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DOI:

[10.1016/j.ijmultiphaseflow.2018.07.006](https://doi.org/10.1016/j.ijmultiphaseflow.2018.07.006)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Aziz, R., Joekar-Niasar, V., & Martinez-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. <https://doi.org/10.1016/j.ijmultiphaseflow.2018.07.006>

Published in:

International Journal of Multiphase Flow

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Pore-scale insights into transport and mixing in steady-state two-phase flow in porous media

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Abstract

Hydrodynamic dispersion and mixing under two-phase flow can be found in many natural, industrial, and engineering processes such as the modified salinity water flooding (MSWF). In MSWF the injected water displaces the formation brine and will interact with the crude oil and rock to improve the oil recovery. We show throughout numerical simulations that access of the injection water to the available pore space is not homogeneous, even in homogeneous porous media, and it is controlled by the saturation topology and pore-scale velocity field.

Under the steady-state two-phase flow in a homogeneous porous medium, the velocity field has a bimodal distribution. **The bimodal distribution of pore-scale velocity** dictates two different transport time scales spatially distributed over the stagnant and flowing regions at a given saturation topology. These distinctly different transport time scales lead to a non-Fickian transport, which cannot be captured using the conventional advection-dispersion equation.

Using the volume-of-fluid method implemented in the OpenFOAM (ver. 4.0), we simulated pore-scale two-phase flow and the hydrodynamic transport at different saturations. We have investigated the impact of stagnant saturation and the tortuosity of flow pathways on the dispersion coefficient and the mass exchange rate - as the two major parameters controlling transport and mixing - under steady-state two-phase flow. At the Darcy scale,

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different theories such as the mobile-immobile (MIM) theory have been proposed to capture the non-Fickian transport and mixing in two-phase flow through porous media. Based on the simulation results, we assess the validity of the assumptions employed in MIM to define the stagnant saturation and mass exchange rate coefficient. The results of this research provide fresh insights into the potential impact of saturation topology on mixing between the modified salinity water and the formation brine under steady-state flow conditions, which has not been investigated and reported in the literature.

Keywords: Porous media, dispersion, two-phase flow, non-Fickian, pore-scale, mixing

1. Introduction

Hydrodynamic dispersion and mixing in two-phase flow through porous media are found in many natural, industrial, and engineering processes such as contaminant transport in the vadose zone where the infiltrated water carries the contaminants and mixes with the resident water, while air has filled some part of the pore space [37, 4, 23]. Another example is the modified- (or low-) salinity water flooding (MSWF) as one of the enhanced oil recovery techniques, in which injection water with a tuned chemical composition is injected into the reservoir filled originally with the formation brine and the crude oil [31, 1, 29, 42]. The performance of MSWF depends on many pore-scale physio-chemical factors such as crude oil chemistry, formation brine and injection water chemistry, temperature, and rock mineralogy, which have been extensively studied [33, 2, 25]. However, the larger-scale mechanical factors such as transport and mixing of the modified-salinity water have not been extensively studied.

Under single-phase flow conditions, transport strongly depends on the Péclet number (ratio of the advective to the diffusive transport). However, under two-phase conditions, transport and mixing will change strongly with saturation in addition to the Péclet number [11]. While in a homogeneous saturated porous medium, a Fickian transport regime is expected, under two-phase flow conditions due to the presence of regions with distinctly different transport time scales, the transport becomes non-Fickian [17, 35, 21], which is saturation- and flow rate-dependent [26, 27].

The void space filled by the carrier fluid (e.g. water) can be decomposed into the backbone, dead-end and disconnected regions [9, 11, 17, 37]. From

the hydrodynamic point-of-view, they are referred to as flowing (mobile), stagnant (immobile) and non-percolating regions, respectively[17, 27]. The flowing regions contribute to the hydrodynamic solute transport as well as the effective phase permeability, which is captured in the relative permeability curves. The hydrodynamically stagnant regions behave as a sink/source term for the transport process. They do not contribute to flow through a porous medium and consequently they do not contribute to the relative permeability. Finally, the trapped regions contribute neither to transport nor to flow processes. Thus, the total water saturation (S_w) can be decomposed to the flowing saturation (S_{fw}), stagnant saturation (S_{sw}), and disconnected saturation (S_{dw}) such that $S_w = S_{fw} + S_{sw} + S_{dw}$. Additionally, while the transport in the flowing region is controlled by the advection, a mass exchange will occur between the flowing and stagnant regions, **due to the concentration gradient across the interface between these two regions**.

To evaluate the transport parameters, namely dispersion coefficient, effective pore velocity, stagnant saturation, and mass exchange rate coefficient, different models such as the dead-end pore (DEP)[9] and mobile-immobile (MIM)[17] models were proposed. Details of these proposed models can be found in the supplementary information section. Compared to the DEP model, MIM has clear advantages as it captures the non-Fickian behaviour using a non-equilibrium mass exchange between the flowing and stagnant regions [17, 35, 37]. Thus, in several studies the transport and mixing parameters in column-scale two-phase flow experiments were determined using the inverse modelling of the MIM theory[12, 17, 5, 15, 13, 14, 35, 32]. Satisfactory results of the inverse modelling were interpreted as an indication of the validity of MIM, although unrealistic values (e.g. the stagnant saturation larger than 1) were reported [32].

Recent direct analysis of micro-scale experiments showed that for a given saturation topology at different flow rates, the same stagnant saturation values were obtained [27]. This is in contradiction with the MIM theory, in which different Péclet numbers would lead to different stagnant saturations, regardless of two-phase flow conditions. Another potential misconception in underlying assumptions employed in MIM is related to the non-equilibrium mass exchange, from inverse modeling a constant mass exchange rate coefficient is obtained, expressed based on the following equation:

$$S_{sw}\varphi\frac{\partial C_{sw}}{\partial t} = \gamma(C_{fw} - C_{sw}), \quad (1)$$

where S_{sw} , φ , C_{fw} , and C_{sw} are stagnant saturation, porosity, average Darcy-scale concentrations of flowing and stagnant regions, respectively. In Equation 1, the rate coefficient, γ is assumed to be a constant[17]. However, the first direct experimental analysis did not validate this assumption [26].

Former experimental data [27] suggest a non-monotonic trend between the dispersion coefficient and total saturation, as well as the stagnant saturation versus the total saturation. Since the full computational fluid dynamics provides much more detailed information compared to the experiments (such as the detailed velocity field, streamlines and tortuosity), it can be used to evaluate the impact of the velocity field on the delineation of stagnant saturation. Also, change of tortuosity as a function of saturation and its contribution to the transport can be investigated using the CFD simulations. Thus, we employed the direct numerical simulations of hydrodynamic dispersion in two-phase flow through a two-dimensional porous medium using the volume of fluid method implemented in the OpenFOAM software (version 4.0). Furthermore, we explored whether the water relative permeability (as a two-phase flow property) is related to the stagnant saturation.

To achieve these objectives, first, we simulated different steady-state saturation states. Then, at each saturation, hydrodynamic transport at three different injection rates was simulated. Since the numerical grid resolution was much smaller than the smallest pore (15 cells in the smallest pore throat), it enabled us to simulate the detailed sub-pore-scale physics in contrast with the pore-network models where the sub-pore-scale mechanisms have been ignored. We simulated two-phase flow in a two-dimensional domain using the volume-of-fluid method implemented in OpenFOAM. Two-phase flow simulations were performed to establish different steady-state saturations, ranging from 0.34 to 1.0. At each saturation topology, we simulated the advection-diffusion transport at 3 different injection rates which provided three different macroscopic Péclet numbers of 7, 70, and 700. The Péclet number is defined at the pore scale as well as at the macro scale. At the pore scale, the Péclet number is defined as $P_e = \frac{u_p \bar{R}}{D_m}$, where u_p denotes the effective pore velocity, $\bar{R}$ is the mean pore radius, and D_m denotes the diffusion coefficient. At the macro scale the Péclet number is defined as $\tilde{P}_e = \frac{qL}{D_m}$, where q denotes the injection flow rate, L is the macroscopic characteristic length (averaging length), and D_m is the diffusion coefficient. For transport simulations, constant concentration and no diffusion boundary conditions were imposed at inlet and outlet, respectively.

98 We upscaled the pore-scale simulation results to calculate the relative
 99 permeability of the carrier fluid at each steady-state saturation. We also
 100 simulated the streamlines at each saturation to obtain the average tortuos-
 101 ity at each saturation. To obtain the dispersion coefficient (as a result of
 102 variable flow field), we used an analytical solution to fit the average resident
 103 concentration in the flowing region resulted from the pore-scale simulations.
 104 The fitting results were excellent with RMSE ranging from 10^{-7} to 10^{-5} . All
 105 details covering the theoretical, and computational aspects of the methods,
 106 upscaling approach and curve fitting analysis are presented in the following
 107 subsections.

108 1.1. Volume of Fluid Method

109 We simulated immiscible and incompressible two-phase flow in porous
 110 media using VoF [40], implemented in OpenFOAM in a solver called inter-
 111 FOAM [43]. In the two-phase VoF method, each fluid phase is represented by
 112 its volume fraction, α . For example, value 1 represents water and value 0 rep-
 113 represents oil. In grid cells containing the intermediate values of α ($0 < \alpha < 1$),
 114 the interface is constructed. The volume fraction α is transported using
 115 Equation (2):

$$\frac{\partial \alpha}{\partial t} + \nabla \cdot (\alpha \mathbf{u}) + \nabla \cdot (\alpha(1 - \alpha) \mathbf{u}_r) = 0, \quad (2)$$

116 where $\mathbf{u}$ and $\mathbf{u}_r$ are referred to as the velocity field and relative velocity
 117 between the two fluids ($\mathbf{u}_r = \mathbf{u}_1 - \mathbf{u}_2$), respectively.

118 The partial time derivatives in Equation (2) were discretized using the
 119 Euler scheme (1^{st} order bounded, implicit scheme). The second term in
 120 Equation (2) was interpolated using the van Leer flux limiter (2^{nd} order
 121 accuracy and bounded) and the third term was linearly interpolated (2^{nd}
 122 order accuracy) [43].

123 The fluids density (ρ) and viscosity (μ) at the interface were calculated
 124 using the weighted averaging represented by $\rho = \rho_1 \alpha + (1 - \alpha) \rho_2$ and $\mu =$
 125 $\mu_1 \alpha + (1 - \alpha) \mu_2$. ρ_i and μ_i denote density and viscosity of fluid i , respectively.

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \left[\nabla \cdot \left(\mu (\nabla \mathbf{u} + \nabla \mathbf{u}^T) \right) \right] + \mathbf{F}_{sa} \quad (3a)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (3b)$$

126 Solving the coupled Navier-Stokes (3a) and continuity equations (3b),
 127 pressure (p) and velocity ($\mathbf{u}$) were calculated. $\mathbf{F}_{sa}$ represents the body force,
 128 which includes interfacial forces. The second term on the rhs of Equation (3a)
 129 was interpolated using the 2^{nd} order bounded self-filtering central differencing
 130 scheme. The second term on the lhs was interpolated using the linear scheme.
 131 The pressure field was solved using the bi-conjugate gradient method with a
 132 relative tolerance of 10^{-5} . The velocity field was solved using smooth solver
 133 with the relative tolerance of 10^{-10} . Coupling of pressure and velocity was
 134 done using the merged PISO-SIMPLE (PIMPLE) algorithm [40].

135 The body force, $\mathbf{F}_{sa}$, in Equation (3a) is defined as

$$\mathbf{F}_{sa} = \rho \mathbf{g} \cdot \mathbf{n}_z + \int_{\Gamma} \sigma \kappa \delta(x - x_s) \hat{\mathbf{n}} d\Gamma(x_s), \quad (4)$$

136 where Γ is the liquid-liquid interface, and $\delta(x - x_s)$ is the Dirac delta function,
 137 κ is the curvature of interface, and σ is the interfacial tension between the
 138 two fluids. Curvature of the interface is $\kappa = -\nabla \cdot \left(\frac{\nabla \alpha}{|\nabla \alpha|} \right)$ and the unit vector
 139 $\hat{\mathbf{n}}$ is defined as $\hat{\mathbf{n}} = \frac{\nabla \alpha}{|\nabla \alpha|}$.

140 The contact angle is defined at the solid boundaries, and is used to deter-
 141 mine the volume fraction gradient such that the contact angle satisfies the
 142 following equation:

$$\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}_s = \cos \theta, \quad (5)$$

143 where $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}_s$ are vectors normal to the interface and solid wall, respectively.

144 The time step (δt) in simulations was determined such that Courant num-
 145 ber, defined as $Co = \frac{\delta t U}{\delta x} < 0.5$. U denotes the magnitude of velocity, δx is
 146 the cell size. The time steps were around 10^{-6} s.

147 1.2. Advection-Diffusion Transport

148 Advection-diffusion of a tracer (passive scalar) within the carrier fluid was
 149 simulated using Equation (6), where C is the concentration of the tracer and
 150 D_m is the molecular diffusion coefficient, which is typically $10^{-9} \text{m}^2/\text{s}$ [10].

$$\frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C - \nabla \cdot (D_m \nabla C) = 0 \quad (6)$$

151 The steady-state velocity field at each saturation was used to simulate
 152 transient advection-diffusion in the domain using *scalarTransportFoam* solver.

153 Simulated concentration field at each time scale was averaged to obtained the
154 Darcy-scale resident concentration curves. The resulted concentration-time
155 curves were used to estimate the hydrodynamic dispersion and mass exchange
156 rate of the domain.

157 The advective term was interpolated using upwind (1^{st} order, explicit)
158 method and the diffusive term was discretized using Gaussian linear corrected
159 scheme (2^{nd} order). The time derivative (for concentration) was discretized
160 using the Euler (1^{st} order) scheme. The transport matrix was solved using
161 *smoothSolver* due to the sharp gradient of concentration between stagnant
162 and flowing saturation with the relative tolerance of 10^{-16} .

163 1.3. Numerical domain, boundary, and initial conditions

164 The numerical domain had a square 2D geometry. The domain has been
165 shown in Figure S1 in the Supporting Information. Since at each direc-
166 tion there were more than 30 pores and the grains were homogeneously
167 distributed, the domain is definitely larger than Representative Elementary
168 Area (REA) [24]. Top and bottom boundaries shared no-flow conditions.
169 The right boundary was at constant pressure with zero gradient of solute
170 concentration normal to the boundary. The left boundary was at constant
171 inlet injection velocity and constant dimensionless solute concentration. Ini-
172 tially, the domain was fully saturated with the wetting phase ($\alpha = 0$) with
173 a contact angle of 140 degrees (measured through the non-wetting phase).
174 The non-wetting phase (i.e. water in an oil-wet medium) was injected at a
175 constant rate.

176 The domain was meshed using the OpenFOAM utility *snappyHexMesh*.
177 This tool allowed the refinement of grain edges to ensure a high-quality mesh
178 in narrower pore throats. We performed the grid convergence analysis in a
179 sub-section of the original domain (Figure S2 in the Supporting Information).
180 Based on the grid convergence analysis, we chose a mesh with 3.6 million cells,
181 which allows at least 15 cells in the narrowest pore throat. Different steady-
182 state two-phase saturation topologies were established (ranged between 0.34-
183 1) to be used for transport simulations.

184 1.4. Material properties

185 The density and viscosity of 998 (kgm^{-3}) and 10^{-3} ($\text{kgm}^{-1}\text{s}^{-1}$), respec-
186 tively, were assigned to the advancing fluid, which carried the solute. The
187 receding fluid had the density and viscosity of 844 (kgm^{-3}) and 1.910×10^{-2}
188 ($\text{kgm}^{-1}\text{s}^{-1}$), respectively. The interfacial tension, σ , was 0.07 (kgs^{-2}) and

189 the solid surface had affinity to the receding phase with a contact angle of
 190 140 degrees, measured through the advancing phase. The diffusion coefficient
 191 (D_m) of 10^{-9} (m^2s^{-1}) was assumed [10]. The concentration reported in the
 192 study is dimensionless, therefore the maximum value is 1 and minimum is 0.

193 1.5. Upscaling the simulation results

194 The MIM theory is a Darcy-scale model, while the numerical results are
 195 defined in grid cells much smaller than a pore. To evaluate the parameters at
 196 the Darcy scale, it is essential to upscale (average) the sub-pore-scale entities.
 197 We averaged the grid-based results to estimate the transport parameters at
 198 the Representative Elementary Area (REA) scale, which represents the Darcy
 199 scale.

200 1.5.1. Dispersion coefficient of the flowing network

201 Combined effects of heterogeneous velocity distribution and tortuosity
 202 lead to the hydrodynamic dispersion. It is known that the hydrodynamic
 203 dispersion is strongly flow-rate dependent [38]. To obtain the hydrodynamic
 204 dispersion either the method of moments [6] or fitting the data to the an-
 205 alytical solutions [3] can be used. For the Dirichlet boundary condition of
 206 our simulations, the one-dimensional analytical solution developed by Ogata
 207 and Banks was used [34]. This equation is originally developed for the single-
 208 phase flow in semi-infinite domain. There is a complicated analytical solution
 209 for finite domain as discussed in the literature [16]. However, breakthrough
 210 analysis shown in the literature illustrate that the results of the complicated
 211 analytical solution for a finite domain will be identical to the results of the
 212 Ogata-Bank equation for Péclet numbers larger than 5 [16]. Therefore, given
 213 the simplicity and better convergence of the Ogata-Banks equation for curve
 214 fitting and since the macroscopic Péclet number is much larger than 5 in our
 215 simulations, we performed the curve fitting using the Ogata-Banks equation.
 216 Under two-phase flow, this equation can only be used to estimate the dis-
 217 persion coefficient of the flowing network, as the flowing network in a fixed
 218 saturation topology obeys the Fickian transport [17, 11, 26]. Note that due
 219 to the injection of the solute from the whole cross section and no-flow side
 220 boundaries, the lateral dispersion was negligible.

$$\begin{aligned}
\langle C_f(t) \rangle &= \frac{1}{L} \int C_f(x, t) dx \\
&= 0.5 \frac{1}{L} \left[\left(\left(\frac{2\sqrt{Dt}}{\sqrt{\pi}} (e^{-\Lambda_2^2} - e^{-\Lambda_1^2}) \right) + (t\bar{u}) \operatorname{erfc}[-\Lambda_2] \right. \right. \\
&\quad \left. \left. + (L - t\bar{u}) \operatorname{erfc}[\Lambda_1] \right) + \left(\frac{D}{\bar{u}} \left(\operatorname{erf}[\Lambda_2] + \operatorname{erf}[\Lambda_1] - \operatorname{erfc}[\Lambda_2] \right) \right. \right. \\
&\quad \left. \left. + e^{\frac{L\bar{u}}{D}} \operatorname{erfc}[\Lambda_3] \right) \right], x \\
&\in \Omega_{S_f} \\
\Lambda_1 &= \frac{L - t\bar{u}}{2\sqrt{Dt}}; \\
\Lambda_2 &= \frac{t\bar{u}}{2\sqrt{Dt}}; \\
\Lambda_3 &= \frac{L + t\bar{u}}{2\sqrt{Dt}}
\end{aligned}
\tag{7b}$$

This analytical equation captures the Fickian spatio-temporal evolution of the resident concentration and in order to avoid the uncertainty of the fitting results in early times, we used the analytical solution integrated over the domain (L). Since the resulted equation can only capture the Fickian transport, it is only applicable to the transport in flowing regions. Thus, the average resident concentration in the flowing regions, $\langle C_f(t) \rangle$, was calculated from the simulation results using the cell area-weighted averaging. $\langle C_f(t) \rangle = \Sigma(C_i(t)A_i)/\Sigma A_i$, $A_i \in \Omega_f$. C_i is the concentration in cell i with the surface area of A_i . Ω_f represents the domain of flowing regions. By fitting the $\langle C_f(t) \rangle$ using Equation (7), effective pore velocity, $\bar{u}$, and dispersion coefficient, D , were obtained.

In all cases, the curve fitting results were excellent with RMSE ranging from 10^{-7} - 10^{-5} . Two examples of the curve fitting at two different saturations at the Peclet number of 700 are shown in Figure S3 of the Supporting Information.

1.5.2. Relative permeability of the carrier fluid

Since the stagnant regions do not contribute to flow, the relative permeability curves capture the net contribution of the flowing regions. Hence,

relative permeability curves potentially carry important information about the stagnant saturations.

The relative permeability, k_r , is defined as the ratio of the effective permeability at a given saturation $k_{eff}(S)$ to that of a fully-saturated network, as shown in Equation (8). The effective permeability was calculated using Darcy's law, as follows

$$k_r(S) = \frac{k_{eff}(S)}{k_{eff}^*} = \frac{Q(S)A^*(P_{in} - P_{out})}{Q^*A(S)(P_{in}^* - P_{out}^*)}, \quad (8)$$

where $*$ denotes the values calculated/used under the fully-saturated conditions and A refers to the cross-sectional area at the inlet filled with the invading fluid. Inlet and outlet pressures are denoted by P_{in} and P_{out} , respectively. Total flow rate is illustrated by Q . Note that since the relative permeability was calculated under steady-state conditions, no dynamic effect was included.

1.5.3. Tortuosity

Tortuosity is a measure of the sinuosity of flowing network pathways. To calculate the tortuosity at steady-state saturations, the steady-state velocity field within the carrier (invading) fluid was used to construct the streamlines (following the streamline equation $\frac{dx}{u_x} = \frac{dy}{u_y}$ in a 2D velocity field $u = (u_x, u_y)$). The total number of streamlines ($N = 5000$) was fixed for the fully saturated case. Based on the value of N for the fully saturated case, the density of streamlines was calculated. Then using the same density, number of streamlines was scaled for each saturation case. The tortuosity at each saturation was calculated as the average length of all streamlines divided by the domain length. Sensitivity analysis was performed by increasing the density of streamlines in the inlet, which did not show any impact on the results.

2. Results and discussion

Figure 1 visualises simulation results at 4 different saturations. This figure matrix shows the Péclet number fields, stagnant and flowing regions, stagnant and total saturation, streamlines and tortuosity, and transient concentration fields at 4 different saturation topologies. Rows 1 and 2 show the amount of total and stagnant saturation, respectively. The method to estimate the stagnant saturation will be explained later in detail. Row 3 shows the spatial distribution of the pore-scale Péclet number. It is clearly visible that the

Figure 1: Simulation results for 4 different saturation topologies. Row 1: values of the total water saturation (S_w). Row 2: stagnant water saturation (S_{sw}). Row 3: topology of the two fluid phases (black: receding fluid) and the local Péclet number distribution in water phase shown by the logarithmic-scale colour coding. Row 4: concentration fields at the total resident concentration of 0.5 and the macro-scale Péclet number of 700. Row 5: the concentration profile at the moment of the full development of the concentration field in the flowing network at the Péclet number of 700. Stagnant and flowing regions are shown in red and blue, respectively. Row 6: streamlines within the water phase. **The values under the visualisation of streamlines show the corresponding average tortuosity values.**

pore-scale Péclet number (and the velocity field) spatially varies by orders of magnitude in steady-state two-phase flow. Row 4 shows the snapshots of concentration field when the total resident concentration is 0.5. The figures qualitatively show that under two-phase flow conditions the spatial distribution of concentration is more heterogeneous compared to the single-phase flow condition. The stagnant and flowing regions are shown in the 5th row. The dead-end pores, which do not contribute to the flow and have null concentration, are diffusion-controlled and are shown in red and the flowing regions are shown in blue. Finally, the row 6 shows the streamlines at different saturations and the average tortuosity has been shown for each saturation.

2.1. Stagnant saturation as a hydrodynamic entity

In previous macroscopic experimental studies [32, 35, 19, 5], the stagnant saturation was estimated by fitting the resident or breakthrough concentration time series to the MIM model. Note that in the MIM model if the flow rate is very small, the concentration profile does not show significant non-Fickian behaviour. Thus, the MIM fitting results will indicate a very small or zero stagnant saturation. However, by increasing the flow rate at the same steady-state saturation topology, the difference between the transport time scales in the flowing and stagnant regions will increase. This can be interpreted as a flaw, since as long as the saturation topology does not change, the stagnant saturation should not change. This has been verified in a recent experiment[27]. That is potentially the cause of the significant data scattering in the relation between the stagnant saturation and the total saturation (see Fig.5 in the reference [26]). Additionally, it has been proven experimentally that for a given saturation, different saturation topologies are possible [18], which can lead to different stagnant saturation values.

To estimate the stagnant saturation at a given saturation topology, we have simulated the velocity field under the steady-state two-phase flow. The probability distributions of the pore-scale Péclet numbers (for the macro scale Péclet number of 700) at 6 different saturation topologies are shown in Figure 2a and the corresponding cumulative probability distributions have been shown in Figure 2b. These distributions are fundamentally different as they show a single-mode distribution under single-phase flow (Figure 2a-b) and bimodal distributions in the steady-state two-phase flow (two peaks in Figure 2a). The second mode with very small Péclet numbers represents the hydrodynamically stagnant regions (the lhs peak on Figure 2a). Taking the saturation of 0.34 as an example, there are two large peaks, which

Figure 2: a) Probability distribution of the pore-scale Péclet number in the numerical cells. There is a clear shift from single-mode distribution in a fully-saturated porous media to a bimodal distribution under two-phase flow conditions. The probability distribution illustrates the stagnant (the lhs peak) and flowing regions (the rhs peak). The Péclet number ranging from 0.01 to 0.1 shows a transition zone. We have selected the $Pe = 0.1$ as the threshold value that differentiates the flowing and stagnant regions. b) Cumulative probability distribution of results shown in figure (a).

Figure 3: a) Stagnant saturation against the total saturation, which is identical for three different injecting rates representing macro-scale $Pe = 7, 70, 700$ for the same saturation topologies, b) Water relative permeability (which is the advancing fluid) versus the total saturation. The relative permeability and stagnant saturation at two different saturations of 0.53 and 0.54 are shown in red and orange circles, respectively. c and e) Fluids topologies for the saturations of 0.53 and 0.54, respectively, d and f) streamlines of saturations 0.53 and 0.54, respectively.

clearly show dual transport time scales. The bimodal velocity field indicates that some parts of the pore space filled with water (belonging to the flowing domain Ω_{fw}) are highly advective and some other parts belonging to the stagnant regions (Ω_{sw}) are diffusion-controlled, which leads to an upscaled non-Fickian transport process. Single-phase transport experimental and computational data show that the Péclet number of 0.01 to 0.1 is the threshold above which the advective transport starts to be pronounced [3]. Thus, we chose 0.1 as the threshold to differentiate the flowing and stagnant regions.

Note that under the steady-state two-phase flow, the difference between transport time scales in these two regions increases with the increase of flow rate; as the stagnant regions are always diffusion controlled and the transport time scale in the flowing regions becomes smaller with the increase of flow rate.

The relation between the stagnant saturation and total saturation for three different injection rates is shown in Figure 3a. These results are in qualitative agreement with former studies, which showed the stagnant saturation increased with the decrease of the carrier fluid’s saturation [21, 15, 13, 19]. However, unlike the experimental data by [26, 27] which showed a non-monotonic trend, no non-monotonic trend is observed in the numerical simulations. This can be due to the fact that in the micromodel experiments [26, 27], the smallest percolating water saturation was 0.2. However, in our simulations, the smallest percolating saturation is about 0.34. This significant difference between the smallest possible percolating saturations may have potentially led to the difference in trends.

Since the stagnant saturation does not contribute to flow, its signature should be visible in two-phase flow relative permeability curves. To examine the correlation between the stagnant saturation and relative permeability, the steady-state water relative permeability-saturation curve has been shown in Figure 3b. Also, an additional case with the saturation of 0.54 was simulated. Although saturations 0.53 and 0.54 are very similar, their saturation topologies are different. Hence, the relative permeabilities of saturations 0.53 and 0.54 are significantly different, as shown in red and orange circles in Figure 3b, respectively. Also, their stagnant saturations and the streamlines are significantly different (Figure 3c-f). The water relative permeability of the saturation 0.54 is smaller than the water saturation of the case 0.53. Accordingly the stagnant saturation is larger for the case of saturation 0.54 (0.102 versus 0.078, Figure 3a). The topology and streamlines of both cases are shown in Figures 3c-f. As shown in those Figures, the saturation topology is

350 very important and this indicates the reason for non-unique relation between
351 the stagnant saturation and total saturation which has been shown in the
352 literature[26].

353 Our results suggest that the two-phase transport modelling can be in-
354 tegrated with the two-phase flow modelling by establishment of a relation
355 between the stagnant saturation and the water relative permeability. This is
356 an important concept in the modelling as currently the two-phase flow sim-
357 ulations and the solute transport simulations do not communicate with each
358 other through a physically-consistent concept; models such as MIM do not
359 capture any parts of two-phase flow in their formulations. Further research is
360 required to develop full understanding of the correlation between the relative
361 permeability and stagnant saturation and direct estimation of the stagnant
362 saturation from the two-phase flow data.

Figure 4: a) Dispersion coefficient (D) of the flowing network plotted against saturation for the macro scale Péclet numbers of 700, 70 and 7. b) Dispersion coefficient (D) for flowing network plotted against the pore velocity ($\bar{u}$) at different saturations. The yellow circles in figures a and b indicate the case of saturation of 0.54.

364 By decomposing the water saturation to the flowing and stagnant regions,
 365 the transport in the flowing regions follows the Fickian transport. Thus,
 366 the dispersion coefficient and pore velocity can be obtained by the conven-
 367 tional curve fitting to the advection-dispersion equation, as discussed in the
 368 Supplementary Information. Figure 4a shows that under fixed flow bound-
 369 ary conditions, two-phase dispersion coefficient can be orders of magnitude
 370 larger than the dispersion coefficient in a fully-saturated system. Although
 371 all former studies indicate that the dispersion coefficient under two-phase
 372 flow conditions is larger than that under single-phase flow conditions, there
 373 is no clear agreement in the literature on factors controlling the dispersion
 374 coefficient. Some former studies reported that dispersion coefficient decreases
 375 as stagnant saturation increases [15, 22], while some other studies speculated
 376 that dispersion coefficient increases under two-phase conditions due to the
 377 presence of stagnant regions [14, 30, 20]. There are studies which suggest
 378 a non-monotonic relationship between the dispersion coefficient and satura-
 379 tion [41, 26, 27] and conjectured that the non-monotonicity in the stagnant
 380 saturation caused the non-monotonicity in the dispersion coefficient. This
 381 can also be seen in Figure 1, row 4, where the concentration fields at different
 382 saturations are shown under the transient condition. The longitudinal disper-
 383 sion varies significantly between saturation 1 and 0.34. Stagnant saturation
 384 is monotonically increasing with decrease of the carrier fluid’s saturation.
 385 However, there is a slight non-monotonicity in the dispersion coefficient-
 386 saturation relation (Figure 4a).

387 Increase of the dispersion coefficient of the flowing region under two-phase
 388 conditions compared to the single-phase case is due to increase of the tor-
 389 tuosity as well as the increase in the stagnant saturation. Tortuosity of the
 390 water-filled area will change significantly as a function of saturation topology
 391 as shown in Figure 5 and Figure 1, row 6. In contrast to the stagnant satura-
 392 tion, which is monotonically changing with saturation in our simulations,
 393 the tortuosity is a non-monotonic function of saturation and it may explain
 394 the slight non-monotonicity in the dispersion coefficient-saturation relation.
 395 With decrease of the flowing saturation, not only the tortuosity increased
 396 (Figure 5) but also the available flowing path (i.e. relative permeability)
 397 decreases, which leads to a large dispersion coefficient of the flowing region.
 398 This is in agreement with the work of Sahimi et al. [37]. The flowing path-
 399 ways are shown with snapshot of streamlines of water saturation in Figure
 400 1, row 6. The decrease of flowing pathways can clearly be seen in Figure 1,
 401 row 6 between water saturation 0.42 and 0.34. If only the number of flowing

Figure 5: Variation of the average tortuosity with total saturation. The solid circle shows the tortuosity for the case of saturation of 0.54, respectively.

pathways affects dispersion coefficient, we would expect an increase of the dispersion coefficient between water saturation of 0.42 and 0.32. However we observe a decrease in dispersion coefficient. This is because even though the number of pathways are decreasing, the tortuosity of water pathways are also decreasing, which results in a small decrease in dispersion coefficient in Figure 4a. Note that there is not necessarily a relation between the relative permeability and tortuosity. As shown in Figure 5, for the saturation range of 0.7 to 1, the tortuosity is almost constant while the relative permeability (Figure 3) drops significantly in the same range of saturation. That indicates that some of the main flow paths have been completely lost by the decrease of saturation from 1 to 0.7, while their loss does not impact the tortuosity of the remaining flow paths. The trend of tortuosity is our simulation results is fundamentally different from the tortuosity-saturation relation proposed by Burdine [8]. Burdine proposed a linear relation between tortuosity and saturation following the same trend as relative permeability, which does not seem to be correct.

The dispersion coefficient has always been reported to have a linear relation with the pore velocity, regardless of saturation in literature [26, 32, 12, 15, 22, 30, 20, 38, 28, 44, 39, 36, 7]. As shown in Figure 4b, we have got similar trends between the hydrodynamic dispersion and the effective pore velocity at each given saturation. However, the relation is saturation-dependent and

423 non-universal.

424 2.3. Mass exchange rate coefficient

425 As discussed earlier, during the transport process, the injected fluid mixes
426 with the resident fluid. This mixing in two-phase flow is a function of satura-
427 tion as the stagnant saturation varies significantly with the total saturation.
428 The mass exchange rate coefficient (γ) as defined in Equation (1) is an im-
429 portant parameter that controls the mixing between the stagnant and flowing
430 regions [17].

431 Using the detailed numerical results, we evaluated the functionality of
432 γ at different saturations. Knowing the temporal evolution of the resident
433 concentration in the flowing and stagnant regions and the amount of the
434 stagnant saturation, we calculated the mass exchange rate coefficient γ ver-
435 sus time using Equation 1. The results are shown in the inset Figure 6c
436 for four different saturations. Figures 6 a and b show the total residence
437 concentration (C) (blue dashed curve), average resident concentration in the
438 stagnant regions, C_{sw} (yellow dashed curve) and flowing regions, C_{fw} (red
439 dashed curve). The concentrations have been plotted against the dimension-
440 less time (defined as total fluid volume injected by a given time divided by
441 total volume of the carrier fluid in the domain, $\bar{t} = \frac{Q_w t}{V_p S_w}$) in a logarithmic
442 scale. The plots show that the concentration in the flowing regions reach
443 the inlet concentration in a short time (in the order of 2 pore volumes) and
444 follows a Fickian regime. However, the concentration in stagnant regions
445 (yellow dashed curves in Figures 6a and b) build up very slowly that leads
446 to a long tailing (non-Fickian behaviour) in the total concentration profile
447 (dashed blue curve in figure 6a-b). This slow development of concentration
448 in stagnant regions, which is controlled by diffusion, is due to the exchange
449 between the flowing and stagnant region interface. Exchange rate coefficients
450 (γ) calculated for four different saturations, are shown in 6c for the Péclet
451 number 700.

452 Our results clearly shows that γ versus time is not constant, opposed to
453 the assumption of MIM. γ exhibits two stages with time. Stage 1, before the
454 full development of the concentration field in the flowing network: γ increases
455 as the mixing line between the flowing and stagnant regions is increasing.
456 Stage 2, after the full development of the concentration field in the flowing
457 saturation, γ decreases gradually due to the depleting concentration gradient
458 across the interface between the flowing and stagnant regions. Consequently,

Figure 6: a, b) Temporal evolution of total (blue dashed curve), flowing (red dashed curve) and stagnant (yellow dashed curve) concentrations at the macro-scale Péclet number of 700 at saturations of 0.34 and 0.58, respectively. c) Resident concentration in the stagnant regions against the total concentration at four different saturations for the macro-scale Péclet number of 700. The inset plot shows the mass exchange rate coefficient against the dimensionless time at four different saturations and the macro-scale Péclet number of 700. The dimensionless time was defined as total fluid volume injected by a given time divided by total volume of the carrier fluid in the domain. The mass exchange rate has been calculated using Equation 1.

the ever-decreasing γ prolongs the mixing that indicates the overestimation of mass exchange rate in the MIM model.

The variable rate coefficient was also reported in the experimental results [26], although the experiments did not capture the long-term behaviour of the mass exchange due to the short duration of the experiments. Our results support the experimental study and clearly shows that exchange rate varies with time and saturation.

Our results imply that the existing mass exchange models do not capture the long term behaviour of mixing in two-phase flow. This understanding has direct implications for modified salinity water flooding (MSWF) technique. While the injected water can replace the formation brine resident in the flowing regions at a short time scale, the stagnant regions will remain filled by the formation brine for a much longer time. The high salinity water in the stagnant regions will be gradually diluted with the injected modified salinity water, which is controlled by the mass exchange rate. As our results show, the mass exchange rate coefficient decreases with time, which can possibly deplete the MSWF performance at much longer time scales. Moreover, since the amount of stagnant saturation varies with total saturation, it is speculated that the performance of wettability alteration would significantly change at different saturations.

3. Conclusions

Understanding and modelling of hydrodynamic transport and mixing in two-phase flow through porous media are important for many natural, industrial and engineering applications, such as modified salinity water flooding for enhanced oil recovery. Our results and former studies in the literature show that under steady-state two-phase conditions (even in homogeneous porous media), the void space filled by the carrier fluid (e.g. water) will have two hydrodynamically different regions; stagnant regions and flowing regions. These two regions have two different transport time scales that can lead to a non-Fickian transport regime. The stagnant regions are diffusion controlled, while the flowing regions are advection-controlled. Thus, increase of the injection rate will make the transport in the flowing regions faster. Consequently, the non-Fickian behaviour becomes more pronounced with the increase of injection rate.

Moreover, the stagnant saturation varies with total saturation, which means the non-Fickian behaviour strongly depends on saturation.

495 The existing models for transport under two-phase flow conditions such
496 as the Mobile-Immobile (MIM) model do not incorporate any two-phase flow
497 property in their formulations and make some assumptions and their validity
498 has not been addressed in the literature. Our results show that stagnant
499 saturation is inversely proportional to the relative permeability. This implies
500 that a relation should be established to estimate the stagnant saturation from
501 the relative permeability, which allows coupling two-phase flow and transport
502 in a physically-consistent way. This is absolutely absent in the MIM or other
503 transport models.

504 Moreover, our results challenge the assumptions related to the stagnant
505 saturation and mass exchange rate coefficient incorporated in MIM. MIM for-
506 mulations allow having different stagnant saturations for a given saturation
507 topology at two different Peclet numbers, which contradicts the hydrody-
508 namic definition of the stagnant saturation. Experimental data[27] and our
509 numerical simulations indicate that as long as the saturation topology does
510 not change, the stagnant saturation should not change.

511 Additionally, MIM assumes a linear non-equilibrium mass exchange be-
512 tween the flowing and stagnant regions with a constant mass exchange rate
513 coefficient. Our results did not support the MIM's assumptions as the rate
514 coefficients were variable with time. Two stages were identified in rate co-
515 efficients. In the early times, the rate coefficient increased with time until
516 the concentration field in the flowing network was fully developed. Then, it
517 gradually decreased with time. The results showed that the mass exchange
518 rate coefficient in stage 1 was highly dependent on the stagnant saturation's
519 geometrical and topological distribution. But, after full development of the
520 concentration fields in the flowing regions, the trend mass transfer rate coef-
521 ficients at different saturations were not very different.

522 While our results provide fresh insights into the potential mixing and
523 transport processes which are applicable to the modified salinity water flood-
524 ing, we have not yet incorporated the wettability alteration or other induced
525 mechanisms in our model. Transport and mixing under dynamic two-phase
526 flow are integral aspects of modified salinity water flooding, which will be
527 investigated in future publications.

528 4. Acknowledgments

529 The authors would like to acknowledge the UK Engineering and Phys-
530 ical Sciences Research Council (EPSRC) for funding the PhD studentship

531 of Miss Rimsha Aziz. They like to acknowledge the assistance given by IT
532 Services and the use of the Computational Shared Facility at The University
533 of Manchester.

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537 **Author Contributions**

538 Rimsha Aziz performed the numerical simulations, and data analysis. Vahid
539 Joekar-Niasar defined and led the research project and objectives. Pedro
540 J.Martinez Ferrer supported troubleshooting of OpenFOAM simulations. The
541 manuscript was written through the contribution of Vahid Joekar-Niasar,
542 Rimsha Aziz and Pedro J.Martinez Ferrer. All authors have given approval
543 to the final version of the manuscript.

544 **6. Data availability statement**

545 The data will be made available upon publication on the IMPRES group
546 website (<http://personalpages.manchester.ac.uk/staff/vahid.niasar/default.htm>).

547 **Supplementary Information**

548 The supporting document presents the numerical domain, the conver-
549 gence analysis for determining the grid size and the curve fitting results.

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Pore-scale insights into transport and mixing in steady-state two-phase flow in porous media

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Simulation details

The numerical domain is shown in Figure S1. The mean grain size is $50\mu\text{m}$ and the porosity is 52%. The circle packing was generated such that no dead-end pore to be created. the top and bottom boundaries are no-flow boundaries and the inlet and outlet are situated in the left and right, respectively. The porosity analysis has been done to determine the REA size. The selected domain size is roughly 2 REA at each direction (4REAs in total). Only steady-state primary drainage simulations were performed to create the saturation topology.

We performed the grid convergence analysis in a sub-section of the original domain. The grid convergence was done based on the mass balance analysis in a two-phase flow. For different grid resolutions we simulated two-phase flow at the same injection rate on the same domain using the same numerical schemes. We quantified the change of saturation from the simulation results before the breakthrough, referred to as E_i . Also, since the boundary condition was fixed flow rate, we easily calculated the change of saturation before breakthrough based on the injection rate, referred to as E . The relative error (%) at each

Figure S1: 2D demonstration of the numerical domain, α and C are initially set to zero in internal domain.

Figure S2: Grid convergence analysis based on the mass balance in a two-phase flow before breakthrough.

simulation case was calculated as $\text{ABS}(E - E_i)/E \times 100$. Results are shown in Figure S2.

Based on the grid convergence analysis shown in Figure S2, the error minimized after 300,000 grid size. Therefore, we selected this mesh size to perform all our simulations. Maintaining the same grid resolution for the whole domain ($\delta x/L \approx 0.0003$), our final mesh contained 3.6 million cells. This resolution provided at least 15 cells in the narrowest pore throat which ensured the sharp changes in volume fraction were captured accurately.

Curve fitting to estimate the dispersion coefficient D and effective pore velocity v

We established steady-state two-phase saturations, ranging between 0.34 – 1 to be used for transport simulations. We then calculated the resident concentration in the flowing regions and produced the time series of concentration profiles at different Péclet numbers and saturations, which followed the Fickian transport.

To obtain the dispersion coefficient and the effective pore velocity, the resident concentration profiles in the flowing regions were fitted using Equation 7. The curve fitting results were excellent with RMSE ranging from 10^{-7} - 10^{-5} . Two examples of the curve fitting at two different saturation at Péclet number of 700 are shown in Figure S3.

Figure S3: Curve fitting of the resident concentration in the flowing region at saturations of 0.34 and 0.76 at Peclet number of 700.

Dead-End Pore (DEP) and Mobile-Immobile (MIM) models

The dead-end pore (DEP) [1] and the mobile-immobile model (MIM) [2] are the two notable Darcy-scale models to estimate transport parameters as well as stagnant saturation in two-phase flow. The differences between the two models are highlighted below.

The DEP model uses the following equations to simulate transport in two-phase flow.

$$S_{fw} \frac{\partial C}{\partial t} + S_{sw} \frac{\partial C_{sw}}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (S1)$$

$$S_{sw} \frac{\partial C}{\partial t} = \gamma_{dep}(C - C_{sw}) \quad (S2)$$

In Equation S1, S_{fw} is saturation of the flowing water, C is the total concentration in water, t is time, S_{sw} is saturation of the stagnant water, C_{sw} is the concentration in the stagnant water, D is the longitudinal dispersion coefficient, v is the effective pore velocity and x is the direction parallel to flow. To account for mixing, γ_{dep} (exchange rate coefficient) was introduced. S_{sw} , v , D and γ_{dep} were estimated using curve fitting to match the experimental data. Note that the exchange rate is introduced between the total concentration and the stagnant concentration.

In the MIM model, the authors improved equations of the DEP model by decoupling the water domain to the immobile (stagnant) and mobile (flowing) regions. They clearly distinguished the concentration in the flowing (C_{fw}) and stagnant regions (C_{sw}). The equations for MIM are given as follows:

$$S_{fw} \frac{\partial C_{fw}}{\partial t} + S_{sw} \frac{\partial C_{sw}}{\partial t} = S_{fw} D \frac{\partial^2 C_{fw}}{\partial x^2} - v S_{fw} \frac{\partial C_{fw}}{\partial x} \quad (S3)$$

$$S_{sw} \varphi \frac{\partial C_{sw}}{\partial t} = \gamma(C_{fw} - C_{sw}) \quad (S4)$$

In literature, either the resident or breakthrough concentration profiles were fitted using the MIM model to estimate S_{sw} , γ , v , and D and none of these parameters were directly estimated for laboratorial experiments.

-There are two main drawbacks in the DEP and MIM models, which are explained here. If the flow rate is at the same scale of diffusion in experimental data (i.e. P_e is small), the curve fitting will result a small dispersion coefficient and smaller stagnant saturation. This implies that for the same saturation topology, P_e is controlling the stagnant saturation and not the saturation topology. We interpret this as a main flaw in the MIM model, as the stagnant saturation should not change as long as the saturation topology does not change. Also, the MIM model does not have any link with the two-phase flow properties and it does not explain how the transport properties are changing as a consequence of two-phase flow properties. Our results clearly highlight the first drawback that the stagnant saturation is a function of saturation topology and as long as the saturation does not change the stagnant saturation should not change with P_e number. Regarding the second drawback, we have shown that there is a correlation between the relative permeability curves and the stagnant saturation.

References

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