Unravelling Effects of the Pore-Size Correlation Length on the Two-Phase Flow and Solute Transport Properties: GPU-based Pore-Network Modeling

Senyou An1, Sharul Hasan1, Hamidreza Erfani1, Masoud Babaei1, and Vahid Niasar1

1Department of Chemical Engineering and Analytical Science, University of Manchester, Manchester, UK

Abstract

Continuum-scale models for two-phase flow and transport in porous media are based on the empirical constitutive relations that highly depend on the porous medium heterogeneity at multiple scales including the microscale pore-size correlation length. The pore-size correlation length determines the representative elementary volume and controls the immiscible two-phase invasion pattern and fluids occupancy. The fluids occupancy controls not only the shape of relative permeability curves but also the transport zonation under two-phase flow conditions, which results in the non-Fickian transport. This study aims to quantify the signature of the pore-size correlation length on two-phase flow and solute transport properties such as the capillary pressure-and relative permeability-saturation, dispersivity, stagnant saturation, and mass transfer rate. Given the capability of pore-scale models in capturing the pore morphology and detailed physics of flow and transport, a novel graphics processing unit (GPU)-based pore-network model has been developed. This GPU-based model allows us to simulate flow and transport in networks with multimillions pores, equivalent to the centimeter length scale. The impact of the pore-size correlation length on all aforementioned properties was studied and quantified. Moreover, by classification of the pore space to flowing and stagnant regions, a simple semianalytical relation for the mass transfer between the flowing and stagnant regions was derived, which showed a very good agreement with pore-network simulation results. Results indicate that the characterization of the topology of the stagnant regions as a function of pore-size correlation length is essential for a better estimation of the two-phase flow and solute transport properties.

1. Introduction

1.1. Correlation Length and Constitutive Relations

The constitutive relations for two-phase flow and solute transport in porous media (e.g., capillary pressure-saturation curves, relative permeability-saturation curves, dispersivity-saturation, and mass transfer rates) are the cornerstones of the Darcy-scale flow and transport models. These relations link the pore-scale physics and porous medium characteristics to the macroscopic variables in flow and transport simulations (Blunt, 2001; Miller et al., 1998). The complex nature of heterogeneity inherent to natural porous media can be found in multiple scales including the pore scale (Cushman, 2013) that controls the two-phase flow and solute transport in porous media (Miller et al., 1998). One ubiquitous form of the pore-scale heterogeneity is the pore size spatial correlation in natural rocks, which can be inferred and characterized using the non-invasive and invasive pore-scale imaging and visualization techniques (e.g., X-ray imaging or thin sections) (Lindqvist et al., 2000; White & Sully, 1987; Yao et al., 1997). A valid question is how the constitutive relations, which are empirically obtained from the laboratory experiments, depend on the inherent spatial correlation. Unlike the large-scale heterogeneity, the effects of pore size spatial correlation on flow and transport properties at the pore scale have been much less studied. The knowledge of the impacts of pore-size spatial correlation length on transport properties in contrast to two-phase flow properties is even more limited. This can be due to the limitations of experimental and computational facilities resolving the pore-scale features or simple assumptions of the negligible role of the pore-scale heterogeneity compared to the large-scale heterogeneity.

Using pore network modeling, the physics of fluid flow in correlated samples has been investigated in a few previous studies. Pore network modeling work by Ferrand and Celia (1992) showed pronounced effects of heterogeneity on the capillary pressure-saturation curve. Flow patterns and relative permeability curves...
were studied in heterogeneous rocks based on correlated networks and compared to experimental results (Chauouche et al., 1993; Jerauld & Salter, 1990). Blunt (1997) analyzed the hysteresis in capillary-pressure and relative permeability curves by simulating primary drainage and imbibition cycles in the networks with different correlation lengths, ranging from 0 to 5 pores. They stated that the model showed qualitative differences when consolidated media with different spatial correlations were considered. There are few studies to investigate the effect of pore-scale heterogeneity on solute transport. Bernabé and Bruderer (1998) evaluated the effect of the variance of pore size distribution on the transport properties based on 2-D designed heterogeneous networks. Le Borgne et al. (2011) showed that the correlation of the spatial velocity should be explicitly included in the representation of incomplete mixing in the pore throats in 2-D models. Babaei and Joekar-Niasar (2016) studied the effect of Péclet number on the advection-diffusion regime for different correlation lengths based on the transport simulation in 3-D pore networks. Recently, Erfani et al. (2019) studied the impact of correlation length on reactive solute transport in sandstone samples and showed that the existence of micro-scale heterogeneity and stagnant zones increases the discrepancy between batch experiment and effective reaction rates in the porous media. All these studies considered either the single-phase flow and transport in porous media or were limited to 2-D domains. In this study, we aim to expand the former studies by investigation of two-phase flow and transport in the 3-D correlated and uncorrelated pore networks.

1.2. Pore-Scale Simulation Approaches

There is a variety of pore-scale simulation approaches for modeling multiphase flow and transport in porous media, such as lattice Boltzmann (Chen & Doolen, 1998), level set (Prodanović & Bryant, 2006), smoothed particle hydrodynamics (Tartakovsky & Meakin, 2006), volume of fluid (Huang et al., 2005), and pore-network modeling (Blunt, 2001; Joekar-Niasar et al., 2012). The major difference between pore-network modeling and other schemes is the input requirements regarding the pore morphology. In pore-network modeling, simplified conservation laws are solved in idealized networks, generated based on either X-ray images or statistical methods. The direct simulation methods can use the segmented X-ray images as input; however, they usually require extensive computational cost and suffer from numerical instabilities depending on the dynamic conditions and irregularity of the pore morphology. Also, there is no consensus on whether any of these techniques have a clear advantage in the predictive capability of pore-scale phenomena (Oostrom et al., 2016; Zhao et al., 2019). In this study, we chose to use pore-network modeling mostly due to its low computational cost compared to other simulation schemes and the possibility to simulate much larger physical scales.

Pore-network modeling has been evolving for over six decades as a tool to investigate flow and transport processes in porous media (Fatt, 1956; Oostrom et al., 2016; Zhao et al., 2019). Given the assumptions used in pore-network models compared to other pore-scale models (Joekar-Niasar et al., 2012), it is possible to simulate flow and transport at much larger physical scales (Babaei & Joekar-Niasar, 2016; Liu & Mostaghimi, 2017; Mani & Mohanty, 1999). This feature has provided the flexibility to use pore-network modeling as a technique to investigate the constitutive two-phase flow and transport relations (Bijeljic et al., 2013; Celia et al., 1995; Ioannidis & Chatzis, 1993; Jiménez-Martínez et al., 2017; Joekar-Niasar et al., 2008; Reeves & Celia, 1996). The first pore-network simulation of dispersion in two-phase flow was reported by Sahimi et al. (1983), using 3-D pore networks. However, they ignored the effect of dead-end (stagnant) pores. Later, Raof and Hassanizadeh (2013) employed a pore-network model to simulate transport in an unsaturated network and used the mobile-immobile model (MIM) to fit their simulation data and estimated the upscaled transport properties, without questioning the validity of the MIM model. Recently, Hasan et al. (2019) simulated transport in 3-D random pore networks and compared the directly estimated dispersion coefficient, stagnant saturation, and mass transfer rate against the values obtained from fitting the MIM model. They found a clear disagreement between the directly estimated parameters and those obtained by the MIM-based inverse modeling and emphasized on the importance of the stagnant regions in the macroscopic transport regimes. Similar disagreements were highlighted by Karadimitriou et al. (2016) using micromodel solute transport experiments under two-phase condition.

1.3. This Study

It is known that the pore-size correlation length influences the representative elementary volume (REV) size. In immiscible two-phase flow, the pore-size correlation length controls the invasion pattern and
stagnant regions as a result of immiscible fluids topology and displacement pattern. Throughout this paper, the stagnant regions refer to the pores, which contribute to the invading phase saturation but are practically either rate-limited or totally inaccessible to solute via advection and accessible only via diffusion (they are hydrodynamically stagnant and referred to as dead-end or immobile zones Coats & Smith, 1964; Gaudet et al., 1977; Krupp & Elrick, 1968). The stagnant saturation is defined as the ratio of the pore volume of stagnant regions to the volume of the pore space in the whole domain. In the context of solute transport, these stagnant regions directly impact the non-Fickian transport and the mass transfer between the flowing and stagnant regions (Bromly & Hinz, 2004; Mayes et al., 2003; Padilla et al., 1999; Sander & Braddock, 2005; Toride et al., 2003). Non-Fickian transport in porous media is the result of different transport time scales in different regions of a porous medium. Consequently, the breakthrough or resident concentration profiles do not follow the “S-shape” profiles and cannot be fitted with advection-dispersion equation.

The stagnant regions are the common topological characteristic of porous media that have a clear and undeniable signature on all constitutive relations of two-phase flow and transport in porous media. The patterns of stagnant regions are usually dendritic (dead-end clusters connected to the main flow path), and their boundary with the receding phase bears the highest capillary pressure at a given state of saturation. Furthermore, these regions mostly form dead-end zones, and thus, they do not contribute to relative permeability values. Moreover, under the advective solute transport in unsaturated (or immiscible two-phase flow) conditions, the stagnant regions are predominantly diffusion-controlled, while the flowing regions are advection-controlled. In this study, we aim to evaluate the variation of all constitutive equations for flow and transport as a function of pore-size correlation length, with the emphasis on the stagnant regions.

The major contributions of this study are summarized as follows:

- The stagnant regions have a critical role in the hysteresis of constitutive two-phase flow relations (Khayrat & Jenny, 2016) as well as discrepancy in transport time scales in the flowing and stagnant regions leading to the non-Fickian transport (Aziz et al., 2018; Hasan et al., 2019; Karadimitriou et al., 2017). This study delineates impacts of the pore-size correlation length on the stagnant regions and their signature on the relative permeability curves, capillary pressure curves, dispersivity, and mass transfer between flowing and stagnant regions.

- A simple semianalytical equation is provided that can address how the stagnant regions’ topology can be incorporated to quantify the mass transfer at different saturation states. Results of the semianalytical approach have been successfully validated against the results of the numerical simulations.

- Previous studies of pore-scale correlated networks were limited by size due to the architecture of the simulation codes or and computational costs. Dashtian and Sahimi (2019) developed a GPU-based pore-network to simulate flow in porous networks. We present a novel fully GPU-based pore-network model to simulate both quasi-static two-phase flow and transport in porous networks at the centimeter scale.

In the following sections, we first briefly present the generation of uncorrelated and correlated networks with identical network topology. Next, the velocity field is solved for the single-phase and two-phase flow in the uncorrelated and correlated networks. Based on the velocity field, the solute transport in the invading phase is simulated using the advection-dispersion equation. Both flow and transport simulation algorithms are parallelized based on the GPU-CUDA technology to accelerate the calculation and enlarge the simulation domain. In the results section, we analyze the effects of pore-scale correlation length on the absolute permeability, capillary pressure curves, relative permeability curves, stagnant saturation, and the transport characterization (dispersion coefficient and mass transfer rate). We also present a semianalytical approach to estimate the mass transfer rate using the effective lengths of stagnant regions, and the estimated results are compared to the results from pore-network simulations.

2. Methodology

2.1. Pore Network Generation

An algorithm is proposed to generate the unstructured networks with various correlation lengths and millions of pores. The correlation length and network size are chosen such that the network is representative
for given spatial statistics. The algorithm mainly includes three steps: the generation of correlated field, the design of topology, and the mapping between topology and pore radius field. To generate the correlated pore radius field, the statistics of pore size distribution are taken from the Berea sandstone (mean radius of $1.57 \times 10^{-5}$ m and variance of $7.9 \times 10^{-11}$ m$^2$). After transferring these statistics to the second-order stationary field (Babaei & Joekar-Niasar, 2016), the anisotropic exponential variogram equation (Nowak et al., 2008) is solved. The solution provides a normal distribution field for pore radii with a specific correlation length. The second-order stationary field is then transferred back to the pore radius field, the size of which has a log-normal distribution, which is comparable to a typical pore size distribution for sandstone (Ioannidis & Chatzis, 1993). During the transformation, the largest pore radius is set to $7.02 \times 10^{-5}$ m.

Once the pore size distribution has been determined, the pore network topology (location of the pores and their connectivity) is established. First, the locations of pore bodies are generated randomly in a $15 \times 15 \times 15$ mm$^3$ cube, based on an on-chip entropy source (Holcomb et al., 2007). Then the throats are generated to connect pore bodies using the Delaunay triangulation method. The Delaunay triangulation method can find all unique convex hull for a given set of points. The number of throats should be reduced to a specific coordination number to represent the natural porous media. Sok et al. (2002) gave the relation between porosity and average coordination number for sandstones. In a natural porous material, it is possible to have morphologically dead-end pores. However, in this study, to avoid the influence of topologically dead-end pores, we removed the isolated pores and kept the minimum coordination number as 2 to generate well-connected networks. That means under fully saturated conditions, there would not be any stagnant regions.

Therefore in a processing step, the pore throats were randomly removed to reach the realistic average coordination number of 4 and the maximum number of 12. After mapping the correlated field and topology information, we obtained the pore radii with specific correlation length. Then, the throats' length and radii were calculated using the locations and radii of the connecting pore bodies (Acharya et al., 2004; Joekar-Niasar et al., 2008). As the first-order approximation of the pore network of a real porous medium, we assumed the pore network comprises cylindrical pore throats and spherical pore bodies. The angularity of the pore elements would not play a significant role in the transport in this study, since transport happens through the nonwetting phase. The networks generated in this paper include 1.2 million pores with variable correlation lengths. Three examples of pore networks with correlation lengths of 0.0.15 and 0.3 mm are shown in Figure 1. All these networks have the identical statistical distribution of radii as shown in Figure 1.

### 2.2. GPU-Based Two-Phase Flow and Transport Simulations

The quasi-static, two-phase drainage algorithm (controlled by the entry capillary pressure) was used to determine the saturation topology under controlled pressure conditions, resembling water flooding in an oil-wet system (e.g., low salinity waterflooding Aziz et al., 2019; Karadimitriou et al., 2019; Morrow & Buckley, 2011), as well as surfactant transport in NAPL-contaminated soils (hydrophobic soil surface) (Powers et al., 1996). Assuming Hagen-Poiseuille flow in pore throats and mass balance in pore bodies, the pressure field and velocity distributions were computed within the water-filled pores similar to Joekar-Niasar et al. (2008) and Hasan et al. (2019). We developed the GPU-CUDA parallelized Jacobi preconditioned conjugation gradient (PCG) to solve the linear system of equations for the pressure in pore bodies.

After breakthrough of the nonwetting phase, the pressure distribution and velocity field for the nonwetting phase were calculated as well. Combining the Hagen-Poiseuille equation and the mass balance equation for the pore units (a pore body and half length of the connecting throats), we obtained a set of linear equations, where pressure values at pore bodies were unknown. By solving the pressure field, the flow through each pore throat was calculated, and finally, the effective permeability for each phase was computed. By dividing the effective permeability to the absolute permeability, the relative permeability at each saturation was calculated. Then, the transport of a conservative solute was simulated in the nonwetting phase for each saturation using the advection-diffusion equation. The same initially concentration (equal to zero) was applied to all saturation cases to avoid discrepancies in the initial concentration conditions, representing different saturation states at different depths at the same initial concentrations.
\[
V_i \frac{dC_i}{dt} = \sum_{q_{ij} < 0} q_{ij} C_i + \sum_{q_{ij} > 0} q_{ij} C_j + \sum_{j \in N_i} \pi r_{ij}^2 D_{ij}^\text{eff} \frac{c_i - c_j}{l_{ij}}, \quad (i, j \in \Omega \text{ invading phase}),
\]

\[
D_{ij}^\text{eff} = D_m (1 + \kappa Pe_{ij}),
\]

where \(c_i\) represents the concentration at pore unit \(i\), \(V_i\) is the volume of pore unit \(i\), \(q_{ij}\) represents the volumetric flow rate in the throat \(ij\), \(r_{ij}\) and \(l_{ij}\) are radius and length of the corresponding throat \(ij\), and \(N_i\) is the coordination number for the pore body \(i\). On the right hand side, \(D_{ij}^\text{eff}\) is the effective dispersion coefficient in a capillary tube considering the Taylor-Aris correction (Aris, 1956; Taylor, 1953). \(D_m\) is the molecular diffusion coefficient, \(\kappa\) is a geometrical factor analytically calculated for a cylindrical capillary tube as \(\kappa = 1/192\). \(Pe_{ij} = 2v_{ij}r_{ij}/D_m\) is the local pore-scale Péclet number, where \(v_{ij}\) is the average pore velocity in the pore throat \(ij\) with the radius of \(r_{ij}\). The time step of each pore \(i\) is determined based on the residence time (the time required to reach the concentration of 1 for loading or 0 for unloading pores). The global time step is the smallest local time steps, considering both loading (concentration increase) and unloading (concentration decrease) in pore units. Equation 1 is explicitly solved for all pore bodies in every time step based on the velocity field and concentration distribution in the last time step. The explicit calculation is a typical high-density system, which is ideally suitable for parallelization. Therefore, we used the GPU-CUDA technique to parallelize the algorithm to expand the loop calculation by allocating pore bodies to different kernels. All calculations were carried out on a NVIDIA Tesla P100 GPU card, which has 3,584 CUDA cores with 1,190 MHz clock frequency, and 16 GB of global memory. Calculation of the velocity field was done once per saturation status (given the steady-state flow condition). However, the transport was dynamically solved; thus, it was computationally more expensive than the quasi-static two-phase flow simulations. For a network with 1.2 million pore bodies, each transport simulation took about 2 min on average using the aforementioned hardware.

2.3. Upscaling the Simulation Results

Average saturation of the network is simply the volume of the fluid at each pore divided by the summation of pore volume of the network. The relative permeability and capillary pressure values directly resulted from the simulations. Thus, the relative permeability-saturation and capillary pressure-saturation curves for the network were outputs of the simulations. Note that in quasi-static pore-network modeling, such curves do not capture the dynamic effects, and they are steady-state solutions using very small increments in boundary pressures (Joekar-Niasar et al., 2008).

At the continuum scale, average concentration is measured either as a resident concentration or as the flux-average concentration. Similarly, the pore-scale concentrations can be upscaled to produce the average concentration profiles. This is a common method to evaluate the longitudinal dispersion coefficient in laboratory and simulation studies (Babaei & Joekar-Niasar, 2016; Oostrom et al., 2016). For the resident concentration within a specific region (e.g., flowing or stagnant regions), the average concentration in the
domain was calculated as \( \bar{C} = \frac{\sum V_i c_i}{\sum V_i} \). Also, the average concentration in the outlet pore throats \( j \) was calculated based on the flux \( q_{ij} \), as \( \bar{C}_e = \frac{\sum q_{ij} c_{ij}}{\sum q_{ij}} \). At the outlet, throat concentration \( c_{ij} \) was set to the concentration at the upstream pore body.

The longitudinal dispersion coefficient \( (D_f) \) and macroscopic effective velocity \( (v) \) were estimated by fitting the analytical solution proposed by Ogata and Banks (1961) (Equation 2) to the simulation results. Note that this equation is only valid for Fickian behavior. Thus, it can be fitted to the Fickian part of the breakthrough curve or the resident concentration in the flowing regions.

\[
\langle C(L, t) \rangle = 0.5C_{\text{max}} \left[ \text{erfc} \left( \frac{L - vt}{2\sqrt{D_f t}} \right) + \exp \left( \frac{Lv}{D_f} \right) \text{erfc} \left( \frac{L + vt}{2\sqrt{D_f t}} \right) \right],
\]

where \( C \) is the macroscopic concentration, \( L \) is the length of the sample along the flowing direction, and \( C_{\text{max}} \) is the maximum concentration (inlet concentration).

### 2.4. A Semianalytical Solution for the Mass Transfer Between Flowing and Stagnant Regions

Mass transfer rate was estimated directly from the pore-network simulations. However, we aim to provide a simple semianalytical solution for the mass transfer rate based on the pore-scale information and verify the solution with the pore-network simulations. We have made several assumptions as follows: (i) each stagnant cluster, as a dead-end dendrite, can be represented by a finite one-dimensional domain with an effective length of \( L_i \); (ii) \( L_i \) has a statistical distribution that can be obtained from the percolation theory (Hunt et al., 2014; Ohtsuki & Keyes, 1984) or directly from the pore network. Since we want to evaluate the analytical solution against the pore-network simulations, we extract the statistics of the stagnant regions from the pore-network simulations. We have made several assumptions as follows: (i) each stagnant cluster is in contact with the flow field; (ii) all stagnant clusters are in contact with the flow region and have the concentration of 0 at \( t = 0 \); (iv) the time scale required to fill the flow region compared to the stagnant regions is very small thus assumed negligible; (v) stagnant regions are assumed to be diffusion-dominated.

The diffusion equation within a stagnant cluster can be written as \( \frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial x^2} \). Each stagnant cluster is finite and assumed to be in contact with the concentration equal to one from one side. At the end of the cluster \( \frac{dC}{dx} = 0 \), the initial resident concentration is equal to zero. Using the Fourier series, the analytical solution for concentration transport in a given stagnant cluster with the effective length of \( L_i \) reads as (similar to 1-D heat diffusion):

\[
C_i(x, t) = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n(2n-1)} \sin \left( \frac{\pi(2n-1)x}{2L_i} \right) e^{-\pi^2 (2n-1)^2 \frac{t}{t_i}}.
\]

The average concentration in the cluster \( i \) at a given time, is given by \( \langle C_i(t) \rangle \) as

\[
\langle C_i(t) \rangle = \frac{1}{L_i} \int_0^{L_i} C_i(x, t) dx = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(1-2n)^2} e^{-\pi^2 (2n-1)^2 \frac{t}{t_i}}.
\]

Assuming \( N \) stagnant clusters with the length \( L_i \), the average concentration over the whole stagnant clusters, \( \langle C_d(t) \rangle \), reads as

\[
\langle C_d(t) \rangle = \frac{\sum_{i=1}^{N} L_i \langle C_i(t) \rangle}{\sum_{i=1}^{N} L_i}.
\]

A nonequilibrium mass transfer calculation between stagnant and flowing regions can be written as Equation 6.
\[ \alpha(t) = \frac{\partial(C_f(t))}{\partial t} \left( \frac{(C_f(t)) - (C_i(t))}{(C_i(t))} \right)^{-1}, \]  

(6)

where \( \alpha \) is the mass transfer rate \([T^{-1}]\). Based on the assumption that the solute in the flowing zones is highly advective, the \( \langle C_f(t) \rangle \) is equal to inlet concentration after solute breakthrough. Therefore, Equation 6 can be solved for mass transfer rate at each time \( t \).

The estimation of mass transfer rate in a system with a normal distribution for the stagnant clusters is shown in Supporting Information, Section A. In order to employ the semianalytical solution of Equation 5 for any given pore network model, we need to estimate the effective length \( L_i \) for each stagnant cluster. From the network topology at each saturation, we estimate the effective length of each cluster as follows:

\[ L_i = \sum_{j=1}^{N_{ph,i}} (L_{ph,j}) + \sum_{k=1}^{N_{pb,i}} (D_{pb,k}), \]

(7)

where \( L_{ph,j} \) is the length of the pore throat \( j \), \( D_{pb,k} \) is the diameter of the pore body \( k \) in the stagnant cluster \( i \), \( N_{ph,i} \) and \( N_{pb,i} \) are the number of pore throats and pore bodies in cluster \( i \), respectively, and \( \zeta_i \) is the average coordination number of the stagnant cluster \( i \). Then, Equation 5 was used to estimate \( \langle C_f(t) \rangle \) with which \( \alpha \) was calculated as \( \alpha(t) = \frac{\partial(C_f(t))}{\partial t} \left(1 - \langle C_f(t) \rangle \right)^{-1} \). Note that this is based on the assumption that the transport time scale in the flowing region is much shorter than that of the stagnant regions.

3. Results and Discussion

3.1. Two-Phase Flow Constitutive Relations

The pore networks with the dimensions of 15×15×15 mm³ and correlation lengths of 0, 0.375, 0.75, 1.5, 2.25, and 3 mm were generated. All networks were hydrophobic, and water was injected from the boundary at a constant pressure. This scenario mimics water flooding or clean-up process in oil-wet systems; for example, low salinity water flooding in natural oil reservoirs. To evaluate the average behavior, 10 realizations for each correlation length (60 networks in total) were generated and used in two-phase flow simulation. To ensure that the domain size was sufficiently large (beyond REV size) and independent of the network realization at a given correlation length, the capillary pressure-saturation curve and absolute permeability were calculated for each realization. Also, the capillary pressure at breakthrough and saturation of the domain at breakthrough have been used as measures of analysis of REV size. Details can be found in the Supporting Information, Section B. Results show that with the increase of the correlation length, the variation across realizations increases. Figure B1 (Supporting Information) shows that the breakthrough pressure and saturation of the invading phase decrease as the correlation length increases from 0 to 0.75 mm. Given the large variation in results for the correlation lengths larger than 0.75 mm (1/20 total length), we conclude that pore networks with the correlation length larger than 1/20 total length are not quantitatively representative. These results imply that in order to analyze the rock properties using laboratory experiments, it is essential to have the minimal dimension of the sample at least 20 times larger than the pore-size correlation length. We can conclude that many sandstone and especially carbonate rock samples used for X-ray microtomography imaging are not representative for the large correlation lengths, because the microCT sample diameters are normally within 1 or 2 mm. The sandstone rocks can have the pore-size correlation length of 50 to 220 μm (Blair et al., 1996; Ioannidis et al., 1996), which means the sample should have a diameter of 1 to 4 mm. This can be much larger for carbonate rocks, given their large heterogeneity. Additionally, it is important to include the analysis of spatial correlation length in the digital rock physics workflow (Andrä et al., 2013; Wu et al., 2019).

Absolute permeability versus correlation length is shown in Figure 2a. Within the range of correlation length below 0.75 mm, with an increase of the correlation length, absolute permeability increases, and macroscopic entry capillary pressure decreases (Figure 2b). As a result, the breakthrough saturation and breakthrough capillary pressure decrease as well. Figure 2b shows that the capillary pressure-saturation curve for the uncorrelated fields lays above other curves, which indicates that at larger correlation lengths, presence of the preferential paths lead to the smaller breakthrough capillary pressure. Jerauld and Salter (1990) used a consolidated media to perform simulations and found that the increase in absolute permeability ranged
from 10% to 60% depending upon the degree of correlation. Our simulation results show an increase in the absolute permeability of up to 60.7% in the network with correlation length of 0.75 mm compared to the uncorrelated network, despite all networks having the same statistical pore size distributions and

![Figure 2](image)

**Figure 2.** (a) The averaged absolute permeability for six correlation lengths and 10 realizations per group. (b) Capillary pressure-saturation curves for the correlation lengths of 0, 0.375, and 0.75 mm in a 15×15×15 mm³ network. The black filled points represent breakthrough points. (c) Averaged relative permeability-saturation curves for three correlation lengths. Bottom row: Snapshots of the velocity field within the nonwetting phase for three correlation lengths (from 1 to 3) at the same nonwetting phase saturation of 60%. Darker color represents higher velocity.

![Figure 3](image)

**Figure 3.** (a) The stagnant saturation versus invading phase saturation for different correlated networks. (b) The stagnant saturation versus total relative permeability deficit. There are good linear relations between $\sqrt{1 - k_{total}}$ and $\sqrt{S_{stagnant}}$ for both uncorrelated and correlated networks. $y_1, y_2, y_3$ represent uncorrelated, correlation length of 0.375 and 0.75 mm, respectively.
topology. In correlated networks, the hydraulic conductivity of the system is controlled by relatively few paths with high local hydraulic conductivity. Therefore, we conclude that the spatial correlation length increases the hydraulic conductivity of such flow paths.

The relative permeability-saturation curve is an essential constitutive relation to simulate the Darcy-scale two-phase flow in porous media. Three relative permeability-saturation curves are shown in Figure 2c with the correlation lengths of 0, 0.375, and 0.75 mm, respectively. Comparing the relative permeability curves for these networks, with an increase of the spatial correlation length, the crossover saturation (with respect to the nonwetting phase) decreases. These observations are consistent with the results of Kirkpatrick (1973), who found that the effective conductivity (analogous to the relative permeability) was higher in the correlated sample. Similar results have been reported in previous studies such as unconsolidated glass beads (Naar et al., 1962) versus consolidated sandstone (Talash, 1976). Also, the nonwetting (invading) phase relative permeability shows a higher sensitivity to the correlation length compared to the wetting phase relative permeability, as the wetting phase resides in the smaller pores due to their higher throat entry capillary pressures.

Connectivity of the larger pores plays a significant role in the shape of the relative permeability and capillary pressure curves. With the increase of the correlation length, large pores and small pores create separated clusters, which leads to a lower entry capillary pressure for the large pore clusters and consequently channelized pathways for the nonwetting fluid. To capture the flow pathways at different correlation lengths, pore-scale velocity distributions are plotted as shown in Figure 2 (bottom row) for three snapshots with the nonwetting saturation of 0.6 (§ to §). The velocity field is important not only for relative permeability curves but also for solute transport as the variation in the pore velocity increases with an increase of the correlation length, having a direct impact on solute transport. Furthermore, since the crossover relative permeability values increase with an increase in the correlation length, less stagnant regions (smaller stagnant saturation) are present at the higher correlation lengths.

### 3.2. Estimation of the Stagnant Saturation

As shown in Figure 2c, the relative permeability-saturation curves reflect the spatial pore size distribution at different saturation status, which is also the reason for the change of stagnant saturation (shown in Figure 3a). Figure 3a shows that the stagnant saturation versus the nonwetting phase saturation has a non-monotonic trend and with an increase of the pore-size correlation length, the stagnant saturation decreases. To illustrate the relation between the relative permeability and the stagnant saturation, we plotted the stagnant saturation versus the deficit of the total relative permeability (the summation of wetting phase and nonwetting phase permeabilities at given saturation) in Figure 3b and found a linear relationship

\[ \sqrt{1 - k_{\text{total}}} \propto \sqrt{S_{\text{stagnant}}} \],

which was obtained by Hasan et al. (2019) for the uncorrelated pore networks. In the uncorrelated network, this linear relation is satisfactory with \( R^2 = 0.99 \). In the correlated networks, the linear relationship is well satisfied for both high and low saturations. Near the crossover point (same permeability for both phases) in Figure 2c, there is a slight hysteresis behavior in Figure 3b that deviates from the linear relation when \( \sqrt{1 - k_{\text{total}}} \) is around 0.8. This deviation is induced by the presence of the transition zone (refer to section 3.3) in the correlated fields. Additionally, with the increase of the correlation length, the slope of the fitted trends decreases. These results indicate that stagnant saturation can link the two-phase flow modeling using the Darcy’s law to the transport modeling under two-phase flow condition, which is non-Fickian and caused by the presence of the stagnant saturation. This concept (not yet been implemented in the continuum-scale modeling of transport) brings the phenomenological modeling closer to the physics of the two-phase flow in porous media.

### 3.3. Temporal Change of Concentration in the Flowing and Stagnant Regions

After generating the velocity fields of two immiscible fluids under pressure difference of 0.1 MPa, we conducted the GPU-parallelized solute transport simulation of a nonreactive solute in the invading phase with a molecular diffusion coefficient of \( 1.16 \times 10^{-3} \text{ mm}^2/\text{s} \) and calculated the average resident concentration. Figure 4 shows the histogram of the pore-scale Péclet number for a case with correlation length of 0.375 mm. Three zones were identified from the histogram. The boundary between the zones has been defined based on two definitions. Boundary between Zone 1 and Zone 2 is the Péclet number of 0.01 defined as a threshold value below which diffusion role becomes important. The boundary between Zone 2 and Zone 3
is based on the statistical information. Transport in Zone 1 is purely advection-dominated, Zone 3 is absolutely diffusion-dominated, and Zone 2 is the transition zone from the advection-dominated to the diffusion-dominated region. In the uncorrelated network, no transition zone was observed, and separation of the advection-dominated and diffusion-dominated zones was straightforward (pattern can be found in Hasan et al., 2019). However, for the case of correlated networks, it is important to estimate the transport dynamics in the transition regions. Thus, we plotted the resident concentrations, as shown in Figures 4b–4f. In Zone 1, the change of total resident concentration has a clear Fickian behavior (Figure 4b), which can be directly fitted using the Ogata-Banks equation (Ogata & Banks, 1961). Conversely, the non-Fickian behavior of Zone 3 can be observed in Figure 4d. Zone 3 is fully diffusion-controlled and requires a long time to reach the steady-state concentration. Compared with the concentration change in Zone 1 and Zone 3, Zone 2 is a transition region with both advective and diffusive behaviors (Figure 4c) with intermediate transport time scale.

Next, we calculated the resident concentration in Zone 1 + Zone 2 and Zone 3 + Zone 2 as shown in Figures 4e and 4f, respectively. Resident concentration in Zone 1 + Zone 2 still shows the Fickian behavior at the early stage, while the non-Fickian behavior occurs as the solute reaches Zone 2. Considering the different resident concentration profiles as well as the definition of threshold Péclet number of 0.01, we classified Zone 2 as a part of stagnant region. For a better illustration, the flowing and stagnant regions of the invading phase are visualized in the top row of Figure 5 for all three spatial correlation lengths. It is clear that the structure of the invading phase during drainage is dendritic, meaning that the invading phase has several stagnant clusters along the flowing zones. In the uncorrelated network, the invading phase distributes uniformly in the whole domain with a homogeneous spread of the flowing and stagnant regions. As the correlation length increases, the invading phase tends to first occupy the large-pore clusters and then invades other regions.

Two stages of the resident concentration are visualized at each given saturation. At a small saturation of the invading phase, advective transport occurs only through some certain pathways, as most of the network is

---

**Figure 4.** (a) Histogram of the local Péclet number at the breakthrough saturation in one realization with correlation length of 0.375 mm (1/40 of domain size). The black lines show the resident concentrations at different times. (b) The concentration at various saturations for the flowing region Zone 1. (c) The concentration for the transition Zone 2. (d) The concentration for Zone 3 with non-Fickian phenomenon. (e) The concentration for Zone 1 + Zone 2. (f) The concentration for Zone 2 + Zone 3.
not yet accessible by advection. From the concentration fields at different saturations and correlation lengths, we can conclude that with an increase of the correlation length, clusters of slow (or stagnant) regions become larger in size and less in total number. As a result, the concentration front becomes more heterogeneous with the increase of the correlation length. This is obvious from the concentration fronts at the concentration of 60% for all three correlation lengths; as for the uncorrelated network the front seems more homogeneous, but with a large number of spatially distributed stagnant regions. These visualizations clearly underpin the importance of the spatial distribution of flowing and stagnant regions due to various pore-size correlation lengths.

To compare the effect of the pore-size correlation length on transport, four types of average concentrations were calculated versus dimensionless time, as shown in Figure 6. The dimensionless time is defined as the ratio of the injected volume of a fluid divided by the total void space available to the injected fluid, $\tau = \frac{Qt}{V_{S_{nw}}}$, where $Q$ is the volumetric flux at the invading phase saturation of $S_{nw}$, $t$ is time, and $V_{S_{nw}}$ represents the pore volume filled with the invading phase. From left to right, the total resident concentration, resident concentration in the flowing regions, resident concentration in the stagnant region, and flux-averaged effluent concentration, $C_e$, were illustrated, respectively. Considering the total resident concentration profiles, at any correlation length, the transport under steady-state two-phase flow is non-Fickian and it strongly changes with saturation. For the flowing regions, both uncorrelated and correlated networks follow the cumulative normal distribution. These concentration profiles show a Fickian behavior and can be fitted using the analytical solution (Equation 2). In the diffusion-dominated regions, the non-Fickian

| Correlation length | 0        | 0.375 mm | 0.75 mm |
|--------------------|----------|----------|---------|
| Nonwetting phase saturation | 41%      | 36%      | 31%     |
| Classification of regions |         |          |         |
| Stagnant (black)    |          |          |         |
| Flowing (green)     |          |          |         |
| Average concentration 0.2 |        |          |         |
| Average concentration 0.6 |        |          |         |

Figure 5. 3-D visualizations of stagnant (black) and flowing (green) regions (top row), concentration fields at resident concentrations of 0.2 (middle row) and 0.6 (bottom row). For each correlation length, two steady-state saturation have been shown. Pores with zero concentration are not displayed.
phenomenon can be observed even at the beginning of the tracer injection. The flux-averaged effluent concentration profiles show similar non-Fickian behavior. After the tracer reaches the outlet, the profiles are first dominated by the concentrations of the outlet pores belonging to the flowing regions. Then the concentration profiles further develop by the change of concentrations in the outlet pores that belong to the stagnant regions.

Comparing the overall trends between the uncorrelated and the correlated networks, we can conclude that at a given flow rate, the time needed for the average resident concentration to reach steady state is longer for the correlated networks due to the presence of larger clusters of stagnant regions; thus, larger times are required for transport in stagnant regions. This highlights the importance of the size and spatial distribution of the stagnant regions and estimation of mass transfer rate between the flowing and stagnant regions.

3.4. Dispersivity Under Two-Phase Flow Conditions

The saturation-dependence of the longitudinal dispersion coefficient in two-phase flow has been studied with 2-D micromodels (Karadimitriou et al., 2016, 2017), pore-network modeling (Hasan et al., 2019; Raoof & Hassanizadeh, 2013), as well as in sand columns (e.g., Delshad et al., 1996; Padilla et al., 1999; Salter & Mohanty, 1982). Dispersion coefficient was obtained from the fitted Ogata-Banks equation (Equation 2) to the effluent concentration, which follows the Fickian regime (Benson et al., 2000). The accuracy of the fitted curves was calculated based on the normalized mean square error (NMSE), which was smaller than 0.01 for every single case.

Figures 7a–7c show the calculated dispersion coefficient for the uncorrelated and correlated networks at different pressure drops. All curves have similar nonmonotonic trends, and their peak values are at nonwetting
phase saturation of 0.6 or higher. Also, as expected, with an increase of the pressure drop (increase of the pore velocity), the dispersion coefficient increases as well. Note that for an applied pressure drop, an increase of the correlation length leads to the increase of the dispersion coefficient. In the literature, dispersion coefficient is usually linked to the material properties and dispersivity ($\alpha$) as $D_f = \alpha v^n$, where $n$ is an empirical parameter usually assumed to be equal to 1 and $v$ is the effective pore velocity. Assuming such relation, the dispersivity versus saturation has been plotted in Figures 7d–7f for different pressure drops. By comparing the trends and values of dispersivity, the curves are nonmonotonic for uncorrelated and correlated networks. Previous studies made a similar conclusion for the uncorrelated networks (Delshad et al., 1985; Hasan et al., 2019; Karadimitriou et al., 2017; Salter & Mohanty, 1982). In all curves, the maximum dispersivity is observed at a saturation larger than the crossover point of relative permeability curves. Also, the dispersivity increases with the increase of correlation length. Another important result is that dispersivity does not significantly change with the pressure drop, which means the initial assumption of $D_f = \alpha v$ is valid and dispersivity is shown to be independent of the dynamic conditions.

3.5. Mass Transfer Rate Under Two-Phase Flow Conditions

Mass transfer rate is another important factor that controls the non-Fickian behavior under two-phase flow conditions. Multiple works in the literature estimated that the mass transfer rate varies in orders of magnitude for different samples (Baker, 1977; De Smedt & Wierenga, 1984; Karadimitriou et al., 2016; Li et al., 1994). Additionally, the mass transfer rate is variable with time throughout experiments (Haggerty et al., 2004). In this paper, we examined the variation range and trend of the mass transfer rate throughout the simulations. The mass transfer rate between the flowing and stagnant regions was estimated based on Equation 6, where the average resident concentration of the flowing region and average resident concentration in the stagnant region were calculated from the simulation results. Figure 8 shows the mass transfer rate for different correlation lengths at various saturation values. To demonstrate the capability of the proposed semianalytical model, the mass transfer rate estimated from the semianalytical solutions has been plotted as well. Both uncorrelated and correlated cases displayed a decrease in the mass transfer rate with time changing by several orders of magnitude. Furthermore, the mass transfer rate is smaller in the correlated networks at a given time, compared with the uncorrelated ones. In the uncorrelated networks as shown in Figure 5, the stagnant

![Figure 7](image-url)
clusters are smaller at higher population, meaning that the ratio of the area (between flowing and stagnant regions) to the volume of the stagnant regions is larger compared to that of the correlated networks. Smaller area to volume ratio of the stagnant clusters for the correlated networks leads to a smaller mass transfer rate.

The semianalytical mass transfer rate as a function of time is also calculated for the curves at middle saturation with different correlation lengths. As shown in Figure 8, there is a very good agreement between the semianalytical solution and the simulation results. This simple formulation provides an extra flexibility to simulate the mass transfer between the flowing and stagnant regions based on the local topology. The concentration of diffusion-dominated region can also be estimated from the semianalytical solution (Equation 5). Figure 8a shows the comparison between the semianalytical and computational results for concentration versus time as well as mass transfer rate versus time (more cases are shown in Supporting Information, Figure C1).

4. Conclusions

In this study, extensive simulation results obtained from a novel GPU-based pore-network modeling for the steady-state two-phase flow and transport have been presented. The major established goal was to evaluate the effects of pore-size correlation length on constitutive relations, used for continuum-scale porous media modeling, namely, capillary pressure-saturation curves, relative permeability-saturation curves, dispersivity-saturation relations, and mass transfer rates. Hypothetically stagnant regions are the key elements that are highly influential in both multiphase flow and solute transport through porous media. To evaluate this hypothesis, we performed thorough pore-scale simulations for two-phase flow and transport to explore whether there is a correlation between stagnant saturation and other two-phase flow and transport properties. Following conclusions can be drawn from the results presented in this study:
• In this study, a novel GPU-based pore-network model for transport simulation under steady-state two-phase flow has been developed, which is able to simulate networks with over a million pores. This model can simulate core plugs on centimeter length scale at a reasonable computational time.

• Pore-size correlation length has a direct impact on the REV size. For the assigned statistics for the pore size distribution and the mean coordination number of 4, the smallest sample dimension needs to be at least 20 times larger than correlation length to have a representative elementary volume. This conclusion impacts the minimum sample size required for characterization of porous media using microCT X-ray imaging or pore-scale modeling.

• Increase of the pore-size correlation length leads to the decrease of stagnant regions in the nonwetting phase, which directly influences the relative permeability curves, dispersivity-saturation curves, and mass transfer rates. With the increase of the correlation length, relative permeability of the nonwetting phase significantly changes, while the wetting phase relative permeability shows a minor change. As a result, the crossover point relative permeability increases (more effective contribution of the void space to the nonwetting phase flow) and crossover saturation moves towards larger wetting phase saturation.

• The stagnant regions in uncorrelated networks are more fragmented (larger number of stagnant clusters) compared to the correlated networks; they have smaller sizes but their population is larger. Thus, effectively, the stagnant saturation in uncorrelated networks is larger compared to the correlated networks for a given saturation. Due to the different topology of the stagnant regions in correlated versus uncorrelated networks, the mass transfer rate between the flowing and stagnant regions is larger for uncorrelated networks.

• An acceptable relation between the stagnant regions and the relative permeability curves was presented, showing that the stagnant saturation can be estimated from the two-phase constitutive relations. The relative permeability curves, which are essential constitutive relations for two-phase flow in porous media, carry significant information about the pore-size spatial distribution and the stagnant regions. This can support the assessment of solute transport in unsaturated porous media and reduces the number of fitting parameters for the transport modeling.

• For any correlation length, the advective transport under two-phase flow conditions is non-Fickian. Dispersivity of the flowing regions increase with the increase of the correlation length and shows a non-monotonic trend with saturation. Due to the large size of the stagnant clusters in correlated networks, the tailing of the resident concentration profiles can take almost five orders of magnitude of the pore volume.

• A semianalytical solution for mass transfer rate between flowing and stagnant regions has been developed. Results of this simple model are in good agreement with the numerical simulation results. The mathematical formulation indicates that for the correct estimation of the mass transfer rate, it is vital to have the topological information of the stagnant regions, which can be estimated either from imaging techniques or from the percolation theory. Unlike the mobile-immobile model, which proposes a constant mass transfer rate, the proposed semianalytical solution provides an expression to evaluate the variable mass transfer rate.

**Data Availability Statement**

After publication, the readers can find the data that support the figures and conclusions presented in the manuscript in the Mendeley repository with the doi: 10.17632/5rcpb43g4w.2.

**References**

Acharya, R. C., van der Zee, S. E., & Leijnse, A. (2004). Porosity-permeability properties generated with a new 2-parameter 3d hydraulic pore-network model for consolidated and unconsolidated porous media. *Advances in Water Resources*, 27(7), 707–723.

Andrä, H., Combaret, N., Dvorkin, J., Glatt, E., Han, J., Kabel, M., et al. (2013). Digital rock physics benchmarks part i: Imaging and segmentation. *Computers & Geosciences*, 50, 25–32.

Aris, R. (1956). On the dispersion of a solute in a fluid flowing through a tube. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 235(1200), 67–77.

Aziz, R., Joekar-Niasar, V., Martínez-Ferrer, P. J., Godínez-Brizuela, O. E., Theodoropoulos, C., & Mahani, H. (2019). Novel insights into pore-scale dynamics of wettability alteration during low salinity waterflooding. *Scientific Reports*, 9(1), 9257.

Aziz, R., Joekar-Niasar, V., & Martínez-Ferrer, P. (2018). Pore-scale insights into transport and mixing in steady-state two-phase flow in porous media. *International Journal of Multiphase Flow*, 109, 51–62.

Babaei, M., & Joekar-Niasar, V. (2016). A transport phase diagram for pore-level correlated porous media. *Advances in Water Resources*, 92, 23–29.
Baker, L. E. (1977). Effects of dispersion and dead-end pore volume in miscible flooding. *Society of Petroleum Engineers Journal, 17*(03), 219–227.

Benson, D. A., Wheatcraft, S. W., & Meerschaert, M. M. (2000). The fractional-order governing equation of lévy motion. *Water Resources Research, 36*(6), 1413–1423.

Bernabé, Y., & Bruderer, C. (1998). Effect of the variance of pore size distribution on the transport properties of heterogeneous networks. *Journal of Geophysical Research, 103*(B1), 513–525.

Bijeljic, B., Raeni, A., Mostaghimi, P., & Blunt, M. J. (2013). Predictions of non-Fickian solute transport in different classes of porous media using direct simulation on pore-scale images. *Physical Review E, 87*(1), 013011.

Blai, S. C., Berge, P. A., & Bentlyman, J. G. (1996). Using two-point correlation functions to characterize micrometry and estimate permeabilities of sandstones and porous glass. *Journal of Geophysical Research, 101*(B9), 20,359–20,375.

Blunt, M. J. (1997). Effects of heterogeneity and wetting on relative permeability using pore level modeling. *SPE Journal, 2001*(1), 70–87.

Blunt, M. J. (2001). Flow in porous media pore-network models and multiphase flow. *Current Opinion in Colloid & Interface Science, 6*(3), 197–207.

Bromly, M., & Hinz, C. (2004). Non-Fickian transport in homogeneous unsaturated repacked sand. *Water Resources Research, 40*, W07402. https://doi.org/10.1029/2003WR002579

Celia, M. A., Reeves, P. C., & Ferrand, L. A. (1995). Recent advances in pore scale models for multiphase flow in porous media. *Reviews of Geophysics, 33*(S2), 1049–1057.

Chaouche, M., Rakotomalala, N., Salin, D., Baomin, X., & Vortos, V. C. (1993). Capillary effects in heterogeneous porous media: Experiments, pore network simulations, and continuum modeling. Society of Petroleum Engineers. Spe annual technical conference and exhibition.

Chen, S., & Doolen, G. D. (1998). Lattice Boltzmann method for fluid flows. *Annual Review of Fluid Mechanics, 30*(1), 329–364.

Coats, K. H., & Smith, B. D. (1964). Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineers Journal, 4*(01), 73–84.

Cushman, J. H. (2013). *The physics of fluids in hierarchical porous media: Angstroms to miles* (Vol. 10). Dordrecht: Springer Science & Business Media.

Dashtian, H., & Sahimi, M. (2019). Efficient simulation of fluid flow and transport in heterogeneous media using graphics processing units (GPUs). arXiv Preprint arXiv:1908.03301. https://arxiv.org/abs/1908.03301

De Smedt, F., & Wierenga, P. J. (1984). Solute transfer through columns of glass beads. *Water Resources Research, 20*(2), 225–232.

Delshad, M., MacAllister, D. J., Pope, G. A., & Rouse, B. A. (1985). Multiphase dispersion and relative permeability experiments. *Society of Petroleum Engineers Journal, 25*(04), 524–534.

Delshad, M., Pope, G. A., & Sepehmoori, K. (1996). A compositional simulator for modeling surfactant enhanced aquifer remediation, 1 formulation. *Journal of Contaminant Hydrology, 23*(4), 303–327. https://doi.org/10.1016/0169-7722(95)00106-9

Erfani, H., Joekar-Niasar, V., & Faezajadadeh, R. (2019). Impact of micro-heterogeneity on upscaling reactive transport in geothermal energy. *ACS Earth and Space Chemistry.*

Fatt, I. (1956). The network model of porous media. *Transactions of the AIME, 207*(01), 144–181.

Ferrand, L. A., & Celia, M. A. (1992). The effect of heterogeneity on the drainage capillary pressure-saturation relation. *Water Resources Research, 28*(3), 859–870.

Gaudet, J. P., Jegat, H., Vachaud, G., & Wierenga, P. J. (1977). Solute transfer, with exchange between mobile and stagnant water, through unsaturated sand. *Soil Science Society of America Journal, 41*(4), 665–671.

Haggerty, R., Harvey, C. F., Freiherr von Schwerin, C., & Meigs, L. C. (2004). What controls the apparent timescale of solute mass transfer in aquifers and soils? A comparison of experimental results. *Water Resources Research, 40*, W01510. https://doi.org/10.1029/2002WR001716

Hasan, S., Joekar-Niasar, V., Karadimitriou, N. K., & Sahimi, M. (2019). Subjectation-dependence of non-Fickian transport in porous media. *Water Resources Research, 55*, 1153–1166. https://doi.org/10.1029/2018WR023554

Holcomb, D. E., Burleson, W. F., & Fu, K. (2007). Initial SRAM state as a fingerprint and source of true random numbers for RFID tags. In *Proceedings of the conference on rfid security* (Vol. 7, pp. 1).

Huang, H., Meakin, P., & Liu, M. (2005). Computer simulation of two-phase immiscible fluid motion in unsaturated complex fractures using a volume of fluid method. *Water Resources Research, 41*, W12413. https://doi.org/10.1029/2005WR004204

Hunt, A., Ewing, R., & Ghanbarian, B. (2014). *Percolation theory for flow in porous media* (Vol. 880). Cham: Springer.

Ioannidis, M. A., & Chatzis, I. (1993). Network modelling of pore structure and transport properties of porous media. *Chemical Engineering Science, 48*(5), 951–972.

Ioannidis, M. A., Kwiecien, M. J., & Chatzis, I. (1996). Statistical analysis of the porous microstructure as a method for estimating reservoir permeability. *Journal of Petroleum Science and Engineering, 16*, 251–261.

Jeralud, G. R., & Salter, S. J. (1990). The effect of pore-structure on hysteresis in relative permeability and capillary pressure: Pore-level modeling. *Transport in Porous Media, 2*(2), 103–151.

Jiménez-Martínez, J., Le Borgne, T., Tabuteau, H., & Méheust, Y. (2017). Impact of saturation on dispersion and mixing in porous media: Photobleaching pulse injection experiments and shear-enhanced mixing model. *Water Resources Research, 53*, 1457–1472. https://doi.org/10.1002/2016WR018489

Joekar-Niasar, V., Hassanizadeh, S. M., & Leijen, A. (2008). Insights into the relationships among capillary pressure, saturation, interfacial area and relative permeability using pore-network modeling. *Transport in Porous Media, 74*(2), 201–219.

Joekar-Niasar, V., van Dijke, M. I. J., & Hassanizadeh, S. M. (2012). Pore-scale modeling of multiphase flow and transport: Achievements and perspectives. *Transport in Porous Media, 94*, 461–464.

Karadimitriou, N. K., Joekar-Niasar, V., Babaie, M., & Shore, C. A. (2016). Critical role of the immobile zone in non-Fickian two-phase transport: A new paradigm. *Environmental Science & Technology, 50*(8), 4384–4392.

Karadimitriou, N. K., Joekar-Niasar, V., & Brizuela, O. G. (2017). Hydro-dynamic solute transport under two-phase flow conditions. *Scientific Reports, 7*(1), 6624.

Karadimitriou, N. K., Mahani, H., Steeb, H., & Niasar, V. (2019). Nonmonotonic effects of salinity on wettability alteration and two-phase flow dynamics in pmds micromodels. *Water Resources Research, 55*, 9826–9837. https://doi.org/10.1029/2018WR024252

Khayrat, K., & Jenny, P. (2016). Subphase approach to model hysteretic two-phase flow in porous media. *Transport in Porous Media, 111*(1), 1–25. https://doi.org/10.1007/s11242-015-0578-6

Kirkpatrick, S. (1973). Percolation and conduction. *Reviews of Modern Physics, 45*(4), 574.

Krupp, H. K., & Elrick, D. E. (1968). Miscible displacement in an unsaturated glass bead medium. *Water Resources Research, 4*(4), 809–815.
Le Borgne, T., Bolster, D., Dentsz, M., De Anna, P., & Tartakovsky, A. (2011). Effective pore-scale dispersion upscaling with a correlated continuous time random walk approach. Water Resources Research, 47, W12538. https://doi.org/10.1029/2011WR010457

Li, L., Barry, D. A., Culligan-Hensley, P. J., & Bajracharya, K. (1994). Mass transfer in soils with local stratification of hydraulic conductivity. Water Resources Research, 30(11), 2891–2900.

Lindquist, W. B., Venkataraman, A., Dunsmuir, J., & Wong, T. (2000). Pore and throat size distributions measured from synchrotron X-ray tomographic images of Fontainebleau sandstones. Journal of Geophysical Research, 105(B9), 21,509–21,527.

Liu, M., & Mostaghimi, P. (2017). Characterization of reactive transport in pore-scale correlated porous media. Chemical Engineering Science, 173, 121–130.

Mani, V., & Mohanty, K. K. (1999). Effect of pore-space spatial correlations on two-phase flow in porous media. Journal of Petroleum Science and Engineering, 28(3), 173–188.

Mayes, M. A., Jardine, P. M., Mehlhorn, T. L., Bjornstad, B. N., Ladd, J. L., & Zachara, J. M. (2003). Transport of multiple tracers in variably saturated humid region structured soils and semi-arid region laminated sediments. Journal of Hydrology, 278(3-4), 141–161.

Miller, C. T., Christakos, G., Imhoff, P. T., McBride, J. F., Pedit, J. A., & Trangenstein, J. A. (1998). Multiphase flow and transport modeling in heterogeneous porous media: Challenges and approaches. Advances in Water Resources, 21(2), 77–120.

Morrow, N., & Buckley, J. (2011). Improved oil recovery by low-salinity waterflooding. Journal of Petroleum Technology, 63(05), 106–112.

Naar, J., Wygal, R. J., & Henderson, J. H. (1962). Imbibition relative permeability in unconsolidated porous media. Society of Petroleum Engineers Journal, 20(1), 13–17.

Nowak, W., Schwede, R. L., Cirpka, O. A., & Neuwiler, I. (2008). Probability density functions of hydraulic head and velocity in three-dimensional heterogeneous porous media. Water Resources Research, 44, W08452. https://doi.org/10.1029/2007WR006383

Ogata, A., & Banks, R. B. (1961). A solution of the differential equation of longitudinal dispersion in porous media: Fluid movement in earth materials. US Government Printing Office 411.

Ohtsuki, T., & Keyes, T. (1984). Scaling theory of dead-end distribution in percolation clusters. Journal of Physics A: Mathematical and General, 17(5), L267.

Oostrom, M., Mehnani, Y., Romero-Gomez, P., Tang, Y., Liu, H., Yoon, H., et al. (2016). Pore-scale and continuum simulations of solute transport micromodel benchmark experiments. Computational Geosciences, 20(4), 857–879.

Padilla, I. Y., Yeh, T.-C. J., & Conklin, M. H. (1999). The effect of water content on solute transport in unsaturated porous media. Water Resources Research, 35(11), 3309–3313.

Powers, S. E., Anneckner, W. H., & Seacord, T. F. (1996). Wettability of NAPL-contaminated sands. Journal of Environmental Engineering, 122(10), 889–896.

Raoof, A., & Hassanizadeh, S. M. (2013). Saturation dependent solute dispersivity in porous media: Pore scale processes. Water Resources Research, 49, 1943–1951. https://doi.org/10.1002/wrcr.20152

Reeves, P. C., & Celia, M. A. (1996). A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore-scale network model. Water Resources Research, 32(8), 2345–2358.

Sahimi, M., Davis, H. T., & Scriven, L. E. (1983). Dispersion in disordered porous media. Chemical Engineering Communications, 23(4-6), 329–341. https://doi.org/10.1080/009864844030840483

Salter, S. J., & Mohanty, K. K. (1982). Multiphase flow in porous media. I. Macroscopic observation and modeling. SPE Annual Technical Conference and Exhibition, 26-29 September, New Orleans, Louisiana, paper 11017.

Sander, G. C., & Braddock, R. D. (2005). Analytical solutions to the transient, unsaturated transport of water and contaminants through horizontal porous media. Advances in Water Resources, 28(10), 1102–1111.

Sok, R. M., Knackstedt, M. A., Sheppard, A. P., Pinczewski, W. V., Lindquist, W. B., Venkataraman, A., & Paterson, L. (2002). Direct and stochastic generation of network models from tomographic images; effect of topology on residual saturations. Transport in Porous Media, 46(2-3), 345–371.

Talash, A. W. (1976). Experimental and calculated relative permeability data for systems containing tension additives. In Spe improved oil recovery symposium. Society of Petroleum Engineers.

Tartakovsky, A. M., & Meakin, P. (2006). Pore scale modeling of immiscible and miscible fluid flows using smoothed particle hydrodynamics. Advances in Water Resources, 29(10), 1446–1478.

Taylor, G. I. (1953). Dispersion of soluble matter in solvent flowing slowly through a tube. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 219(1137), 186–203.

Ursic, N., Inoue, M., & Leij, F. J. (2003). Hydrodynamic dispersion in an unsaturated dune sand. Soil Science Society of America Journal, 67(3), 703–712.

White, I., & Sully, M. J. (1987). Macroscopic and microscopic capillary length and time scales from field infiltration. Water Resources Research, 23(8), 1514–1522.

Wu, Y., Tahmasebi, P., Lin, C., Zahid, M. A., Dong, C., Golab, A. N., & Ren, L. (2019). A comprehensive study on geometric, topological and fractal characterizations of pore systems in low-permeability reservoirs based on sem, micp, nmr, and X-ray CT experiments. Marine and Petroleum Geology, 103, 12–28.

Yao, J., Thoulet, J. F., & Adler, P. M. (1997). Characterization, reconstruction and transport properties of vugs sandstones. Revue-Institut Français du Pétrole, 52, 3–22.

Zhao, B., MacMinn, C. W., Primkulov, B. K., Chen, Y., Valocchi, A. J., Zhao, J., et al. (2019). Comprehensive comparison of pore-scale models for multiphase flow in porous media. Proceedings of the National Academy of Sciences, 116, 13,799–13,806.