Pore-scale Transport in Rocks of Different Complexity Modeled by Random Walk Methods

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1 Pore-scale transport in rocks of different complexity 2 modelled by random walk methods

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7 **Abstract** We investigate pore-scale transport of a passive solute in three types
8 of reservoir rocks of distinctly different heterogeneity characteristics, using both
9 Random Walk Particle Tracking (RWPT), a Lagrangian method free of numerical
10 dispersion, and Time Domain Random Walk (TDRW), a regular-lattice-based ap-
11 proximation of the advection-diffusion equation. The transport behavior is probed
12 in terms of solute breakthrough curves for a large range of values of the Péclet
13 number, and for both flux weighted and uniform injection conditions. We compare
14 the two numerical modeling approaches, and thereby highlight the impact of the
15 distribution of pore-scale flow velocities on the large scale transport behavior. We
16 discuss the properties of two numerical approaches, and analyze the influence of
17 the numerical resolution of the velocity field on the simulated transport behaviors.
18 A main difference consists in the presence of numerical dispersion in the TDRW
19 method in contrast to the RWPT method. We find that this feature does not af-
20 fect the simulated large scale transport compared to the RWPT method, because
21 numerical dispersion is negligible compared to the impact of the broad spectra of
22 velocity fluctuations, which leads to heavy-tailed breakthrough curves and broad
23 peak behaviors determined by hydrodynamic dispersion. The two random walk
24 methods can be equivalently used to simulate hydrodynamic transport at pore
25 scale. The direct simulations provide breakthrough curves that cover up to ten
26 orders of magnitude in time. The tailing behavior is directly related to the distri-
27 bution of pore-scale flow velocities using a continuous time random walk approach.
28 The comparison of breakthrough curves and velocity distributions for three dif-

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ferent rock types, indicates that the solute breakthrough behavior can be used to infer the pore-scale velocity distribution and the medium structure.

Keywords Advection-diffusion equation · Porous media · Dispersion · Numerical methods

1 Introduction

Hydrodynamic dispersion results from the interplay between pore-scale diffusion and advection in the spatially variable pore-scale fluid flow (Whitaker, 1967; Bear, 1972; Sahimi et al, 1983; De Anna et al, 2013; Meyer and Bijeljic, 2016). Laboratory experiments (Moroni and Cushman, 2001; Seymour et al, 2004; Morales et al, 2017; Holzner et al, 2015), and numerical simulations (Bijeljic and Blunt, 2006; Bijeljic et al, 2011; Kang et al, 2014; Puyguiraud et al, 2019c) of pore-scale solute and particle transport have shown that observed solute breakthrough, spatial concentration and particle distributions, and spatial moments show non-Fickian behaviors. Breakthrough curves may show power-law tails at long times, the second centered spatial moments may scale non-linearly with time, and spatial distribution have distinct non-Gaussian tails characterized by forward or backward tails.

Recent works converge toward the idea that pore-scale transport in porous media can be upscaled by a Continuous Time Random Walk (CTRW) approach (Bijeljic and Blunt, 2006, 2007; De Anna et al, 2013; Kang et al, 2014; Puyguiraud et al, 2019a, 2021). The general picture of the posited stochastic process is the following: the speed of a solute particle changes at a given distance that is of the order of the throat length, thus defining the transition time in the CTRW formalism. Diffusion tends to increase particle path tortuosity, smooths particle speed contrasts and sets a maximum time for their transitions (Puyguiraud et al, 2021).

The verisimilitude of the upscaled (CTRW) model and the pertinence of the underlying assumptions that define how the model is parameterized cannot be evaluated only from the robustness of the mathematical reasoning, but requires being tested against direct simulations of solute transport in real porous media. These direct simulations must be free of numerical dispersion from diffusion-dominant to advection-dominant systems and accurate for several orders of magnitude of concentration in order to tackle the power tails of the breakthrough curve that contains information on the velocity field heterogeneity and diffusive mass transfer.

Random walk (RW) approaches associated or not to particle tracking methods have been used to solve the hydrodynamic transport of solutes in porous media for hydrology and engineering applications in general (Salamon et al, 2006; de Dreuzy et al, 2007; Kinzelbach, 1988), and specifically for modeling pore-scale transport (Mostaghimi et al, 2012a) where the solid and the void fractions are usually mapped from X-ray microtomography images or produced from (statistical) models (Blunt et al, 2013). Such pore-scale transport simulations have been used to investigate mixing and dispersion as well as reaction processes and test upscaling approaches (Bijeljic et al, 2004, 2011, 2013; Gouze et al, 2008b; Kang et al, 2014; Meyer and Bijeljic, 2016; Kang et al, 2019; Puyguiraud et al, 2019c, 2020, 2021).

RW methods are based on the displacement of many random walkers, sometimes called probes but more usually named particles, that follow motion rules defined such that the ensemble of particles displacement reproduces advective and/or diffusive transport. In this work, we focus on RW methods that apply to spatially discretized media at pore scale. An extended discussion of the conceptual features of the different RW methods and of their implementation into numerical simulators as well as examples of applications at different scales can be found in Salamon et al (2006) and Noettinger et al (2016). Some of the issues mentioned in the op. cit. review papers will be further discussed. However, as a simple introduction to RW methods, it is important to recall the five main reasons that make RW methods appealing, for instance compared to standard meshed methods such as finite volume (FV), finite-difference (FD), finite element (FE) or higher orders methods. First, RW methods are quite easy to implement (albeit implementing the boundary conditions can be cumbersome in certain cases) and are specifically adapted to massively parallel computing using symmetric multiprocessing approaches because RW methods are based on the displacement of independent particles, at least for the modeling of passive solute transport. When interactions between particles are involved, such as for the modeling of chemical reactions, then the performance of the parallelization decreases. Second, RW methods are specifically adapted to capture the elementary transport mechanisms by computing spatial and temporal statistics of the particle displacement. As such, it is a unique means for probing the different components of pore-scale mass transfer and analyzing how they depend on the structural and compositional heterogeneities (see for example Gouze et al (2020)). Third, RW methods allow for an easy implementation of particle motion rules that take into account mass transfers that occur at scales smaller than that of the considered RW method discretization, such as trapping (Dentz et al, 2012). This allows simple upscaling of transfers processes and tackling a large spectrum of pre-asymptotic behaviors at any scales (Dentz et al, 2018). Fourth, RW methods perform well even for large values of the Péclet number, i.e., advection dominant transport, while FV, FD and FE approaches are usually affected by numerical dispersion that can produce inaccurate solution. This limitation can be overcome by increasing the grid resolution and/or decreasing the time steps, but at the expense of higher, often unrealistic, computational cost. Furthermore, RW methods are globally mass conservative (such as FV) whereas FE and FD schemes are often not. Fifth, RW methods are adapted for solving problems displaying strong heterogeneities using noticeably coarser grid than standard approaches (Noettinger et al, 2016).

The first goal of this article is to compare two RW methods: the time domain random walk (TDRW) and the random walk particle tracking (RWPT). While these two methods tackle the same transport problems, they are conceptually very different. The RWPT is a true Lagrangian method based on some kinds of velocity interpolation for the advective part and a random walk for the diffusive motion (Perez et al, 2019; Puyguiraud et al, 2019b), while the TDRW is based on a finite volume approximation of the Fickian diffusion-advection equation in each of the mesh cell (Russian et al, 2016; Dentz et al, 2012). Thus, the spatial discretization is a key issue for TDRW because the fundamental assumption is that the mass exchange at the scale of a single grid element is Fickian or characterized by a fixed residence time distribution (Russian et al, 2016). Another notable difference is the fact that the TDRW is based on spatial steps while most RWPT use temporal

steps for the simulations. The second goal is to systematically study the control of medium structure and flow field characteristics on dispersion by comparing velocity distributions and breakthrough curves for three distinct rock types. To this end, we employ the recent theory proposed by Puyguiraud et al (2021) that derives a link between the velocity distribution, imposed by the medium heterogeneity, and the dispersion behavior characterized for instance by the slope of the power law behavior of the breakthrough curves.

This paper is organized as follows. The formulation of the RWPT and of the TDRW methods implemented for this study are presented in Section 2. In Section 3, we detail the different setups that are used for the simulations including the boundary conditions as well as the parameters for the two different numerical approaches. In Section 4, we analyze the results of a large set of RWPT and TDRW simulations for three rock samples of varying heterogeneity. Then, the CTRW up-scaled model is discussed in relation with the flow field properties and compared to the RWPT and TDRW direct simulations in Section 5. Finally, Section 6 presents the conclusions of the study.

2 Random walk methods for pore-scale transport

2.1 RWPT formulation

For pore-scale modeling where the connected porosity is represented by *void* voxels embedded in *solid* voxels, hydrodynamic transport is classically modeled by the advection-diffusion equation

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} - \nabla \cdot [D_0 \nabla + \mathbf{v}(\mathbf{x})] c(\mathbf{x}, t) = 0, \quad (1)$$

where $c(\mathbf{x}, t)$ is the solute concentration at position $\mathbf{x}$ and time t , D_0 is the molecular diffusion coefficient and $\mathbf{v}(\mathbf{x})$ is the flow velocity at position $\mathbf{x}$ which is obtained by solving the Stokes problem. The random walk particle tracking simulations are based on the equivalence between the advection-diffusion equation (1) and the Langevin equation,

$$\frac{d\mathbf{x}(t)}{dt} = \mathbf{v}[\mathbf{x}(t)] + \sqrt{2D_0}\boldsymbol{\xi}(t), \quad (2)$$

where $\boldsymbol{\xi}(t)$ is a vectorial Gaussian white noise characterized by zero mean $\langle \boldsymbol{\xi}(t) \rangle = 0$ and covariance $\langle \xi_j(t) \xi_k(t') \rangle = \delta_{jk} \delta(t - t')$, where δ_{jk} is the Kronecker delta. We can then discretize the Langevin equations using an Euler scheme as the current position $\mathbf{x}(t)$ plus an advective and a diffusive component as

$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \mathbf{v}[\mathbf{x}(t)]\Delta t + \sqrt{2D_0\Delta t}\boldsymbol{\zeta}(t). \quad (3)$$

The advective term (second term on the right hand of the equation) is based on an extension of the Pollock's algorithm (Pollock, 1988; Mostaghimi et al, 2012b; Puyguiraud et al, 2019b, 2020). The original Pollock's algorithm assumes a linear variation of velocity within a cubic mesh cell in each direction. It is used for modeling flow path at Darcy's scale and for very high porosity structures. However, this linear interpolation causes precision errors in the vicinity of solid surfaces since

a linear interpolation is no longer accurate for reproducing the Poiseuille velocity profile. This is why Mostaghimi et al (2012b) extended the methodology by introducing quadratic interpolations in voxels in contact with solid. This therefore renders this methodology accurate even for low porosity media. With the RWPT method, the position $\mathbf{x}(t)$ of a particle is known analytically for any t . This permits splitting the trajectory in small time intervals Δt . Thus, the advective and diffusive operators can be split on this Δt basis, allowing for the computation of the diffusive jumps between advective steps. Note that there exists other possible interpolation schemes for the velocity. The diffusive jumps are computed following the third term on the right side of equation (3) where $\boldsymbol{\zeta} = (\zeta_1, \zeta_2, \zeta_3)$ with ζ_i being uniform random variables in $[-\sqrt{3}, \sqrt{3}]$ with $\langle \boldsymbol{\zeta}(t) \rangle = \mathbf{0}$. The central limit theorem guarantees that the sum of the random motions is Gaussian. Using uniformly generated random variables rather than Gaussian presents two main advantages. The computational cost is reduced and there is a better control on the maximum displacement jump that a particle can do. This avoids unexpectedly large displacement that could cross solid cells and thus, allows using not-too-small Δt .

The algorithm reads as follow. Each jump of the particle comprises an advective and a diffusive step. First, for the advective motion, the type of voxel the particle is in is detected. The type of voxel is determined by the neighboring voxels being void or solid. For the general method as described by Mostaghimi et al (2012b), there is 48 possibilities corresponding to a void voxel bounded by 1 to 4 solid faces (flow is null by definition in case of 5 solid faces). Once the voxel type is identified, then the appropriate velocity interpolation is used. However, as we ensure that the smallest throats are characterized by three voxels at least (see Section 3.2), there cannot be any void voxels with opposite solid-solid faces thus a void voxel can be bounded by 1 to 3 solid faces only. Accordingly, the number of different interpolations to be considered drops to 27. After integration of the velocity equation, we obtain an analytical equation for the trajectory of a particle within the voxel. The elapsed time is then updated by adding the time step Δt to the running time. Then, the diffusive step is computed according to (3). As particles are independent from each other, the algorithm is efficiently parallelizable and the computational time decreases almost linearly with the number of processors. Simulations can be handle on standard multi-processor computers. Let us assume a cubic sample of size l^3 voxels. The memory load for running RWPT simulations is primarily due to the vector (of type *char*) of size l^3 that describes the type of voxel (void or solid) and the three vectors (of type *float32*) of size $l^2(l+1)$ that describe the velocity vector components at the voxel edges. For a domain of size 900^3 the memory requirement is about 12 to 14 GB depending on the number of particles involved.

2.2 TDRW formulation

The time domain random walk (TDRW) method for pore-scale simulation of solute transport is based on a finite volume discretization of the advection-diffusion equation (1) which is considered to apply at the scale of each voxel (Delay et al, 2005). A detailed description of the TDRW method foundations and its implementation using voxelized images of porous media can be found in Dentz et al (2012) and Russian et al (2016). The main features of the method applied for modeling pore-scale transport in binary (void-solid) systems are given below. The

domain discretization used for transport is the same as the one used for computing the flow. The TDRW approach models the displacement of particles in space and time, their ensemble average giving the solution of the transport equation for the considered media. For each particle, each motion event is denoted by a single transition from one voxel to one of the 6 face-neighboring voxels. As such, the transition distance ξ is constant and equal to the voxel side length. The direction and the transition duration are random variables ruled by the local properties of the voxels, i.e. the fluid velocity at the voxel interface and the diffusion coefficient D_0 if the neighboring voxel belongs to the void phase, or 0 if it is solid. The recursive relations that describe the random walk from position $\mathbf{x}_j$ to position $\mathbf{x}_i$ of a given particle for transition n is

$$\mathbf{x}_i(n+1) = \mathbf{x}_j(n) + \boldsymbol{\xi}, \quad t(n+1) = t(n) + \tau_j, \quad (4)$$

where $|\boldsymbol{\xi}| = \xi$ denotes the transition length. Assuming that the local transport follows (1), the transition time τ_j is exponentially distributed:

$$\psi_{\tau_j}(t) = \bar{\tau}_j \exp(-t/\bar{\tau}_j), \quad (5)$$

where the mean transition time $\bar{\tau}_j$ for each voxel j is given by

$$\bar{\tau}_j = \frac{1}{\sum_{[jk]} b_{kj}}. \quad (6)$$

The notation $\sum_{[jk]}$ indicates the summation over the nearest neighbors of voxel j . The probability p_{ij} for a transition of length ξ from voxel j to voxel i is

$$p_{ij} = \frac{b_{ij}}{\sum_{[jk]} b_{kj}}, \quad (7)$$

where the b_{ij} are given by Russian et al (2016):

$$b_{ij} = \frac{D_{eij}}{\xi^2} + \frac{|\mathbf{v}_{ij}|}{2\xi} \left(\frac{\mathbf{v}_{ij}}{|\mathbf{v}_{ij}|} + 1 \right). \quad (8)$$

In (8), $D_{eij} = D_0$ if voxel i is a void voxel and 0 otherwise and $\mathbf{v}_{ij}$ denotes the velocity component of $\mathbf{v}_j$ in the direction of voxel i , $\mathbf{v}_{ij} = \mathbf{v}_j \cdot \boldsymbol{\xi}_{ij}$. Voxel i is downstream from voxel j if $\mathbf{v}_{ij} > 0$, as a convention. The velocity at the solid-void interface is zero.

The algorithm is quite simple and consists in computing once the probability p_{ij} (7) and the mean transition time $\bar{\tau}_j$ (6) for each of the voxels belonging to the pore space and then solving the random walk in which the direction for each particle jump is drawn from the p_{ij} vector and the transition time is drawn from the exponential distribution (5) of mean $\bar{\tau}_j$. For a cubic sample of size l^3 voxels, the memory maximum load for running TDRW simulations is equivalent to that of the RWPT, plus the memory required for storing the vector (of type *float32*) of probability p_{ij} (7) of size $6l^3$ as well as the vector (of type *float32*) of the transition time $\bar{\tau}_j$ (6) of size l^3 . At this stage, before freeing the memory from the velocity and the descriptor vectors, the memory demand is about 32 Go for a 900^3 image. Both the construction of the probability and transition time vectors and the RW motion computations can be easily parallelized using shared-memory multiprocessing programming to efficiently reduce computation time. Furthermore, the simulations are performed using the dimensionless form of the problem where $\xi = 1$, in order to increase computation efficiency.

2.3 Key differences between the two methods

From the description (above) of the two methods it can be recognized that the TDRW method gives a priori an approximation of the transport problem whereas the RWPT method provides the exact solution corresponding to a given flow field. Indeed, on a conceptual point of view the RWPT method is solving the hydrodynamic transport problem without any other approximation than that resulting from the accuracy and spatial resolution of the velocity field, providing Δt is small enough.

Thus, the first important difference between TDRW and RWPT concerns the velocity values possibly sampled by the particles while moving in the system. For TDRW, particles sample the Eulerian velocity field exported from the flow calculation only. For RWPT, particles may experience a denser distribution of values because of the velocity interpolation, including the quadratic interpolation in the voxels adjacent to the solid phase that reproduces better the no-slip boundary condition. In other words, the particles can only access a discrete distribution of speeds bounded by the maximum and minimum values prescribed by the Stokes computation for TDRW simulations, while the particles can access to a continuum of speed values bounded by the maximum one only, for RWPT simulations. As such, one can anticipate that the resolution of the image, that will determine in how many locations the velocity variability will be defined in the throats, will have a larger impact on the accuracy of the results in the TDRW than in the RWPT.

A second noticeable difference concerns the fact that by construction RWPT is exempt of numerical dispersion because the advective particle velocity is that of the flow lines, whereas TDRW is not free of numerical dispersion. Numerical dispersion arises because the particle motion is performed on a lattice. Russian et al (2015) showed that for a given transition the numerical dispersion is of the order of $v(\mathbf{x})\xi$, where ξ is the lattice spacing and $v(\mathbf{x})$ the local velocity. Thus, numerical dispersion affects only regions of high flow rate. In low flow regions where $v(\mathbf{x}) < D/\xi$, it can be disregarded. This means that numerical dispersion does not affect breakthrough curve tailing and anomalous dispersion behaviors that are caused by solute retention in low flow zones. The peak behavior of breakthrough curves, and the asymptotic dispersion of the solute distribution may be affected by numerical dispersion. In order to assess the importance of this effect, we compare numerical dispersion to the physical hydrodynamic dispersion that is caused by the fluctuations of the flow velocity. A conservative estimate for the hydrodynamic dispersion coefficient is $D^* = \bar{u}\ell_c$, where $\bar{u}$ is the sample-scale mean streamwise flow velocity and ℓ_c is the correlation length of the velocity fluctuations which is of the order of magnitude of ℓ_0 , the average pore size (Puyguiraud et al, 2021). The typical numerical dispersion coefficient is $D^{\text{num}} = \bar{u}\xi$. Thus, as long as $\xi \ll \ell_c$, which is the case for the three samples studied, the impact of numerical dispersion on the actual large scale normal and anomalous dispersion behaviors can be disregarded.

3 Simulation setup

In order to give a thorough comparison of the numerical methods, we ran simulations for three media of increasing heterogeneity: a sand-pack (SP), a Berea

298 sandstone (BS) and a reefal carbonate (RC). Figure 1 displays in columns 1 and 2
 299 the three-dimensional geometry of the void space for the 3 samples. The two rock
 300 samples (RC and BS) show similar porosity value, 0.18, but distinctly different
 301 pore geometry. The porosity of the sand-pack is 0.37, i.e. about twice the porosity
 302 of the rock samples and displays more homogeneous pore shape. The Berea sand-
 303 stone sample is the same used by Puyguiraud et al (2021). The reefal carbonate
 304 sample comes from the Majorca test site where tracer tests were performed some
 305 years ago; the description of the reservoir rock in its geological context as well as
 306 the evidenced site-scale non-Fickian dispersion behavior can be found in Gouze
 307 et al (2008a). The sand-pack image (Sand Pack LV60C) comes from the Imperial
 308 College image repository (Mostaghimi et al, 2012b).

Fig. 1 Illustration of the heterogeneity of the three $900 \times 900 \times 900$ voxels samples: the reefal carbonate (top row), the Berea sandstone (middle row) and the sand-pack (bottom row). From left to right: porosity (light blue) projected on the sample boundaries, three-dimensional geometry of the void space (shaded blue) and the flow path from the left side (inlet) to the right side (outlet). The color scale from dark-blue to white to red denotes the normalized particle speed ($v/\langle v \rangle$) from $10^{-4}\langle v \rangle$ to v_{max} ; the corresponding distributions $v/\langle v \rangle$ are given in Figure 2.

3.1 Flow

Flow simulations are performed on the three-dimensional binary image of the rock samples obtained by identifying the connected void phase and the solid phase by processing a X-Ray microtomography image (see for example Gouze et al (2008b) and references therein). The binary images are composed of 300^3 regular voxels (cubes) that are either void or solid. The mesh used for solving flow is obtained by dividing each of the image voxels by 3 in each of the directions so that 1 voxel of the image is represented by 27 cubic cells of size $\Delta x = \Delta y = \Delta z = 1.05 \times 10^{-6}$ m for BS, 1.69×10^{-6} m for RC and 5.001×10^{-6} m for SP. This discretization level is operated for improving the resolution of the flow field in the smallest throats, see Gjetvåg et al (2015) for details on mesh refinement. Thus, the resulting discretization for the regular grid consists of 900^3 cubic cells. We first solve the flow using the SIMPLEFOAM solver (using the SemiImplicit Method for Pressure Linked Equations algorithm) implemented in the OpenFOAM platform (Weller et al, 1998). Twenty layers are added at the inlet and outlet in order to minimize boundary effects (Guibert et al, 2016). We prescribe pressure boundary conditions at the inlet and outlet, and no-slip conditions at the void-solid interfaces and at the remaining domain boundaries. A pressure gradient is set between the inlet ($z = 0$) and the outlet ($z = Lz$) boundary conditions such that the Reynolds number Re is smaller than 10^{-6} , i.e. laminar flow. After convergence, that is, once the (normalized) residual of the pressure and flow between two consecutive steps is below 10^{-5} , we extract the x-y-z components of the velocity at all the interfaces of the voxels forming the mesh. The resulting flow field is used for both RWPT and TDRW simulations.

Fig. 2 Left: Langrangian speed auto-correlation function. The lag distance is normalized by the mean throat length ($\lambda = 2\ell_0$). Right: distribution $p_e(v)$ of the speed v for RC, BS and SP samples, as well as for the cropped SP sample discussed in Section 4.1.

The computed permeability along the z -direction increases from $1.23 \times 10^{-13} \text{ m}^2$ for RC, to $6.67 \times 10^{-12} \text{ m}^2$ for BS and $2.93 \times 10^{-11} \text{ m}^2$ for SP. The main features of the velocity fields can be appraised from Figure 1, where the column at right displays the same number of randomly chosen flow lines for the 3 samples. The

heterogeneity of the flow field for these 3 types of rocks can be evaluated as well as the velocity fluctuations that are denoted by the color scale applied for each flow line. A more quantitative characterization of the flow field can be obtained from the Eulerian speed (i.e. the norm of the fluid velocity) distribution and the Lagrangian speed autocorrelation function (Puyguiraud et al, 2019b) (Figure 2). Both the Eulerian flow speed distribution $p_e(v)$ and the speed correlation distance are key parameters of the upscaled CTRW model discussed in Section 5.1. The RC and BS display similar porosity and exhibit comparable behaviors of the speed autocorrelation functions with a sharp drop that occurs over about the three first throat lengths. Conversely, the autocorrelation for the SP exhibits a smoother (quasi exponential) decrease. The SP sample displays low tortuosity and higher regularity of the network that triggers a fraction of the particles to conserve speed correlation over four to five throats. The speed distributions for the RC and BS show similar behaviors, which indicates similar pore-scale heterogeneity (De Anna et al, 2017; Dentz et al, 2018). For the sand pack, which is more homogeneous, the speed distribution is flatter at low values.

3.2 Transport

For each sample, we performed simulations for different values of the Péclet number. The Péclet number is defined as $Pe = \langle v \rangle \ell_0 / D_0$ where ℓ_0 is a characteristic length which is taken here as half the average pore throat width and $\langle v \rangle$ denotes the mean speed. The value of ℓ_0 ranges from 3.8×10^{-5} m for BS, 5.4×10^{-5} m for SP and 6.0×10^{-5} m for RC.

The flow fields used for the RW transport simulations at different Péclet numbers are obtained by multiplying the raw flow field resulting from the Stokes simulation by a constant. The corresponding Reynolds numbers range from $Re \approx 10^{-8}$ for $Pe = 10^{-3}$ to $Re \approx 0.1$ for $Pe = 10^4$, which is below the limit for which the Stokes assumption (negligible inertial forces compared to viscous forces) is valid.

A *pulse* of constant concentration at the sample inlet ($z = 0$) is applied at $t = 0$ for both the RWPT and the TDRW simulations. Note that the main flow direction is z . For the TDRW approach the *pulse* is formally an exponential distribution function of characteristic time $\tau_j|_{z=0}$ whose mean value is negligible compared to the mean time required for the particles to move through the sample (Russian et al, 2016). For the RWPT, this injection corresponds to a Dirac delta function at $z = 0$ such that $\delta(z) = 0$ if $z \neq 0$. No-flux boundary condition is set at $x = 0$, $x = L_x$, $y = 0$, $y = L_y$.

Two type of injection conditions at the inlet are investigated: flux-weighted and uniform injections. Flux weighted injection of the particles at $t = 0$ corresponds to that expected when considering the sample as a sub-volume of a more extended medium. This means that the number of particles injected at a location is proportional to the local velocity. This corresponds, for example, to a constant concentration Dirichlet boundary condition in a lab-scale flow experiment. For the uniform injection of particles at $t = 0$, the injection of the particles at $t = 0$ does not depend on the local velocity where the particles are set. Instead, the same number of particles is placed at every location of the inlet, which could be seen as localized an initial condition. In both cases, the speed distribution sampled over

the inlet plane is close to the speed distribution sampled in the entire domain, as shown in Figure 3.

An important point is that the temporal discretization of the RWPT has been set in order to approximately give the same average number of transition per particle than that occurring in the TDRW, for which this number is fixed by the spatial discretization for a given value of Pe . The number of particles is also set similar for the two RW methods for a given Pe number. The typical number of particles ranges from 10^5 for the lowest value of Pe to 3×10^8 for the highest. So, the sampling of the flow field, and thus of the heterogeneity of the porosity, is globally similar for the two methods for each value of the Pe number.

Fig. 3 Left: Map of the speed $v(x, y, 0)$ at the inlet boundary condition for the Berea sandstone (BS) sample with decreasing speed from red to blue. Black color denote the solid phase. Right: Eulerian speed distribution (black solid line) and flux weighted speed (black dashed line) distributions for the entire domain and the corresponding distributions at the inlet for the uniform injection (blue circles for TDRW and red plus (+) symbols for RWPT) and for the flux weighted injection (blue squares for TDRW and red crosses (x) for RWPT).

Hydrodynamic dispersion is characterized by the distribution of first arrival times at the outlet $z = L_z$, whose distribution defines the solute breakthrough curve (BTC) usually measured in laboratory or field tracer tests. This distribution is expressed as the PDF f_t of the time $t(p)$ spent by the particles p to cross the domain.

Transport simulations can also be performed for measuring the advective tortuosity χ which is one of the key parameters of the upscaled model discussed in Section 5.2. The value of χ can be obtained from the ensemble average of the length of the particle trajectories for RWPT simulations performed at $Pe = \infty$ (i.e. assuming $D_0 = 0$). The advective tortuosity values are 2.03 ± 0.03 , 1.68 ± 0.03 and 1.34 ± 0.01 , for RC, BS and SP, respectively. This values are similar to those obtained from the ratio of the mean Eulerian speed v_e to the mean velocity in the direction of the flow v_z (Koponen et al, 1996; Ghanbarian et al, 2014; Puyguiraud et al, 2019c): $\chi_v = \langle v_e \rangle / \langle v_z \rangle$.

406 4 Hydrodynamic transport and RW methods comparison

407 In this section, we study hydrodynamic transport for three different rock types
 408 in terms of the behavior of the solute breakthrough curves, and compare the
 409 performance of the TDRW and RWPT methods from quasi pure diffusion scenarios
 410 ($Pe = 10^{-3}$) to quasi pure advection ($Pe = 10^4$), for both uniform and a flux
 411 weighted injection. Figure 4 displays the first passage time PDF f_t at the outlet
 412 for the three samples: the sand-pack (SP), the Berea sandstone (BS) and the reefal
 413 carbonate (RC). This represents a total of 96 simulations. It is worth noticing that
 414 both the methods (TDRW and RWPT) produce f_t curves that are smooth and
 415 noiseless over up to 10 orders of magnitude.

Fig. 4 First passage time at the outlet f_t for (from top to bottom) the reefal carbonate RC, the Berea sandstone BS and the sand-pack SP, for Péclet values ranging from 10^{-3} (*pure* diffusion, purple color) to 10^4 (*pure* advection, black color). Plain curves and triangles denote f_t for the TDRW and the RWPT simulations, respectively. Left and right columns display results for the flux weighted (FW) and the uniform (UNI) injections, respectively.

The two reservoir rock samples, RC and BS, which display distinctly different structures (characterized by, for instance, different tortuosities and different velocity correlation lengths), have been imaged with resolutions that allow an appropriate characterisation of the pore structure geometry; the ratio of the throat characteristic length to the voxel size ℓ_0/ξ is of 15 and 18 for the Berea sandstone and the reefal carbonate, respectively. But, it is of 3 for the sand-pack. Thus, the flow in the smallest throats will be mapped by 5 to 6 times less voxels than for the reservoir rock samples.

In general, one observes in Figure 4 that both the RW methods identify correctly the time at which the maximum of each of the f_t curves occurs, independently of the value of the Pe number, the characteristics of the sample and the type of injection. This confirms the expected negligible effect (see Section 2.3) of the numerical dispersion on the first passage time distribution. The results from both methods are visually similar for $Pe < 10$ independently of the heterogeneity level and injection mode. For flux-weighted injection, the breakthrough curves coincide at all Pe for RC and BS. Only for SP, we observe differences between RWPT and TDRW at high Pe . For the uniform injection, however, we observe differences between RWPT and TDRW in the tail behavior at $Pe > 100$. In the following, we analyze these differences in more detail.

4.1 Discrepancies in results at high values of the Péclet number

We now discuss the origin of the difference between the two RW methods considering first the reservoir rock samples, RC and BS, that display similar results. The f_t curves computed by the TDRW and the RWPT methods are identical for the flux weighted injection, over the full range of Pe values. Conversely, one observes noticeable differences for $Pe > 100$ at intermediate and late times, for the uniform injection. This highlights the fundamental difference between the two approaches concerning the velocity spectrum accessible for each of the RW methods. The RWPT approach allows for exploring a continuum of (Lagrangian) speeds because of the interpolation procedure, including the quadratic decrease of velocity in the vicinity of the void-solid interface, while the TDRW only uses the spatially discrete distribution of the Eulerian speeds resulting from the Stokes computations (evaluated at the center of the voxel faces). This point is illustrated by the speed distribution at the inlet plane shown in Figure 3. The RWPT can access much smaller speeds than the TDRW, for which the speed distribution is cut-off at a minimum value. For the flux weighted injection, the difference between the two speed distributions has no consequence on the particle motion because the probability of sampling the low velocity values decreases fast for normalized speed below 10^{-6} (positive log-slope of the red cross ($\times$) symbols curve for flux weighted injection in Figure 3). In other words, the blue square curve (TDRW) and the red cross symbols curve (RWPT) are essentially similar in terms of statistical sampling of the low velocities. Conversely, the effect of the extension of the velocity spectrum toward the lowest values (slightly negative log-slope of the red plus (+) symbols curve for uniform injection in Figure 3) induces a consequential different sampling of the velocity distribution at the boundary condition by the two RW methods. Thus, in the RWPT approach particles can sample the low end of the velocity spectrum (including low velocities close to the grain boundaries), while those ve-

locities are excluded in the TDRW approach because it considers the mean fluxes within a voxel. This effect can be reduced by increasing the spatial resolution, as discussed further below. The possibility to sample more low speeds leads to a more pronounced long-time tail in the RWPT approach compared to the TDRW approach as shown in Figure 4 for the RC and BS samples with uniform injection at $Pe = 10^4$. This also explains the little delay associated with the slightly broader peak around the maximum concentration observed at high Pe values.

The importance of the effective velocity distribution potentially experienced by a particle in the respective approaches is further highlighted by the results for the sand-pack sample (last row in Figure 4). Compared to the results obtained for the reservoir rocks, the TDRW and RWPT are much less dissimilar for the uniform injection at $Pe > 100$. However, one observes that for $Pe > 100$ the TDRW method under-evaluates dispersion for short to intermediary times for the flux weighted injection. In order to demonstrate that this feature is linked to the spatial resolution of the flow field, and the different sampling of the velocity field by the particles, we run similar simulations in a sub-volume of the sand-pack structure while keeping the same number of voxels, this means by increasing the resolution. To do so, a 300^3 sub-sample was cropped into the sand-pack sample, then each voxel was divided by 3 in all directions. Thus one obtains a domain whose volume is 27 times smaller, but is resolved with 27 times more voxels. The Stokes flow is computed on this new 900^3 domain. The flow field characteristics in relation to the pore geometry can be appraised from Figure 5; the velocity field of the cropped sand-pack image has similar properties as the reservoir rocks RC and BS in terms of ratio of the throat characteristic length to the voxel size. The resulting domain is discretized finer, but keeps the same hydrodynamic properties of the initial domain such as the permeability, advective tortuosity and speed autocorrelation (Figure 2). The corresponding first passage time PDFs f_t are shown in Figure 6 where it can be seen that now the TDRW method reproduces almost perfectly the RWPT results independently of the value of the Pe number and of the injection type. The higher spatial resolution makes the low end of the velocity spectrum accessible to particle in the TDRW approach, independently of the boundary condition type up to high values of Pe .

Fig. 5 Illustration of the cropped sand-pack with refined discretization. From left to right: porosity (light blue) projected on the sample boundaries, three-dimensional geometry of the void space (shaded blue) and the flow path from the left side (inlet) to the right side (outlet). The color scale from dark-blue to white to red denotes the normalized particle speed $(v/\langle v \rangle)$ from $10^{-4}\langle v \rangle$ to v_{max} ; the corresponding distribution is given in Figure 2.

Fig. 6 First passage time at the outlet f_t for the sand-pack (SP) cropped domain, for Péclet values ranging from 10 to 10^4 . Plain curves and symbols denote f_t for the TDRW and the RWPT simulations, respectively. Figure at left displays the results for flux weighted (FW) injection and figure at right displays results for uniform (UNI) injection.

4.2 Computational performance

Concerning computational performance, the two RW methods are equivalent. TDRW and RWPT require the same number of particles to reach the prescribed accuracy and produce noiseless first passage time curves for a given value of Pe . TDRW is faster than RWPT (factor of about two) because the number of computational operations to be solved at each particle jump is smaller. However, this difference in CPU time is not a crippling criteria for a research tool. Both RW methods are easily implementable for high performance parallel computing with an optimal scalability because particles are independent from each other. The return time using 28 processors of type Intel E5-xxxx is in the order of few hours for TDRW, for high resolution simulations presented here.

It follows that RWPT and TDRW can be indifferently used for running passive tracer dispersion simulations in the range of the Pe values usually encountered in natural active hydrogeologic systems, i.e. $10^{-3} \leq Pe \leq 100$. Yet, RWPT should be preferred 1) for higher Pe value simulations because it is less dependent on the resolution (discretization) of the flow field, and 2) if streamlines properties are required, such as for computing Lagrangian velocity or meaningful velocity correlation functions such as presented in Figure 7, or for investigating dispersion properties using spatial distribution considerations (e.g. spatial variance, see for example Puyguiraud et al (2021)). Conversely, TDRW is ideal for studied mixed pore-scale and Darcy's scale transport, for instance for modeling hydrodynamic dispersion in mobile-immobile-domain systems (see for example Gouze et al (2020)) because it is fast and accurate for problems dealing with intermediate to low Pe values and does not require interpolation which could become cumbersome to implement for mobile-immobile-domain systems using RWPT. The other advantage of TDRW is the easy implementation of sub-resolution trapping processes (see for example Russian et al (2017)).

5 Upscaling of hydrodynamic transport

The results of the previous section emphasize the key role of the full distribution of flow speeds to the understanding of (non-Fickian) hydrodynamic transport in porous media. We analyze the transport in the different rocks in the light of the theory of Puyguiraud et al (2021) that relates the tailing behavior of solute breakthrough curves to the distribution of flow speeds. In the following, we recall quickly the key elements of the model.

5.1 Upscaled Continuous Time Random Walk model

The upscaled model abstracts the porous medium as a network of conducts, which are characterized by the length ℓ and the average flow speed v_m . The constant length ℓ is of the order of the average throat length and represents the distance over which the flow speed is approximately constant (correlation length). Particle motion along trajectories is then modeled through a series of statistically independent transitions of length ℓ and duration τ . The transition time is determined by the mean speed v_m over a conduct and molecular diffusion. The conditional distribution $\psi_0(t|v)$ for a given mean speed can be approximated by an inverse Gaussian distribution truncated at time $\tau_D = \ell^2/D_0$ because the maximum transition times are of the order of τ_D . For high Péclet numbers $Pe = \ell\langle v_m \rangle/D_0$, with $\langle v_m \rangle$ the network-averaged mean speed, particle transitions are advection-dominated. Transition times can be approximated by $\tau = \ell/v_m$ for $\tau \ll \tau_D$ and thus, $\psi_0(t|v) = \delta(t - \ell/v)$. In this case, the unconditional transition time distribution $\psi(t)$ is

$$\psi(t) = \int_0^\infty dv p_v(v) \psi_0(t|v) = \frac{\ell}{t^2} p_v(\ell/t), \quad (9)$$

for $t \ll \tau_D$. The distribution $p_v(v)$ of particles speeds is obtained from the distribution $p_m(v)$ of mean pore speeds by flux-weighting

$$p_v(v) = \frac{v p_m(v)}{\langle v_m \rangle}. \quad (10)$$

This relation accounts for the fact that the partitioning of particles at intersections is proportional to the flow rates into the downstream conducts. Based on Poiseuille's law, the distribution of mean speeds v_m is given in terms of the distribution $p_e(v)$ of Eulerian flow speeds v by

$$p_m(v) = -2v \frac{dp_e(2v)}{dv}. \quad (11)$$

Particle trajectories through the pore space are in general not straight. The ratio between the average trajectory length and the linear length along the mean flow direction defines the tortuosity χ . At high Pe , tortuosity can be determined by the ratio of the mean Eulerian flow speed and the mean velocity in the direction of the flow $\chi_v = \langle v_e \rangle / \langle v_z \rangle$ (see Section 3.2). χ decreases with increasing Pe .

In this framework, the breakthrough curve at a linear distance of $x_c = n\ell/\chi$ is given by the n -fold convolution of the transition time distribution $\psi(t)$. This

allows relating the distribution of Eulerian flow speeds to the large scale transport behavior based on relations (9)-(11), and thus discriminating transport behaviors between different rock types based on the distributions of their flow speed. Specifically, if the distribution $p_m(v)$ of mean flow speeds displays a power-law scaling as $p_m(v) \sim v^{\alpha-1}$ for $v < \langle v_m \rangle$, the transition time distribution (9) scales at high Pe as $\psi(t) \sim t^{-2-\alpha}$. The generalized central limit theorem then predicts that the breakthrough curves, at large Pe , show the scaling behavior as $f_t(t) \sim t^{-2-\alpha}$.

To facilitate the comparison between the Eulerian speed data and solute breakthrough curves for the three different medium types in the following section, we define the inverse speed, or slowness $\sigma = 1/v_m$ (Gotovac et al, 2009), whose distribution $\psi_\sigma(s)$ is directly related to the speed distribution $p_m(v)$ by $\psi_\sigma(s) = s^{-2}p_m(1/s)$. This implies that $\psi_\sigma(s) \sim s^{-1-\alpha}$ for the power-law scaling of $p_m(v)$. Note also that the transition time distribution $\psi(t)$ can be expressed in terms of $\psi_\sigma(t)$ as

$$\psi(t) = \frac{1}{\langle v_m \rangle t} \psi_\sigma(t/\ell). \quad (12)$$

5.2 Flow speed, slowness and breakthrough curves

Now, we probe the distribution of the flow speed or slowness and breakthrough curves in the light of the upscaled model and scaling relations summarized in the previous subsection. An important observation is that the speed correlation is short range and decays fast on distances of the order of magnitude of the mean throat length (i.e. 3 to 5 mean throat length), thus confirming the foundation of the upscaled CTRW model that considers particle transitions of fixed distance with constant speed. The distribution of slowness is shown in the left panel of Figure 7. We can identify clear power-law behaviors as $\psi_\sigma(w) \sim w^{-1-\alpha}$ over 2–4 orders of magnitude. We find for RC, BS and the cropped sand-pack the values $\alpha = 0.37, 0.35$ and $0.63 (\pm 0.01)$, respectively. The breakthrough curves shown in the right panel of Figure 7 show the slopes $f_t(t) \sim t^{-2-\alpha}$ as predicted from the theory. Note that the breakthrough curves are cut-off at the diffusion time scale τ_D ; for decreasing Pe , the time interval over which advective tailing can be observed decreases and eventually disappears as shown in Figures 4 and 6.

Thus, the breakthrough curve behavior gives insights into the behavior of the distribution of low pore-scale flow speeds. At the same time, flow speed distribution (that can be directly translated into the particle mean speed distribution (10,11) and used to determine χ_v) enables classification of large scale transport behaviors; one can see the clear difference between the two rock samples and the sand-pack, for instance.

Fig. 7 Left: Pdf of the normalized slowness ($\psi_\sigma \langle v_m \rangle$) for RC, BS and the cropped SP samples. The slope ($s_\sigma = -1 - \alpha$) of the intermediary mean speed range is indicated by the thin dashed lines ($s_\sigma = -1.38 \pm 0.01$, -1.36 ± 0.01 and -1.63 ± 0.01 for RC, BS and SP, respectively). Right: First passage time at the outlet (f_t) for RC, BS and the cropped SP samples for $Pe = 10^4$. The slope $s_t = 2 - \alpha$ is indicated by the thin dashed lines ($s_t = -2.37 \pm 0.01$, -2.35 ± 0.01 and -2.64 ± 0.01 for RC, BS and SP, respectively)

6 Conclusions

We investigate the transport behavior in three rock types characterized by distinctly different pore structures and velocity distributions. We probe large scale solute dispersion in terms of solute breakthrough curves. To this end, we use numerical simulations that are based on the solution of Stokes equation for fluid flow in the pore space, and two different particle-based simulation methods for passive transport, the RWPT and TDRW approaches. Both methods solve the pore-scale advection-diffusion equation. The RWPT method is based on the Langevin equation that is equivalent to the advection-diffusion equation, and simulates particle motion through the combination of advection along streamlines, and a random walk that models molecular diffusion. The TDRW method is a grid-based method that moves solute particles between cells according to the master equation that results from a finite volume discretization of the advection-diffusion equation. We compare these two methods and investigate the impact of the medium structure and pore-scale velocity distribution on solute breakthrough curves.

RWPT is exempt of numerical dispersion and as such is accurate for modeling transport at high Pe . Conversely, there is numerical dispersion in relation with the finite volume discretization of the transport equation at the voxel scale. But, we show that numerical dispersion, does not noticeably affect the first passage time distribution, because the spreading due the velocity variability is much larger than the one possibly produced by numerical dispersion. Indeed, the RWPT and TDRW approaches provide equal results for the solute breakthrough curves as long as the variability of pore-scale flow velocities is sufficiently well resolved.

As a general rule the accuracy of pore scale hydrodynamic transport results relies on that of the velocity field. At equal spatial resolution of the flow field, RWPT provides a larger spectrum of particle velocities, specifically towards the lower end, because of the velocity interpolation within voxels. As such, this may

lead to differences between the breakthrough curves estimated from RWPT and TDRW in the tail behavior at high Pe , particularly in the case of uniform initial conditions, if the velocity in the throats is not densely enough defined. These results emphasize the eminent role of the full velocity spectrum, not only its mean, for the understanding of non-Fickian transport features such as the long-time tailing of solute breakthrough curves.

The differences in the tailing behaviors of the breakthrough curves for the three different materials can be traced back to their distinctly different speed distributions. These behaviors are analyzed in the light of the CTRW theory of Puyguiraud et al (2021) that provides a quantitative link between the tail behaviors of solute breakthrough curves and the distribution of flow speeds. The results from the direct simulations (both RWPT and TDRW) agree with Puyguiraud et al (2021) theory, such confirming that solute spreading in porous media is controlled by the particle transition time which, at high Pe , is determined by the distribution of flow speeds, and specifically by the low flow speeds. With decreasing Pe , diffusion dominates over low flow speeds, thus cuts off the long time tails and eventually leads to Fickian behavior. Thus, the tail behavior of the breakthrough curves at high Pe is a potential tools for typifying porous media because the distribution of flow speeds is controlled by the porosity structure. Then, to go ahead and eventually being able to evaluate dispersion from pore-scale geometrical properties only, further investigations must focus on how flow speed distribution can be modelled from the pore-throat topology and the distribution of hydraulic apertures and throat lengths, for instance.

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