil simulations for three-component - three-phase flow in fractured porous media, *SPE J.*, 14, 338–354.

- Gelhar, L. W., and M. A. Collins (1971), General analysis of longitudinal dispersion in nonuniform flow, *Water Resour. Res.*, 7, 1511–1521.
- Gerritsen, M. G., and L. J. Durlofsky (2005), Modelling fluid flow in oil reservoirs. *Annu. Rev. Fluid Mech.*, 37(1), 211–238.
- Hiorth, A., L. M. Cathles, and M. V. Madland (2010), The impact of pore water chemistry on carbonate surface charge and oil wettability, *Transp. Porous Media*.
- Hoteit, H., and A. Firoozabadi (2005), Multicomponent fluid flow by discontinuous Galerkin and mixed methods in unfractured and fractured media, *Water Resour. Res.*, 41 (11), W11412. doi:10.1029/2005WR004339.
- Huber, R., and R. Helmig (1999), 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.
- Javadpour, F. (2009), CO<sub>2</sub> Injection in geological formations: Determining macroscale coefficients from pore scale processes, *Transp. Porous Media*, 79(1), 87–105.
- Johansen, T., and R. Winther (1988), The solution of the Riemann problem for a hyperbolic system of conservation laws modeling polymer flooding, *SIAM J. Math. Anal.*, 19(3), 541–566.
- Juanes, R. (2003), Displacement theory and multiscale numerical modeling of three-phase flow in porous media, PhD thesis, University of California, Berkeley.
- Juanes, R., and M. J. Blunt (2006), Analytical solutions to multiphase first-contact miscible models with viscous fingering, *Transp. Porous Media*, 64(3), 339–373.
- Kashchiev, D., and A. Firoozabadi (2002), Analytical solutions for 1-D countercurrent imbibition in water-wet media, *SPE J.*, 8(4), 401–408.
- Kevorkian, J., and J. D. Cole (1981), *Perturbation Methods in Applied Mathematics*, Springer, New York.
- Khan, S. A., G. A. Pope, and J. A. Trangenstein (1996), Micellar/polymer physical-property models for contaminant cleanup problems and enhanced oil recovery, *Transp. Porous Media*, 24(1), 35–79.
- King, M. J., and A. Datta-Gupta (1998), Streamline simulation: A current perspective. *In Situ*, 22(01), 91.
- LaForce, T., and R. T. Johns (2005), Analytical solutions for surfactant-enhanced remediation of nonaqueous phase liquids, *Water Resour. Res.*, 41(10), W10420, doi:10.1029/2004WR003862.
- Lake, L. W., and F. Helfferich (1977), 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.
- Langlo, P., and M. S. Espedal (1994), Macrodispersion for two-phase, immiscible flow in porous media, *Adv. Water Resour.*, 17(5), 297–316.
- Lie, K. A., and R. Juanes (2005), A front-tracking method for the simulation of three-phase flow in porous media, *Computat. Geosci.*, 9(1), 29–59.
- Lunati, I., and P. Jenny (2006), Multiscale finite-volume method for compressible multiphase flow in porous media, *J. Computat. Phys.*, 216(2), 616–636.
- Mackay, E. (2003), Predicting in situ sulphate scale deposition and the impact on produced ion concentrations, *Chem. Eng. Res. Design*, 81(3), 326–332.
- Matthäi, S. K., et al. (2007), Numerical simulation of multi-phase fluid flow in structurally complex reservoirs, *Geol. Soc. Spec. Publ.*, 292(1), 405.
- Matthäi, S. K., H. M. Nick, C. Pain, and I. Neuweiler (2009), 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.
- McWhorter, D. B. (1971), Infiltration affected by flow of air, *Hydrol. Pap.* 49, Colo. State Univ., Fort Collins.
- McWhorter, D. B., and D. K. Sunada (1990), Exact integral solutions for two-phase flow, *Water Resour. Res.*, 26(3), 399–413.
- McWhorter, D. B., and D. K. Sunada (1992), Exact integral solutions for two-phase flow: Reply, *Water Resour. Res.*, 28(5), 1479.
- Muskat, M. (1949), *Physical Principles of Oil Production*, McGraw-Hill, New York.
- Nachabe, M. H., A. L. Islas, and T. H. Illangasekare (1995), Analytical solutions for water flow and solute transport in the unsaturated zone, *Ground Water*, 33, 304–310.
- Neuweiler, I., S. Attinger, W. Kitzelbach, and P. King (2003), Large scale mixing for immiscible displacement in heterogeneous porous media, *Transp. Porous Media*, 51(3) 287–314.
- Panfilov, M., and S. Floriat (2004), Nonlinear two-phase mixing in heterogeneous porous media, *Transp. Porous Media*, 57(3), 347–375.
- Paster, A., and G. Dagan (2008), Mixing at the interface between two fluids in aquifer well upconing steady flow, *Water Resour. Res.*, 44, W05408, doi:10.1029/2007WR006510.
- Philip, J. R. (1960), A very general class of exact solutions in concentration-dependent diffusion. *Nature*, 4708, 233.
- Philip, J. R. (1973), On solving the unsaturated flow equation: 1. The flux-concentration relation. *Soil Sci.*, 116(5), 328.
- Pope, G. (1980), The application of fractional flow theory to enhanced oil recovery, *SPE J.*, 20(3), 191–205.
- Rahman, M., S. C. Jose, W. Nowak, and O. A. Cirpka (2005), Experiments on vertical transverse mixing in a large-scale heterogeneous model aquifer, *J. Contam. Hydrol.*, 80(3-4), 130–148.
- Reichenberger, V., H. Jakobs, P. Bastian, and R. Helmig (2006), A mixed-dimensional finite volume method for two-phase flow in fractured porous media, *Adv. Water Resour.*, 29(7), 1020–1036.
- Seto, C. J., and F. M. Orr (2009), Analytical solutions for multicomponent, two-phase flow in porous media with double contact discontinuities, *Transp. Porous Media*, 78(2), 161–183.
- Sorbie, K. S. (1991), *Polymer-Improved Oil Recovery*, Blackie Acad. and Prof., London.
- Sorbie, K. S., and E. J. Mackay (2000), Mixing of injected, connate and aquifer brines in waterflooding and its relevance to oilfield scaling, *J. Petrol. Sci. Eng.*, 27(1-2), 85–106.
- Stephen, K. D., G. E. Pickup, and K. S. Sorbie (2001), The local analysis of changing force balances in immiscible incompressible two-phase flow, *Transp. Porous Media*, 45, 63–88.
- Stoll, M., J. Hofman, D. Ligthelm, M. Faber, and P. van den Hoek (2008), Toward field-scale wettability modification - the limitations of diffusive transport, *SPE Reservoir Eval. Eng.*, 11(3), 633–640.
- van Duijn, C. J., and M. J. de Neef (1998), Similarity solution for capillary redistribution of two phases in a porous medium with a single discontinuity, *Adv. Water Resour.*, 21(6), 451–461.
- van Duijn, C. J., and L. A. Peletier (1992), A boundary-layer problem in fresh-salt groundwater flow, *Q. J. Mech. Appl. Math.*, 45(1), 1–24.
- Van Dyke, M. (1975), *Perturbation Methods in Fluid Mechanics*, annotated ed., Parabolic Press, Stanford, Calif.
- Welge, H. J. (1952), A simplified method for computing oil recovery by gas or water drive, *Trans. AIME*, 195, 91–98.
- Werth, C. J., O. A. Cirpka, and P. Grathwohl (2006), Enhanced mixing and reaction through flow focusing in heterogeneous porous media, *Water Resour. Res.*, 42, W12414, doi:10.1029/2005WR004511.
- West, C. C., and J. H. Harwell (1992), Surfactants and subsurface remediation. *Environ. Sci. Technol.*, 26(12), 2324–2330.
- Willingham, T. W., C. J. Werth, and A. J. Valocchi (2008), Evaluation of the effects of porous media structure on mixing-controlled reactions using pore-scale modeling and micromodel experiments, *Environ. Sci. Technol.*, 42, 3185–3193.
- Wilson, J. L., and L. W. Gelhar (1974), Dispersive mixing in a partially saturated porous medium. Technical Report, Ralph M. Parsons Lab. for Water Resour. and Hydrodyn., Mass. Inst. of Technol., Cambridge.
- Wilson, J. L., and L. W. Gelhar (1981), Analysis of longitudinal dispersion in unsaturated flow 1. The analytical method, *Water Resour. Res.*, 17(1), 122–130.
- Xu, T., E. Sonnenthal, N. Spycher, and K. Pruess (2006), TOUGHREACT-A simulation program for non-isothermal multiphase reactive geochemical transport in variably saturated geologic media: Applications to geothermal injectivity and CO<sub>2</sub> geological sequestration, *Comput. Geosci.*, 32(2), 145–165.
- Zhang, Y., and N. R. Morrow (2007), Waterflood performance by injection of brine with different salinity for reservoir cores, SPE paper 109849 presented at Annual Technical Conference and Exhibition, Anaheim, Calif.

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