Differential transport and dispersion of colloids relative to solutes in single fractures

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ABSTRACT

This work employed numerical experiments simulating colloid and solute transport in single parallel-plate fractures, using the random walk particle tracking method, to demonstrate that (1) there exists an aspect ratio of the colloid radius to half the fracture aperture, \( \delta_0 \), where the average velocities of colloids and solutes are similar. When \( \delta > \delta_0 \), the velocity distribution assumption is satisfied, and the fact that the ratio of the colloid transport velocity to the solute transport velocity, \( \tau_p \), decreases as \( \delta \) increases is well documented in the literature. However, when \( \delta < \delta_0 \), the velocity distribution assumption is violated, and \( \tau_p \) increases as \( \delta \) increases and (2) the Taylor dispersion coefficient and its extension by James and Chrysikopoulos [S.C. James, C. V. Chrysikopoulos, J. Colloid Interface Sci. 263 (2003) 288] will overestimate the colloid dispersion coefficient significantly. Additionally, numerical experiments simulating colloid and solute transport in variable-aperture fractures demonstrated that \( \tau_p \) and \( \text{St}_{\text{colloid}}/\text{St}_{\text{solute}} \) decrease with increasing CoV, and the anisotropy ratio only plays a minor role compared to the CoV. These observations have important implications towards the interpretation of colloid transport in both porous and fractured media.

1. Introduction

Experimental studies in both porous [1–4] and fractured [e.g., [5–7]] media have demonstrated that the average transport velocity of colloid tracers may be larger than that of both water molecules and molecular-scale conservative tracers. This phenomenon is commonly referred to as differential transport. The pore-water velocity in an ideal pore throat or a parallel-plate fracture is generally parabolically distributed, with the maximum velocity occurring at the centerline and decreasing towards a zero velocity at the walls [8]. The Taylor–Aris transport theory assumes that conservative molecular-scale solutes, due to their relatively large diffusion coefficients, sample nearly the entire distribution of pore-water velocities. Conversely, colloids are prevented from entering the regions nearest to the walls due to their physical size (i.e., size exclusion) or repulsive interaction forces between the colloids and walls (i.e., charge exclusion) (Fig. 1a). Therefore, colloids necessarily sample larger pore-water velocities than the average water molecule or molecular-scale solute. Furthermore, when particulates are sized within the same range as the pore or aperture region in which they are present, they can be excluded from these regions (i.e., pore exclusion) due to either size or charge, which has the potential to enhance the relative velocity of these particulates even further [9].

The quantitative effect of size and charge exclusion on colloid transport in unconsolidated porous media has generally been evaluated through modifying the classical transport or attachment/detachment coefficients [10,1], reducing the kinematic porosity [9], employing a particle-based model [11] or an empirical model of travel time density function [12]. However, the effect of size or charge exclusion on colloid transport in fractured media has been studied by few researchers. Li and Jen [13] and Jen and Li [14] evaluated the effect of size and other external forces on colloid transport in single uniform fractures using a semi-technological technique. James and Chrysikopoulos [15] derived expressions for the effective velocity and the effective dispersion coefficient for finite-sized spherical particles in a uniform-aperture fracture. Additionally, Chrysikopoulos and James [16] investigated the effect of aperture field anisotropy on the transport and dispersion of colloids.

Studies examining the effects of size and charge exclusion on colloid transport are typically based on the hypothesis, either explicitly or implicitly, that the velocity field sampled by colloids is statistically similar to that of the pore-water velocity, except that colloids cannot enter the regions nearest to the walls where the velocity is lowest (e.g., [11]). This hypothesis will hereafter be referred to as velocity distribution assumption. If the velocity distribution assumption is satisfied, and the differential advection is mainly due to size and/or charge exclusion, the difference between the average transport velocities of colloids and solutes will increase with the ratio of colloid radius to fracture aperture (Fig. 1a), which is well documented in the hydrodynamic chromatography (HDC) literature (e.g., [17]). Due to the fact that colloids have very small diffusion coefficients, however, this assumption only holds true under certain conditions. For laminar flow in frac-
Fusion coefficients (approximately 10 is three orders of magnitude less than typical molecular solute diffusion in 20 colloid diameter. For a spherical colloid with a diameter of 1, the velocity distribution assumption will be violated (Fig. 1b). The aperture field statistics for the parallel-plate fractures. Table 1 aperture fractures when the velocity distribution assumption is satisfied and (b) when the velocity distribution assumption is violated. To the best knowledge of the authors, this is the first study of its kind in this field.

2. Methods

To reach the goals of this research, both colloid and solute transport were simulated in a series of parallel-plate fractures with a range of apertures (Table 1), with the purpose of isolating the effect of fracture aperture on differential transport. Three additional numerical experiments (Table 2) were then designed to investigate the effects of the coefficient of variation (CoV = σb/μb, where σb is the standard deviation, and μb is the arithmetic mean of the fracture aperture), and anisotropy ratio (AR = λb/λp, where λb and λp are the correlation lengths of the aperture in the x- and y-directions, respectively) of variable-aperture fields on differential transport. The following sections describe the generation of the aperture fields, flow field calculations, and the determination of colloid and solute transport parameters.

2.1. Fracture aperture field generation

Table 1 shows that aperture fields follow a log-normal distribution; the anisotropic covariance function of the log-aperture has the form [16]:

Table 1
Aperture field statistics for the parallel-plate fractures.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Mean μb (m)</th>
<th>Standard deviation σb (m)</th>
<th>Coefficient of variation (CoV) = σb/μb</th>
<th>Longitudinal correlation length λL (m)</th>
<th>Transverse correlation length λT (m)</th>
<th>Anisotropic ratio AR = λL/λT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00003</td>
<td>1.0E-10</td>
<td>3.33E-06</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.00005</td>
<td>1.0E-10</td>
<td>2.00E-06</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
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<td>1.0E-10</td>
<td>1.43E-06</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.00009</td>
<td>1.0E-10</td>
<td>1.11E-06</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.0001</td>
<td>1.0E-10</td>
<td>1.00E-06</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>0.00015</td>
<td>1.0E-10</td>
<td>6.67E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>0.0002</td>
<td>1.0E-10</td>
<td>5.08E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>0.0003</td>
<td>1.0E-10</td>
<td>3.33E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>0.0004</td>
<td>1.0E-10</td>
<td>2.50E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>0.0005</td>
<td>1.0E-10</td>
<td>2.00E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>11</td>
<td>0.0006</td>
<td>1.0E-10</td>
<td>1.67E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>12</td>
<td>0.0007</td>
<td>1.0E-10</td>
<td>1.43E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>13</td>
<td>0.0008</td>
<td>1.0E-10</td>
<td>1.25E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
<tr>
<td>14</td>
<td>0.0009</td>
<td>1.0E-10</td>
<td>1.11E-07</td>
<td>0.08</td>
<td>0.08</td>
<td>1.0</td>
</tr>
</tbody>
</table>
such that each 4 cm by 4 cm element had a distinct aperture. The aperture field was discretized into 50 elements (parallel to the direction of flow) (Fig. 2). Each aperture field was discretized into 26 0.0009 0.00008 0.09 0.08 0.40 0.2
25 0.0009 0.00004 0.04 0.08 0.40 0.2
24 0.0009 0.00008 0.09 0.08 0.08 1.0
23 0.0009 0.00004 0.07 0.08 0.40 0.2
22 0.0009 0.00012 0.20 0.08 0.40 0.2
21 0.0009 0.00004 0.04 0.08 0.40 0.2
20 0.0009 0.00008 0.09 0.08 0.08 1.0
19 0.0009 0.00004 0.04 0.08 0.40 0.2
18 0.0009 0.00008 0.09 0.08 0.08 1.0
17 0.0009 0.00004 0.04 0.08 0.40 0.2
16 0.0009 0.00008 0.09 0.08 0.08 1.0
15 0.0009 0.00004 0.04 0.08 0.40 0.2
14 0.0009 0.00008 0.09 0.08 0.08 1.0
13 0.0009 0.00004 0.04 0.08 0.40 0.2
12 0.0009 0.00008 0.09 0.08 0.08 1.0
11 0.0009 0.00004 0.04 0.08 0.40 0.2
10 0.0009 0.00008 0.09 0.08 0.08 1.0
9 0.0009 0.00004 0.04 0.08 0.40 0.2
8 0.0009 0.00008 0.09 0.08 0.08 1.0
7 0.0009 0.00004 0.04 0.08 0.40 0.2
6 0.0009 0.00008 0.09 0.08 0.08 1.0
5 0.0009 0.00004 0.04 0.08 0.40 0.2
4 0.0009 0.00008 0.09 0.08 0.08 1.0
3 0.0009 0.00004 0.04 0.08 0.40 0.2
2 0.0009 0.00008 0.09 0.08 0.08 1.0
1 0.0009 0.00004 0.04 0.08 0.40 0.2

\[ C_{lnb}(r) = \sigma_{lnb}^2 \exp \left(-\frac{r^2 + r_0^2}{2\lambda_x^2}\right) \]  

where \( b \) [L] is the fracture aperture, \( \sigma_{lnb} \), the variance of the ln-aperture, \( lnb, r = (r_x, r_y)^T \) is a two-dimensional vector whose magnitude is the separation distance between two aperture measurements, and \( \lambda_x, \lambda_y \) [L] are the correlation length scales of \( lnb \) in the \( x \)- and \( y \)-directions, respectively. The arithmetic mean aperture and standard deviation are related to their log-transforms by

\[ \sigma_{lnb} = \left[ \ln \left( \frac{\sigma_{lnb}^2 + 1}{\sigma_{lnb}^2} \right) \right]^{1/2} \]  

\[ \mu_{lnb} = \ln \mu_b - 0.5\sigma_{lnb}^2 \]  

The quasi-three-dimensional fracture aperture fields employed in this research are 16.0 m in the \( x \)-direction (parallel to the direction of flow) by 2.0 m in the \( y \)-direction (perpendicular to the direction of flow) (Fig. 2). Each aperture field was discretized into a grid of 400 elements (\( x \)-direction) by 50 elements (\( y \)-direction) such that each 4 cm by 4 cm element had a distinct aperture. The aperture fields were generated using SPRT2D [18], which is based on the Fast Fourier Transform technique. The parallel-plate fracture aperture fields were generated by assuming a very small \( \sigma_b \) (\( 1 \times 10^{-10} \) m). For variable-aperture fields, fifty aperture field realizations for each set of aperture field statistics were generated by changing the seed number supplied to the random field generator.

2.2. Flow field calculation

The steady state flow field in each fracture plane was obtained by solving the Reynolds equation using a fully implicit finite difference technique [16]:

\[ \frac{\partial}{\partial x} \left[ h^3(x,y) \frac{\partial h(x,y)}{\partial x} \right] + \frac{\partial}{\partial y} \left[ h^3(x,y) \frac{\partial h(x,y)}{\partial y} \right] = 0 \]  

\[ \frac{\partial h(x,y)}{\partial y} \bigg|_{y=0,0} = 0 \]  

\[ \frac{\partial h(x,y)}{\partial y} \bigg|_{y=2,0} = 0 \]  

\[ h(x,y)\big|_{x=0,0} = h_0 \]  

\[ h(x,y)\big|_{x=16,0} = 0 \]  

where \( x \) [L] is the coordinate along the fracture length in the direction of flow, \( y \) [L] the coordinate along the fracture width perpendicular to the direction of flow, \( h(x,y) \) [L] the total head potential, and \( b(x,y) \) [L] is the local fracture aperture. The boundary conditions described in Eq. (5) represent no-flow boundaries on the sides of a horizontal fracture, and constant head upstream and downstream boundaries. The equivalent aperture between adjacent elements, in both the \( x \)- and \( y \)-directions, is approximated by the harmonic mean aperture of the two elements [5]. The average velocity component in both the \( x \)- and \( y \)-directions are calculated by [16]:

\[ \bar{v}_x = -\frac{\gamma b^3(x,y)}{12\eta} \frac{\partial h(x,y)}{\partial x} \]  

\[ \bar{v}_y = -\frac{\gamma b^3(x,y)}{12\eta} \frac{\partial h(x,y)}{\partial y} \]  

### Fig. 2. Schematic illustration of the coordinate system and boundary conditions for the flow and transport simulations.
where \( \gamma \) [M L^{-2} t^{-2}] is the specific weight of the fluid, and \( \eta \) [M L^{-1} t^{-1}] is the dynamic viscosity of the fluid.

In order to obtain a three-dimensional velocity field from (6a) and (6b), it is assumed that a fully developed Poiseuille velocity distribution (parabolic velocity profile) exists within each element. This assumption holds true for flow in both the parallel-plate and variable-aperture [38] fractures employed in this work, since the Reynolds numbers in this work are well within the laminar range (Re < 1), and the no-slip condition is applied at the fracture walls. With this assumption, the parabolic velocities in the \( x \)- and \( y \)-directions are expressed in terms of the \( v_x \) and \( v_y \) as

\[
v_x = \frac{3}{2} \left( 1 - 4 \frac{z}{h(x,y)} \right) \quad (6c)
\]

\[
v_y = \frac{3}{2} \left( 1 - 4 \frac{z}{h(x,y)} \right) \quad (6d)
\]

where \( z \) [L] is the coordinate perpendicular to the fracture plane. Fig. 2 gives a schematic illustration of the coordinate system and boundary conditions employed in this work, and Table 3 lists the parameters employed in the model.

It is well-recognized that the Reynolds equation employs numerous simplifying assumptions, the most limiting of which is that inertial forces are negligible. Several studies have demonstrated that the Reynolds equation over-predicts the flow rate by up to twice the actual value (e.g., [39,40]). However, Brush and Thomson [38] conducted simulations to compare the Reynolds equation to both the Stokes and Navier Stokes equations under various geometric and kinematic conditions, and concluded that the Reynolds equation may be considered valid when the following criteria are satisfied:

\[
Re < 1; \quad Re(b)/a < 1; \quad Re \sigma b/(ab) < 1
\]

The further beyond these ranges the parameters get, the more the Reynolds equation will over predict the flow. These conditions are met in the simulations conducted here. Therefore, in this work, it is sound to assume that the Reynolds equation is a reasonable approach for modeling the flow field.

2.3. Transport simulations

In this work, the random walk particle tracking (RWPT) technique was used to simulate the colloidal and molecular-scale solute transport in single fractures, based on the following assumptions: (1) both colloids and molecular-scale solutes were considered to be conservative, (2) the colloids are neutrally buoyant, and therefore sedimentation was neglected, and (3) the colloid suspension is dilute, and the fracture aperture is large relative to the colloid radius, and therefore the colloid–colloid and colloid–fracture wall interactions were neglected. In very confined parallel-plate fractures, where the colloid radius is comparable in size to the fracture aperture, the hydrodynamic particle/wall interactions play a significant role (e.g., [41–44]). However, when the fracture aperture is much larger than the colloid radius, the hydrodynamic particle/wall interactions can be neglected. For example, James and Chrysiikopoulos [15] ignored the hydrodynamic particle/wall interaction when deriving the effective velocity and effective dispersion coefficient for finite-sized colloids.

The size exclusion processes were implemented into the RWPT technique by preventing colloid particles from entering the region near the wall where the velocity is very small. In vector form, the RWPT equation is given by [19]:

\[
X^n = X^{n-1} + A(X^{n-1})\Delta t + B(X^{n-1}) \cdot Z\sqrt{\Delta t}
\]  

(7)

where \( n \) [-] refers to the time step, \( X \) [L = \((x^n, y^n, z^n)\)] is the three-dimensional particle position vector with \( x^n, y^n, \) and \( z^n \) representing the Cartesian coordinate of the centroid of a particle at time \( n\Delta t \), \( A(X^{n-1}) \) is the absolute forcing vector (i.e., the velocity profile) evaluated at \( X^{n-1} \), \( B(X^{n-1}) \) is a deterministic scaling second-order tensor (i.e., a function of the molecular diffusion coefficient) evaluated at \( X^{n-1} \), and \( Z \) is a vector of three independent normally distributed random numbers with a mean of zero and a unit variance. The terms of the diagonal second tensor \( B(X^{n-1}) \) are equal to \( \sqrt{2D_i} \), where \( D_i \) is given by Eq. (1).

The same discretization scheme was employed for both the transport and flow simulations, and the aperture within each discretized element remained constant. It was assumed that the aperture field is symmetric about the center plane of the fracture. Upon substituting Eqs. (6c) and (6d) into Eq. (7), the quasi-three-dimensional RWPT vector equations may be represented by the following directional particle tracking Eqs. [20]:

\[
x^n = x^{n-1} + \bar{v}_x(x^{n-1}, y^{n-1}, z^{n-1}) \frac{3}{2} \left[ 1 - 4 \frac{z}{h(x,y)} \right]^2 \Delta t + Z(0,1)\sqrt{2D_x \Delta t}
\]  

(8a)

\[
y^n = y^{n-1} + \bar{v}_y(x^{n-1}, y^{n-1}, z^{n-1}) \frac{3}{2} \left[ 1 - 4 \frac{z}{h(x,y)} \right]^2 \Delta t + Z(0,1)\sqrt{2D_y \Delta t}
\]  

(8b)

\[
z^n = z^{n-1} + Z(0,1)\sqrt{2D_z \Delta t}
\]  

(8c)

where \( D_i \) [L^2 t^{-1}] is the diffusion coefficient (\( D^c \) for colloids and \( D^m \) for molecular-scale solutes, where \( D^m \) is the molecular diffusion coefficient).

The initial condition involves the instantaneous release of 10,000 conservative particles across the inlet of the fracture. The particles are then distributed according to the local volumetric flow rate in both the \( y \)- and \( z \)-directions as detailed by James et al. [20]. As a result, the average concentration of colloids or solutes at the fracture inlet elements is uniform. However, at each element, the particle concentration distribution across the aperture (i.e., in the \( z \)-direction) is proportional to the local flow rate in the corresponding parabolic velocity profile, with the highest concentration at the centerline and lowest concentration adjacent to the walls.

A constant time step of \( \Delta t = 0.1 \) s was employed in these simulations to achieve a balance between solution accuracy and computational efficiency. The random noise present in the stochastic simulations was smoothed out by using ensemble averages of the breakthrough curves generated by each of the 50 aperture field realizations [20]. Table 3 lists the RWPT model parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow simulation</td>
<td></td>
</tr>
<tr>
<td>Fracture dimensions (length × width)</td>
<td>16.0 m × 2.0 m</td>
</tr>
<tr>
<td>Fracture discretization (elements × elements)</td>
<td>400 × 50</td>
</tr>
<tr>
<td>Element size (dx × dy)</td>
<td>0.04 m × 0.04 m</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 °C</td>
</tr>
<tr>
<td>Dynamic viscosity</td>
<td>1.002 × 10^{-3} N m/s²</td>
</tr>
<tr>
<td>Specific weight</td>
<td>9789 N m⁻¹</td>
</tr>
<tr>
<td>Hydraulic gradient</td>
<td>0.25/16 for parallel-plate fractures, and 0.025/16 for variable-aperture fractures</td>
</tr>
<tr>
<td>Transport simulation</td>
<td></td>
</tr>
<tr>
<td>Molecular diffusion coefficient ( D_m )</td>
<td>9.0 × 10^{-10} m²/s</td>
</tr>
<tr>
<td>Time step ( \Delta t )</td>
<td>0.1 s for parallel-plate fractures, and 1.0 s for variable-aperture fractures</td>
</tr>
</tbody>
</table>
2.4. Determination of the average transport velocities and dispersion coefficients for solute and colloid particles

The effluent breakthrough curves from the RWPT simulations were fit to the one-dimensional advection–dispersion equation (ADE) in order to obtain the average transport velocity and effective dispersion coefficient. The ADE is given by:

\[
\frac{\partial C}{\partial t} = D_t \frac{\partial^2 C}{\partial x^2} - v_L \frac{\partial C}{\partial x} \quad \text{(9a)}
\]

\[
C(0, t) = \frac{M}{Q} \delta(t) \quad \text{(9b)}
\]

\[
C(x, 0) = 0 \quad x > 0 \quad \text{(9c)}
\]

\[
\lim_{b \to 0} C(x, t) = 0 \quad \text{(9d)}
\]

where \( C(x, t) \) [M L\(^{-3}\)] is the tracer concentration, \( v_L \) [L t\(^{-1}\)] the mean tracer transport velocity (\( v_L = v_{L, \text{colloid}} \) for colloids and \( v_L = v_L, \text{solute} \) for molecular-scale solute), \( D_t \) [L\(^2\) t\(^{-1}\)] the longitudinal dispersion coefficient (\( D_t = D_{t, \text{colloid}} \) for colloids and \( D_t = D_{t, \text{solute}} \) for molecular-scale solute), \( M \) [M] the mass of tracer injected, \( Q \) [L t\(^{-1}\)] the volumetric flow rate, \( x \) [L] the spatial coordinate in the direction of flow, \( t \) [t] the time, and \( \delta(t) \) is the Dirac delta function for the time variable.

The analytical solution for Eqs. (9a–d) is given by [21]

\[
C(x, t) = \frac{M}{Q} \frac{x}{\sqrt{4 \pi D_t t}} \exp \left( -\frac{(x - v_L t)^2}{4D_t t} \right) \quad \text{(10)}
\]

Although both the conventional procedures of fitting the one-dimensional analytical solution to the numerically generated breakthrough curves and the ordinary moment method (e.g., [22]) yielded satisfactory results for symmetrically distributed breakthrough curves (e.g., Fig. 3a), these techniques were not suitable for the colloid breakthrough curves, which were seriously skewed (e.g., Fig. 3b). The ordinary moment method put a large weight on the tail portion of these skewed breakthrough curves, particularly for higher moments, resulting in unreasonably large dispersion coefficients and low velocities. In order to circumvent these shortcomings, the weighted moment method was employed to calculate the average transport velocity and dispersion coefficients for all breakthrough curves (both colloid and solute).

The nth weighted moment method is defined as [23]:

\[
m_n = \int_0^\infty C^n \exp(-st) dt \quad \text{where } s [-] \text{ is a weighting factor. Eq. (11) was applied to the one-dimensional analytical solution (Eq. (10)) for transport in parallel-plate fractures, and the 0th, 1st and 2nd weighted moments were obtained as:}
\]

\[
m_0 = \exp \left( \frac{x v_L - x \sqrt{4 D_s + v_L^2}}{2 D_s} \right) \quad \text{(12a)}
\]

\[
m_1 = \frac{x}{\sqrt{4 D_s + v_L^2}} \exp \left( \frac{x v_L - x \sqrt{4 D_s + v_L^2}}{2 D_s} \right) \quad \text{(12b)}
\]

\[
m_2 = \exp \left( \frac{x v_L - x \sqrt{4 D_s + v_L^2}}{2 D_s} \right) \frac{\left( 4 D_s + v_L^2 \right)}{\left( 4 D_s + v_L^2 \right)} \quad \text{(12c)}
\]

The optimal determination of the weighting factor \( s \) is essential to the success of the weighted moment method. Anderson and White [24] suggested an empirical approximation for optimal \( s \) values:

\[
s = \frac{n_{\text{highest}}}{t_{\text{max,input}} + t_{\text{max,output}} - \Delta t_D} \quad \text{(13a)}
\]

where \( n_{\text{highest}} \) is the highest order of moment used to estimate the parameter, \( t_{\text{max,input}} \) and \( t_{\text{max,output}} \) are the times when the input and output signals reach their maximum values, respectively, and \( \Delta t_D \) is the difference in time delay between the input and output signals. For the delta pulse input employed in this work, however, \( t_{\text{max,input}} \) is zero. Additionally, some of the output signals have no rising limb, and therefore \( t_{\text{max,output}} \) for these output signals is equal to \( \Delta t_D \). This would result in the denominator in Eq. (13a) equaling zero. In order to avoid this issue, a modified form of Eq. (13a) was employed:

\[
s = \frac{n_{\text{highest}}}{t_{\text{max,output}}} \quad \text{(13b)}
\]

The average transport velocity, \( v_L \), and dispersion coefficient, \( D_t \), can be calculated from the combination of any two of the three weighted moments in Eq. (12). When calculating \( v_L \) and \( D_t \) for solute transport in parallel-plate fractures, however, it was found that the combination of \( m_0 \) and \( m_1 \) gave the best results (i.e., \( v_L \) agrees very well with the fluid velocity, and \( D_t \) agrees very well with the Taylor dispersion coefficient for solute transport through parallel-plate fractures). This validated the use of Eq. (13b) in determining the weighting factor \( s \). Therefore, \( m_0 \) and \( m_1 \) were employed as the weighted moments in this work for calculating \( v_L \) and \( D_t \) exclusively.

### 3. Results and analysis

Differential advection between colloids and solutes in parallel-plate channels/fractures is well documented in the HDC literature.
(e.g., [25,26]), and is characterized by the calibration relationship between the relative retention time, $\tau_p$, [-], and the relative colloid size with respect to the channel aperture, $\delta$ [1]:

$$
\tau_p = \frac{t_{c,\text{peak}}}{t_{s,\text{peak}}} = \frac{1}{1 + \Phi_0 - G \delta^p}
$$

(14a)

$$
\tau_p = \frac{t_{c,\text{peak}}}{t_{s,\text{peak}}} = \frac{L_x/V_{c,\text{peak}}}{L_x/V_{s,\text{peak}}} = \frac{V_{c,\text{peak}}}{V_{s,\text{peak}}}
$$

(14b)

$$
t_{c,\text{peak}} = L_x/V_{c,\text{peak}}
$$

(14c)

$$
t_{s,\text{peak}} = L_x/V_{s,\text{peak}}
$$

(14d)

where $L_x$ [L] is the fracture length in the x-direction and, $t_{c,\text{peak}}$ [t] and $t_{s,\text{peak}}$ [t] are the retention times of the colloids and molecular-scale solutes, respectively. The retention time of a particle is referred to as the time elapsed between the injection and elution of the maximum peak of that particle, and it is determined through visual inspection of the breakthrough curves. Eqs. (14c) and (14d) relate the retention times, $t_{c,\text{peak}}$ and $t_{s,\text{peak}}$, to their respective mean transport velocities, $V_{c,\text{peak}}$ and $V_{s,\text{peak}}$. The constants $F$ and $G$ are dependent on the conduit symmetry and $G$ also depends on a retention model, $\delta$ [-] is the ratio of the colloid radius to half of the height of the channel through which it is traveling. For parallel-plate fractures, $\delta$ is defined as:

$$
\delta = \frac{r_c}{R}
$$

(15)

where $r_c$ [L] is the radius of the colloid particles, and $R$ [L] refers to half of the actual aperture, $b$, for parallel-plate fracture. For variable-aperture fractures, $R$ [L] represents the half of the arithmetic mean aperture, $\mu_b$, in this work. For impermeable hard spheres transported through a parallel-plate fracture, Eq. (14a) becomes [25]:

$$
\tau_p = \frac{1}{1 + \delta - \delta^p}
$$

(16a)

Additionally, $\tau_m$, the ratio of colloid to molecular-scale solute mean residence time, can be also employed to characterize the differential transport of colloids and molecular-scale solutes, and is defined as:

$$
\tau_m = \frac{t_{c,\text{mean}}}{t_{s,\text{mean}}} = \frac{L_x/V_{c,\text{mean}}}{L_x/V_{s,\text{mean}}} = \frac{V_{c,\text{mean}}}{V_{s,\text{mean}}}
$$

(16b)

where $t_{c,\text{mean}}$ [t] and $t_{s,\text{mean}}$ [t] represent the mean residence times for colloids and solutes, respectively, $V_{c,\text{mean}}$ [Lt$^{-1}$] and $V_{s,\text{mean}}$ [Lt$^{-1}$] are the mean transport velocities for colloids and solutes, respectively, and are based on the mean residence time. Fig. 3 shows that the molecular-scale solute breakthrough curves are nearly normally distributed; however, the colloid breakthrough curves are typically skewed to the right with sharp fronts and long tails, particularly when the velocity distribution assumption is not satisfied. As a result, $\tau_m$ is similar to $\tau_p$ for molecular-scale solutes, but is much larger than $\tau_p$ for colloids due to the long tail of breakthrough curves. Since the determination of $t_{c,\text{mean}}$ depends on the weighting factor $s$, there is a degree of uncertainty in its calculation. By contrast, the determination of $t_{c,\text{peak}}$ is straightforward. Therefore, $\tau_p$ and not $\tau_m$ is used in this work.

3.1. Method employed to determine the validity of the velocity distribution assumption

James and Chrysikopoulos [27] derived an empirical expression to calculate the time, $\Delta t_c$, [t], necessary for a colloid to travel, by diffusivity alone, a specified distance, $L_x$ [L], in the z-direction within an aperture:

$$
\Delta t_c = \exp \left\{ \ln \left( \frac{L_x^2}{2} \right) - 0.978 + 0.787Z(0, 1) \right\}
$$

(17a)

Eq. (17a) shows that, if the Brownian motion is the only driving force, $\Delta t_c$ depends on $L_x$ and $D_c$. To determine if the velocity distribution assumption is satisfied when colloid particles are transported in single fractures, $L_x$ is replaced by the aperture, $b$, for parallel-plate fractures, or the arithmetic mean aperture, $\mu_b$, for variable-aperture fractures. Five thousand realizations of $Z(0, 1)$ were generated, resulting in 5000 realizations of $\Delta t_c$, $\Delta t_c$, the arithmetic mean value of $\Delta t_c$, is then compared with the colloid retention time, $t_{c,\text{peak}}$, to determine the validity of the velocity distribution assumption:

$$
\begin{cases} 
\Delta t_c < t_{c,\text{peak}} & \text{Taylor—Aris assumption satisfied} \\
\Delta t_c > t_{c,\text{peak}} & \text{Taylor—Aris assumption not satisfied}
\end{cases}
$$

(17b)

A value of $\Delta t_c$ greater than $t_{c,\text{peak}}$ indicates that the colloid cannot sample the entire velocity profile across the aperture during the time it is traveling in the fracture, and the velocity distribution assumption is not satisfied. Conversely, if $\Delta t_c$ is less than $t_{c,\text{peak}}$, the velocity distribution assumption is satisfied.

3.2. Mechanisms causing differential transport in parallel-plate fractures

Eq. (17a) shows that the variables $R$ (refer to $b$ for parallel-plate fractures), $D_c$, (thus $r_c$) and $t_{c,\text{peak}}$ are all required to determine the validity of the velocity distribution assumption. To investigate the dependence of $\tau_p$ on $r_c$, $R$, and $t_{c,\text{peak}}$, two groups of simulations were conducted in parallel-plate fractures, as shown in Table 4. In Group I, $r_c$ was kept constant, and four different average fluid velocities across the aperture, $v_s$, were applied to a series of parallel-plate fractures ($v_b = 0$ for parallel-plate fracture). In Group II, $R$ and the average fluid velocity, $v_s$, remained unchanged, and seven different values of $r_c$ were employed.

3.2.1. Group I simulations

The results from the Group I simulations are shown in Fig. 4a, together with a HDC calibration curve based on Eq. (16a), which illustrates the dependence of $\tau_p$ on $\delta$. Fig. 4a clearly shows that, for each case with a specific average fluid velocity, there exists a threshold value of $\delta_0$. The determination of $\delta_0$ for the case when $v_s = 1.14 \times 10^{-3}$ m/s and $d_s = 1$ μm is shown in Table 5 and Fig. 5. For each specific aperture $b$, $L_x$ is replaced by $b$ in Eq. (17a). Five thousand realizations of $Z(0, 1)$ were generated, resulting in 5000 realizations of $\Delta t_c$, and therefore $\Delta t_c$, the arithmetic mean value of $\Delta t_c$, could be calculated. $\Delta t_c/t_{c,\text{peak}}$ was then plotted against $b$. The critical fracture aperture, $b_0$, and therefore $\delta_0 = (r_c/b_0)$ since $r_c$ is constant) can then be determined by setting $\Delta t_c/t_{c,\text{peak}} = 1$ (Fig. 5).

Fig. 4a shows that, when $\delta < \delta_0$, the simulation results follow the same trend as that of the HDC calibration curve, that is, $\tau_p$ increases with decreasing $\delta$. However, when $\delta > \delta_0$, the simulation results display an opposite trend to that of HDC curve, that is, $\tau_p$ increases with increasing $\delta$, and reaches a constant value asymptotically. This phenomenon is not represented by the HDC calibration curve, and has never been reported before to the knowledge of these authors. Fig. 4a also shows that the threshold value, $\delta_0$, increases with increasing average fluid velocity in the fractures. This phenomenon can be explained by considering the velocity distribution assumption.

The average velocity, $v_{UL}$ [Lt$^{-1}$], for a colloid transported in parallel-plate fracture is evaluated by:

$$
v_{UL} = \frac{1}{2} \int_{L_x}^{2L_x} [v(z)dz]
$$

(18)
Table 4
Transport simulation in parallel-plate fractures: Groups I and II simulations.

<table>
<thead>
<tr>
<th>Group I</th>
<th>Group II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$ (μm)</td>
<td>$r_c$ (μm)</td>
</tr>
<tr>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>70</td>
<td>1.5</td>
</tr>
<tr>
<td>90</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fig. 4. Dependence of $\delta$ on $r_p$ based on (a) Group I simulation results with constant $r_c$. $-$: HDC calibration curve based on Eq. (16a), ◆: simulation results with $v_x = 1.14 \times 10^{-3}$ m/s, ×: simulation results with $v_x = 3.18 \times 10^{-3}$ m/s, ◆: simulation results with $v_x = 1.14 \times 10^{-3}$ m/s. Δ: simulation results with $v_x = 1.03 \times 10^{-3}$ m/s. (b) Group II simulation results with a constant $b$ and $v_x = 1.14 \times 10^{-3}$ m/s. $-$: HDC calibration curve based on Eq. (16a), ◆: simulation results.

Table 5
Determination of $\Delta_0$ (for Group I simulation with $v_x = 1.14 \times 10^{-3}$ m/s).

<table>
<thead>
<tr>
<th>$h$ (μm)</th>
<th>$\delta$ [-]</th>
<th>$\Delta t$ (s)</th>
<th>$t_{peak}$ (s)</th>
<th>$\Delta t_{peak}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.33E-02</td>
<td>1.09E+03</td>
<td>1.36E+04</td>
<td>0.1</td>
</tr>
<tr>
<td>50</td>
<td>2.00E-02</td>
<td>3.03E+03</td>
<td>1.36E+04</td>
<td>0.2</td>
</tr>
<tr>
<td>70</td>
<td>1.43E-02</td>
<td>5.93E+03</td>
<td>1.37E+04</td>
<td>0.4</td>
</tr>
<tr>
<td>90</td>
<td>1.11E-02</td>
<td>9.81E+03</td>
<td>1.35E+04</td>
<td>0.7</td>
</tr>
<tr>
<td>150</td>
<td>1.00E-02</td>
<td>1.21E+04</td>
<td>1.35E+04</td>
<td>0.9</td>
</tr>
<tr>
<td>200</td>
<td>6.67E-03</td>
<td>4.84E+04</td>
<td>9.94E+03</td>
<td>4.9</td>
</tr>
<tr>
<td>300</td>
<td>3.33E-03</td>
<td>1.09E+05</td>
<td>9.84E+03</td>
<td>11.1</td>
</tr>
<tr>
<td>400</td>
<td>2.50E-03</td>
<td>1.94E+05</td>
<td>9.57E+03</td>
<td>20.2</td>
</tr>
<tr>
<td>500</td>
<td>2.00E-03</td>
<td>3.03E+05</td>
<td>9.56E+03</td>
<td>31.7</td>
</tr>
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<td>9.49E+03</td>
<td>45.9</td>
</tr>
<tr>
<td>700</td>
<td>1.43E-03</td>
<td>9.38E+05</td>
<td>9.50E+03</td>
<td>62.5</td>
</tr>
<tr>
<td>800</td>
<td>1.25E-03</td>
<td>7.75E+05</td>
<td>9.50E+03</td>
<td>81.6</td>
</tr>
<tr>
<td>900</td>
<td>1.11E-03</td>
<td>9.81E+05</td>
<td>9.45E+03</td>
<td>103.8</td>
</tr>
</tbody>
</table>

Fig. 5. Determination of $\Delta_0$ based on data in Table 5.
where $v(z)$ [L t$^{-1}$] is the colloid transport velocity at $z$, and $z_c$ [L] and $z_l$ [L] are the $z$ coordinates indicating the upper and lower limit of the colloid particle transport zone, as shown in Fig. 1. When $\delta > \delta_0$ (correspondingly $b > b_0$ since the colloid size is constant in Group I), $\Delta t_c < t_{c,\text{peak}}$, thereby satisfying the velocity distribution assumption, and the colloid is able to sample the entire velocity profile (except the region very near the wall due to charge and/or size exclusion) before it exits the fracture (Fig. 1a). Under such conditions, the average transport velocity of colloids will be larger than that of molecular-scale solutes due to size and/or charge exclusion according to Eq. (18). This phenomenon coincides with the main retention mechanism of HDC, and therefore follows the same trend as that of HDC. It should be pointed out here that the velocity distribution assumption is satisfied for all molecular-scale solutes employed in these simulations.

However, when $\delta < \delta_0$ (and correspondingly $b < b_0$), the velocity distribution assumption is violated, and colloids are only able to traverse a fraction of the aperture in the $z$-direction before they exit the fracture due to their low diffusivities (as illustrated in Fig. 1b). This results in the following two consequences.

The first consequence of violating the velocity distribution assumption is that the dispersion coefficients of colloid particles within the fracture will be smaller than the Taylor dispersion coefficient, $D_{\text{Taylor}}$, calculated using the following equation:

$$D_{\text{Taylor}} = D_c + \frac{1}{2} \frac{\nu^2 b^2}{D_c}$$

where $\nu$ [L t$^{-1}$] is the mean fluid velocity across the aperture. This will be further discussed in Section 3.3.

Another consequence is that the colloid breakthrough curves will have sharp fronts and long tails, and the peak arrival time of the colloids will be earlier than that of molecular-scale solutes. Furthermore, the difference between peak arrival times of colloids and molecular-scale solutes is larger than that which can be explained by size and/or charge exclusion. For example, for the case of $r_c = 1 \mu m$ and $v_s = 1.14 \times 10^{-3}$ m/s, the RWPT simulation (Fig. 4a) shows that, when $\delta < \delta_0 = 9.0 \times 10^{-3}$ (i.e., the velocity distribution assumption is violated), $\tau_d$ decreases dramatically and is much different from 1. However, the HDC calibration curve (in which the difference between peak arrival times of colloids and molecular-scale solutes is primarily caused by size and/or charge exclusion) shows that $\tau_d$ approaches 1 when $\delta < \delta_0 = 9.0 \times 10^{-3}$ and decreases. This is due to the facts that: (1) A colloid with an initial position at the centerline will travel in a zone near the centerline until it exits the fracture (i.e., the velocity distribution assumption is violated) due to its small dispersion coefficient. Therefore, its average transport velocity will be much larger than that of a solute. Similarly, a colloid starting in a region near a wall will travel in the region near that wall. Therefore, its average transport velocity will be much smaller than that of molecular solutes. (2) The particle concentration distribution across the aperture is somewhat similar to that of the fluid velocity, with highest concentration at the centerline and lowest concentration near the walls [5,25]. These two factors result in the fact that the faster moving colloids near the centerline lead to sharper breakthrough curve fronts and earlier peak arrival times than molecular-scale solutes, and the slower moving colloids near the wall result in a long tail in the breakthrough curves. Another consequence is that the colloid residence time distribution is wider, and its macro-dispersion coefficient larger than that of a solute.

Several explanations have been proposed for the long tail observed for colloid breakthrough curves in fractured media, such as matrix diffusion (e.g., [28,29]), and diffusive exchange of tracer with immobile water in fractures (e.g., [30,31]). Becker and Shapiro [32] attributed the long tails on their breakthrough curves to the differential advection of tracer in channels with very different hydraulic conductivities, and advective mass exchange between mobile and immobile fluid. Harter et al. [33] attributed the long tail in skewed colloid breakthrough curves to reversible attachment. This work, on the other hand, demonstrates that the long tail can also be caused by the very different average colloid velocities across the aperture (i.e., larger average velocities at the centerline and smaller average velocities near the wall), when the velocity distribution assumption is violated. This effect is expected to be more obvious in less heterogeneous fractures, which will be further discussed in Section 3.4.

Fig. 4a and Table 4 also show the relationship between the threshold value $\delta_0$ (or $b_0$ when $r_c$ remains constant) and the average fluid velocity in the fracture, which is that $\delta_0$ increases with increasing average fluid velocity. This is due to the fact that an increasing average fluid velocity will lead to a smaller $t_{c,\text{peak}}$. By letting $\Delta t_c = t_{c,\text{peak}}$ in Eq. (17a), a smaller $t_{c,\text{peak}}$ will result in a decrease in $b_0$. According to Eq. (15), a decrease in $b_0$ will result in an increase in $\delta_0$ since $d_c = 2(\sigma r_c)$ remains constant (i.e., 1 $\mu m$) in the Group I simulations. The calculated values of $\delta_0$ for the four different average fluid velocities employed in this work are shown in Table 4. It is noted, however, that the calculated threshold values of $\delta_0$ using Eq. (17) are consistently smaller (by a factor of about 3) than those observed in Fig. 4a. One explanation for this discrepancy is that the method to determine the validity of the velocity distribution assumption described in Section 3.1 is only qualitatively correct. For the velocity distribution assumption to be satisfied, the colloid should fully sample the entire velocity profile; however, the method employed to calculate $\delta_0$ in Sections 3.1 and 3.2.1 requires that the colloid only travel a distance of $b$ under the driving force of Brownian diffusion, which would likely not enable the colloid to fully sample the velocity profile. It is also observed from Fig. 4a that, for larger average velocities ($v_s = 1.14 \times 10^{-3}$ and $1.03 \times 10^{-2}$ m/s in this research), $\tau_d$ reaches an asymptotic value (approximately 0.67) as $\delta$ decreases. This is due to the fact that, when the colloid retention time in the fracture is relatively small, colloids near the centerline, where the colloid concentration is the highest, only traverse a small distance in the $z$-direction. Therefore the average colloid velocities are similar in fractures with apertures larger than a certain value, approximately equal to the maximum velocity of the Poiseuille velocity distribution across the aperture, which results in similar peak arrival times. The mean solute velocity, however, is 2/3 of the maximum solute velocity. According to Eq. (14b), $\tau_p$ has an asymptotic value of approximately 2/3. Additionally, Fig. 4a also shows that for a specific $\delta$, and thus $b$, $\tau_p$ decreases with increasing average fluid velocity. This indicates that, when the average fluid velocity increases, the average transport velocity of colloids traveling near the centerline, which determines the peak arrival time, increases to a larger extent than the average transport velocity of solutes.

3.2.2. Group II simulations

These simulations involved situations in which the fracture aperture remained constant while the colloid diameter changed. The results are shown in Table 4 and Fig. 4b. For the range of colloid diameters and fracture apertures used in these simulations, the velocity distribution assumption is only satisfied for $d_c = 0.5 \mu m$. It is clearly shown, however, that the relationship between $\tau_d$ and $\delta$ follows a trend similar to the HDC calibration curve, which is that $\tau_d$ decreases with increasing $\delta$. The simulated results, however, deviate from the theoretical HDC curve significantly. For the HDC calibration curve, the velocity distribution assumption is satisfied, and it is well known that size/charge exclusion results in the fact that the average velocity of larger colloids ($v_{\text{larger}}$), smaller colloids ($v_{\text{smaller}}$), and molecular-scale solutes ($v_{\text{solute}}$) will follow the relationship: $v_{\text{larger}} > v_{\text{smaller}} > v_{\text{solute}}$. Therefore their
respective retention time are: \( t_c \text{ larger} < t_c \text{ smaller} < t_c \text{ solute} \). When the velocity distribution assumption is not satisfied, the above relationship still holds. Because the distance the larger colloids will traverse in the z-direction will be statistically smaller than that of smaller colloids before they exit the fracture, the average velocity of a larger colloid starting from the centerline of the aperture, where the colloid concentration is the highest, is larger than that of a smaller colloid starting from the same position (Eq. (18)). The deviation between the simulations and the HDC calibration curve in Fig. 4b is due to the fact that the velocity distribution assumption is satisfied for the HDC calibration curve, but not for the present simulations.

### 3.2.3. Implications of the simulation results

The findings of this work, combined with the HDC calibration curve, show that when \( R \) in Eq. (15) remains constant, the relationship between \( \tau_p \) and \( \delta \) always follows the same trend as the theoretical HDC calibration curve, whether the velocity distribution assumption is satisfied or not. When \( R \) remains constant in Eq. (15), however, there exists a value of \( \delta_0 \) (thus \( h_0 \)), where the average transport velocity for a colloid is similar to that of a molecular-scale solutes. When \( \delta > \delta_0 \), \( \tau_p \) decreases as \( \delta \) increases; when \( \delta < \delta_0 \), \( \tau_p \) decreases as \( \delta \) decreases.

This finding has significant implications on interpreting the results of colloid and solute tracer tests in single fractures as well as in unconsolidated porous media. For example, Small [17] employed HDC experiments to show that velocity enhancement increases as the mean grain size of the packing bed decreases. However, Harter et al. [33] conducted experimental work on colloid transport in sandy soils and found that velocity enhancement increased as the mean grain size of the soil column increased. This seeming inconsistency disappears upon further analysis.

Following earlier work in the field of HDC, a parallel array of capillaries of equal size were employed to represent the interstitial channels in porous media, and the equivalent capillary radius was represented by the hydraulic radius \( R_0 \) [34]:

\[
R_0 = \frac{d_p \theta}{3 \left( 1 - \theta \right)}
\]

where \( d_p \) [L] is the diameter of the media grains, and \( \theta \) [−] is the porosity. \( \Delta t \) was calculated by replacing the \( L \) in Eq. (17) with \( R_0 \). Comparing \( \Delta t \) with the retention time \( t_c \text{, peak} \), we can determine whether or not the velocity distribution assumption is satisfied. Table 6 shows that the velocity distribution assumption was satisfied in Small’s [17] experiments, and therefore velocity enhancement increased as the mean grain size (thus \( R_0 \)) of the packing bed decreased in his work. However, the velocity distribution assumption was violated in Harter et al.’s experiments [33] (Table 7), and the grain size of the porous media varies while the colloid size remains constant, so velocity enhancement increased as the mean grain size (thus \( R_0 \)) of the soil column increased.

### 3.3. The validity of the Taylor–Aris dispersion coefficient

By implicitly assuming that the velocity distribution assumption is satisfied, James and Chrysikopoulos [15] derived expressions for the effective velocity, \( v_{eff} \) [L T\(^{-1}\)], and the effective dispersion coefficient, \( D_{eff} \) [L\(^2\) T\(^{-1}\)], for neutrally buoyant, finite-sized spherical particles traveling in a uniform-aperture fracture as follows:

\[
v_{eff} = \frac{v_2}{1 + \frac{d_c}{b} \left( 1 - \frac{d_c}{b} \right)^2} \quad \text{(21)}
\]

\[
D_{eff} = D_c \left( 1 - \frac{d_c}{b} \right) \quad \text{(22)}
\]

where \( v_2 \) [L T\(^{-1}\)] is the mean fluid velocity across the aperture. The correction term in Eq. (21) (shown in square brackets) is typically very small and therefore, the difference between \( v_{eff} \) and \( v_2 \) is also very small (up to 3% in this research). By contrast, the ratio of \( D_{eff} \) to \( D_{Taylor} \) varies from 6% to 18% when \( b \) decreased from 100 µm to 30 µm in this research. When \( b \geq 150 \) µm in this work, the difference between \( D_{eff} \) and \( D_{Taylor} \) was negligible (less than 4%).

Fig. 6 compares dispersion coefficients and average transport velocities for solutes and colloids in parallel-plate fractures (Group 1 simulation, \( v_2 = 1.14 \times 10^{-3} \) m/s) obtained using various methods. As shown in Figs. 6a and b, the dispersion coefficient and transport velocity for a solute, calculated by the weighted moment method based on the numerically generated breakthrough curves, agree very well with the Taylor dispersion coefficient and average fluid velocity, respectively. This is expected, and confirms the validity of using the weighted moment method to calculate the dispersion coefficient and average transport velocity in this work. However, the story is very different for colloids. Figs. 6c shows that, when the velocity distribution assumption is satisfied (for \( b = 30 \) µm, 50 µm, 70 µm, 90 µm, and 100 µm in these simulations), \( D_{eff} \) from Eq. (22) agrees very well with \( D_c \) calculated using the weighted moment method based on the numerically generated breakthrough curves, with a difference of less than 5%. However, \( D_c \) is significantly smaller than \( D_{eff} \) by up to 8 times, when the velocity distribution assumption is violated (for \( b \geq 150 \) µm in this simulation). Therefore, Eq. (22) will significantly overestimate the colloid dispersion coefficient when the velocity distribution assumption is violated.

Additionally, the difference between \( v_{c, \text{peak}} \) (the mean colloid transport velocity, which is calculated using the weighted moment method and is based on the mean residence time, \( t_m \)) and \( v_{eff} \) (obtained from Eq. (21)) increases as \( b \) increases (correspondingly as \( \delta \) decreases), but the largest difference is less than 3%. Therefore, \( v_{eff} \) provides a good estimation of \( v_c \) whether or not the velocity distribution assumption is satisfied. However, \( v_{c, \text{peak}} \) (the mean colloid transport velocity based on \( t_c, \text{peak} \) the retention time) is larger than \( v_{eff} \) by up to 32% when the velocity distribution assumption is violated. This is due to the fact that the colloid breakthrough curve is typically skewed right with a sharp front and long tail when the velocity distribution assumption is not satisfied. Therefore, \( t_m \) is typically much larger than \( t_c, \text{peak} \) and \( v_c \) is typically much smaller than \( v_{c, \text{peak}} \).

### 3.4. Differential advection and dispersion through variable-aperture fractures: the effects of CoV and AR

The effect of CoV and AR on \( \tau_p \) when the velocity distribution assumption was violated was also investigated. The experiment design is shown in Table 2, and the results are illustrated in Figs. 7
Several important findings were identified upon examination. It should be pointed out here that $Pe/C_{29}$ in the present simulations, that is, the transport is within the advection-dominated regime.

Fig. 7 shows that $s_p$ decreases with increasing mean fluid velocity in variable-aperture fractures with arithmetic mean apertures of $b_0 = 300 \mu m$, $600 \mu m$, and $900 \mu m$, respectively, which is consistent with the results from the simulations conducted in parallel-plate fractures shown in Fig. 4a. Fig. 7 also shows that for fractures with a specific arithmetic mean aperture, $s_p$ increases with increasing $r_b$. This indicates that the velocity enhancement of colloids relative to conservative molecular-scale solutes decreases with increasing CoV for fractures with a specific average aperture. For $b_0 = 300 \mu m$ and $\sigma_0 = 120 \mu m$ (CoV = 0.4, the largest employed in these simulations), $s_p$ is near unity, which is consistent with experimental observations. Harvey et al. [35] found that flagellated protozoa and microspheres did not exhibit significant velocity enhancement traveling in a sandy aquifer with moderate heterogeneity over a distance of 1–3.6 m. Fig. 7 also shows that AR also plays a role in colloid velocity enhancement relative to solute tracers, however, its effect is much smaller than that of $r_b$. Additionally, the effect of AR is not consistently demonstrated for different combinations of $b_0$ and $r_b$. Therefore, the effect of AR merits further investigation.

Figs. 8a–c show plots of $D_{coll}/D_{solute}$ versus CoV and AR for $b_0 = 300 \mu m$, $600 \mu m$, and $900 \mu m$, respectively. All of these figures show the same trend, which is that the ratio of $D_{coll}/D_{solute}$ decreases (from about 700 to about 1) with increasing CoV. For example, the ratio of $D_{coll}/D_{solute}$ for parallel-plate fractures with $b_0 = 300 \mu m$ and hydraulic gradient = 0.00156 is 551. The ratio of

<table>
<thead>
<tr>
<th>Porous media characteristics</th>
<th>CS fast</th>
<th>MS fast</th>
<th>FS fast</th>
<th>CS slow</th>
<th>MS slow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Velocity enhancement (%)</td>
<td>19</td>
<td>9</td>
<td>0</td>
<td>37</td>
<td>11</td>
</tr>
<tr>
<td>$b_0$ ((\mu m))</td>
<td>467</td>
<td>135</td>
<td>62</td>
<td>467</td>
<td>135</td>
</tr>
<tr>
<td>$\Delta t$ (s)</td>
<td>13,206</td>
<td>110,356</td>
<td>23,276</td>
<td>13,206</td>
<td>110,356</td>
</tr>
<tr>
<td>Actual retention time (s)</td>
<td>1217</td>
<td>1217</td>
<td>1217</td>
<td>12,169</td>
<td>12,169</td>
</tr>
<tr>
<td>Taylor–Aris assumption satisfied?</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

1. This table is based on the data from Harter et al. [33].
2. CS: coarse sand, MS: medium sand, FS: fine sand, fast: high flow rate, slow: low flow rate.

Fig. 6. A comparison of (a) molecular-scale solute dispersion coefficient ($D_{solute}$), (b) molecular-scale solute transport velocity ($v_{L,solute}$), (c) colloid dispersion coefficient ($D_{coll}$), and (d) colloid transport velocity ($v_{L,coll}$) in parallel-plate fractures for Group I simulations with $V_i = 1.14 \times 10^{-2} m/s$. 

Table 7

Interpretation of the experimental results by Harter et al. [33].

<table>
<thead>
<tr>
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<th>FS fast</th>
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<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
for variable-aperture fractures (with the same dimensions and hydraulic gradient, $\mu_b = 300 \mu m$, $\sigma_b = 40 \mu m$, 80 \mu m, and 120 \mu m) decreases from approximately 40 to 2 with increasing CoV. The AR plays a minor role compared to the CoV, and the results show that

$$\frac{D_{L,coll}}{D_{L,solute}}_{\text{AR}=1.0} > \frac{D_{L,coll}}{D_{L,solute}}_{\text{AR}=0.2} > \frac{D_{L,coll}}{D_{L,solute}}_{\text{AR}=5.0}$$

(23)

The above discussion demonstrates a transition of $\tau_p$ and $D_{L,coll}/D_{L,solute}$ from parallel-plate to increasingly variable-aperture fields. In parallel-plate fractures, a comparison of Fig. 6a and c shows that the ratio of $D_{L,coll}/D_{L,solute}$ is much larger than 1, whether or not the velocity distribution assumption is satisfied. Faster breakthrough of colloids relative to conservative solutes in parallel-plate fractures has been demonstrated through numerical simulation in this work (Fig. 4a and b), through experiments (e.g., [25]), and theoretical analysis (e.g., [15]). This phenomenon has been attributed to size and/or charge exclusion when the velocity distribution assumption is satisfied [25,15]. However, this work shows that when the velocity distribution assumption is violated, this phenomenon is due to the combined effect of the large difference between the diffusivity of colloids and solutes, together with the parabolically distributed velocity across the aperture, and size and/or charge exclusion plays a minor role.

In variable-aperture fractures, however, aperture field heterogeneity and, to a lesser extent, anisotropy become more dominant in determining the average transport velocity and macro-dispersion coefficient as these parameters increase [36]. In these circumstances, the effect of size and/or charge exclusion (when the velocity distribution assumption is satisfied) and the combined effect of the large difference between the diffusivity of colloids and solutes together with the parabolically distributed velocity profile across the aperture (when the velocity distribution assumption is not satisfied) will become less important. Therefore, the difference between the breakthrough time and macro-dispersion coefficient
of colloids and solutes becomes smaller with increasing aperture field heterogeneity and anisotropy. It is hypothesized that, when solutes and colloids are transported in relative large scale single fractures and for relatively long time periods, solute will be able to enter small aperture regions while colloids will not be able to due to pore exclusion. Further, solutes will be able to enter stagnant regions while colloids will not due to the fact that colloid dispersion coefficients are significantly smaller than those of solute. Colloids, however, will still breakthrough faster than solutes. Under these conditions, the faster breakthrough and smaller dispersion coefficients of colloids relative to solutes will be similar to those observed in unconsolidated porous media (e.g., [1,37,2]).

4. Summary

Differential transport between colloids and molecular-scale solutes in single fractures was investigated using numerical simulations. The Reynolds equation was solved using a fully implicit finite difference technique to obtain the flow field in saturated single fractures. A quasi-three-dimensional random walk particle tracking technique was employed to simulate colloid and molecular-scale solute transport in both parallel-plate and variable-aperture fractures. The formula developed by James and Chrysikopoulos [15] was employed to determine whether the velocity distribution assumption is satisfied or violated.

For colloid and solute transport in parallel-plate fractures, it was demonstrated that there exists a threshold value of \( d_0 \), the ratio of the colloid radius to half the fracture aperture, where the retention time for solute and colloid particles are very similar. When \( \delta > d_0 \), the velocity distribution assumption is satisfied, and the relative retention time \( \tau_p \) decreases as \( \delta \) increases, as is well documented in the HDC literature. Conversely, when \( \delta < d_0 \), the velocity distribution assumption is violated, and the relative retention time \( \tau_p \) increases as \( \delta \) decreases. To the best knowledge of the authors, this is the first time that this trend has been demonstrated. When the velocity distribution assumption is satisfied, the Taylor dispersion coefficient \( D_{taylor} \) and its extension by James and Chrysikopoulos [15] \( D_{eff} \) give a good estimation of the actual colloid dispersion coefficient, however, when the velocity distribution assumption is violated, both \( D_{taylor} \) and \( D_{eff} \) significantly overestimate the colloid dispersion coefficient. These results have important implications regarding the interpretation of tracer tests in both porous and fractured media, and help to explain previous, seemingly conflicting, results as discussed in Section 3.2.3.

Transport simulations were also conducted in variable-aperture fractures to investigate the influence of CoV and AR on the relative retention time, \( \tau_p \), and the ratio of \( D_{coll}/D_{solute} \) for cases where \( \delta < d_0 \) (i.e., the velocity distribution assumption is violated). These results show that \( \tau_p \) increases with increasing CoV, which means that the velocity enhancement of colloids relative to solutes decreases with increasing heterogeneity. On the other hand, the ratio of \( D_{coll}/D_{solute} \) decreases by several orders of magnitude to about 1 with increasing CoV, which means that the difference between dispersion coefficients of colloids and solutes becomes smaller with increasing aperture field heterogeneity. These results also show that the AR also has an impact on \( \tau_p \) and \( D_{coll}/D_{solute} \); however, its influence is much smaller than that of the CoV.

Acknowledgments

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References