Supporting Information for:

Hemispheres-in-Cell Geometry to Predict Colloid Deposition in Porous Media

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Derivation of relationship between porosity and the fluid shell thickness for the Hemispheres-in-cell

The relationship between porosity (ε), the collector radius (a_c) and the fluid shell radius (b) for the Hemispheres-in-cell geometry is derived via their volumetric analyses as follows:

$$\begin{aligned}\varepsilon &= \frac{\frac{4}{3}\pi b^3 - 2 \times \frac{1}{3}\pi(b-a_c)^2[3b-(b-a_c)] - \frac{4}{3}\pi a_c^3}{\frac{4}{3}\pi b^3 - 2 \times \frac{1}{3}\pi(b-a_c)^2[3b-(b-a_c)]} = \frac{2b^3 - (b-a_c)^2(2b+a_c) - 2a_c^3}{2b^3 - (b-a_c)^2(2b+a_c)} \\ &= \frac{2 - \left(1 - \frac{a_c}{b}\right)^2 \left(2 + \frac{a_c}{b}\right) - 2\left(\frac{a_c}{b}\right)^3}{2 - \left(1 - \frac{a_c}{b}\right)^2 \left(2 + \frac{a_c}{b}\right)} = \frac{3\left(\frac{a}{b}\right) - 3\left(\frac{a}{b}\right)^3}{3\left(\frac{a}{b}\right) - \left(\frac{a}{b}\right)^3} = \frac{3\left(1 - \frac{a_c^2}{b^2}\right)}{3 - \frac{a_c^2}{b^2}} \\ \text{or } \frac{a_c}{b} &= \left(\frac{3-3\varepsilon}{3-\varepsilon}\right)^{1/2} \quad (\text{S1})\end{aligned}$$

Attempts at a closed form solution for the fluid flow field in the Hemispheres-in-cell

To our knowledge, a closed form solution for the flow field does not exist for the Hemispheres-in-cell geometry. The most relevant previous work appears to be Wakiya ([1](#)), who examined the velocity field around two spheres in contact suspended in viscous flow. However, this system differs from the hemisphere-in-cell model due to the undisturbed flow being aligned parallel to the line connecting the sphere centers, rather than perpendicular. Also, the flow-field boundary conditions in the Hemisphere-in-cell model are periodic. Based on the general solution to the Stokes equations provided in Wakiya ([1](#)), we attempted to solve the flow transverse to a fixed doublet of two equal spheres. Coefficients in the trial function solution were determined under the requirement that the solution satisfy the continuity equation and appropriate boundary conditions.

The resulting set of equations for the coefficients became exceedingly complex, requiring numerical solutions of Hankel transformations of expressions involving Bessel functions.

An attempt was also made to develop a flow field surrounding a fixed doublet with a fluid envelope of arbitrary porosity. The two grains comprising the doublet were mirror images of one other, but they were not constrained to be spherical. It was hoped that relaxing this constraint would allow the construction of a flow field for the more general model by simpler methods, while yielding a doublet geometry which would serve our purpose as well as one with spherical grains. The velocity field satisfied the continuity equation and the boundary conditions, but not the Stokes momentum equation, except in a qualitative sense. A trial function was sought to describe the flow field in the fluid envelope surrounding one “spheroid”, and subsequently was superimposed to develop the field surrounding the doublet. We hoped to identify the outer boundary of the fluid envelope as locations where the velocities (radial velocity) produced by the trial function would vanish. Unfortunately we determined that the trial functions for the velocity field were non-monotonic with respect to distance from the center of the spheroid, which prevented determination of the outer boundary of the fluid envelope.

Computational meshes

The guidelines for construction of computational meshes prescribe that cell volume change is within a factor of 1-10 for adjacent cells; cell aspect ratios should be less than 10; and internal angles should not be less than 45° . Because of symmetry on the $x = a_c$ and $y = 0$ planes, mesh

simulations were required only for one quadrant; e.g., the quadrant defined by $(x \in [0, a_c], y \in [-b, 0])$ of the Hemispheres-in-cell (Figure 1b in the Manuscript). Since the balance of fluid drag, Brownian, and colloidal forces near the collector surface controls colloid deposition, the mesh required to support numerical solution of the near-surface flow field must be highly resolved. This was achieved by building 5 layers of prism cells on the grain surface, with the surface boundary layer being $0.5 \mu\text{m}$ thick; and subsequent layers expanding by a factor of 1.2 to yield a total thickness of $3.7 \mu\text{m}$ for the 5-layer prism cells (Figure 1c inset in the Manuscript). Because symmetry planes intersect rear flow stagnation zones and grain to grain contacts, the mesh cells along the symmetry planes were also finely discretized as described above. The bulk mesh consisted of polyhedral cells (approximately $5 \mu\text{m}$ diameter), with approximately one layer of transition from the bulk mesh to the prism cells as moderated by the meshing software. In the Hemispheres-in-cell mesh, the grain to grain contact is represented by a collar of dimension ~ 7 microns in diameter and a thickness of 200 nm (100 nm on each side of the contact) (Figure 1c in the Manuscript).

Fluid flow equations

The steady-state Navier-Stokes equation under laminar flow hydrodynamics describing the fluid flow and the continuity equation can be written as follows:

$$\begin{aligned}
\rho_f \left\{ v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right\} &= -\frac{\partial p}{\partial x} + \mu \left[\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] \\
\rho_f \left\{ v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right\} &= -\frac{\partial p}{\partial y} + \mu \left[\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right] \\
\rho_f \left\{ v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right\} &= -\frac{\partial p}{\partial z} + \mu \left[\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right] \\
\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} &= 0
\end{aligned} \tag{S2}$$

where v_x , v_y , and v_z are the velocity components of the fluid in Cartesian coordinates (x, y, z) ; p is the pressure; ρ_f and μ are the density and dynamic viscosity of the fluid, respectively.

Outer fluid boundary condition

The boundary conditions for the Happel sphere-in-cell model derived directly from the streaming function in eq 2 in Rajagopalan and Tien (2) were given below in terms of spherical coordinates (v_r, v_θ, v_ϕ) :

$$\begin{aligned}
v_r &= 0, \quad v_\theta = 0, \quad v_\phi = 0 & \text{at } r = a_c \\
\left. \begin{aligned} v_r &= U \cos \theta \\ v_\theta &= \frac{U}{2} \sin \theta \left(\frac{-4 + 3\gamma + 5\gamma^3 - 6\gamma^5 + 2\gamma^6}{2 - 3\gamma + 3\gamma^5 - 2\gamma^6} \right) \\ v_\phi &= 0 \end{aligned} \right\} & \text{at } r = b \tag{S3}
\end{aligned}$$

where $\gamma = (1-\varepsilon)^{1/3}$; U is the approach velocity. In the Happel sphere –in-cell model, $v_\phi = 0$ in the entire fluid envelope ($a_c \leq r \leq b$); whereas, the grain-to-grain contact in the Hemispheres-in-cell model cause v_ϕ to vanish only in regions distant from the grain-to-grain contact. To take advantage of closed form boundary conditions (i.e. eq S3) of the outer fluid envelope in the Happel sphere-in-cell model, we adapted this boundary condition to the Hemispheres-in-cell geometry by

approximating v_ϕ equal to zero in the outer fluid boundary; whereas, v_ϕ is allowed to be non-zero inside the fluid shell (during numerical simulation of the flow field).

Comparison of the Happel sphere-in-cell to the hemisphere-in-cell geometry shows that the Hemispheres-in-cell flow field approximates two adjacent Happel flow fields, with compression of flow in the grain to grain contact. Corresponding compression of the boundary condition on the outer fluid boundary of the Happel sphere-in-cell was performed by linear re-distribution of the condition along the approximated streamline arc ([Figure S1a](#)), compressing this flow from the Happel $\pi/2$ radian arc (e.g. arc abc) to a lesser length between the planes $x = 0$ and $x = a_c$ (e.g. arc ab). This redistribution was applied to all arcs comprising the outer fluid envelop from $y = 0$ to y -values at the intersection of the two fluid envelopes. This process forces the fluid velocities at the outer fluid envelope to become tangential to the grain to grain contact plane ($x = a_c$) ([Figure S1b](#)). This approximation satisfies the non-tangential stress boundary condition on the outer fluid envelope of the hemi-sphere in cell. The lack of divergence (that is, $v_\phi = 0$) on the outer fluid envelope on the plane intersecting the grain-to-grain contact ($x = a_c$) is moderated with depth in the fluid envelope, and is expected to have negligible influence on near-surface fluid velocities.

Flow around the grain to grain contact and pressure drop

Representative flow streamlines around the grain to grain contact in the Hemispheres-in-cell model are shown in [Figure S3](#).

The lack of analytical solutions for the flow field for the Hemispheres-in-cell geometry

precludes deriving explicit velocity components that can be used to estimate pressure drop via integration of cumulative drag forces acting on the Hemispheres cell surface. Instead, the pressure differences (i.e. the difference between the minimum and maximum pressure) across a single Hemispheres-in-cell unit cell are estimated from numerical simulations of the flow field at different fluid velocities and porosities; and then fitted with an expression similar to pressure drop for the Happel's model (3). The following pressure drop-flow rate relationship across a Hemispheres-in-cell unit was obtained:

$$-\frac{\Delta P}{L} \approx \left(\frac{3 + 2\gamma^5}{3 - \frac{9}{2}\gamma + \frac{9}{2}\gamma^5 - 3\gamma^6} \right) \frac{58\mu(1 - \varepsilon)U}{d_c^2} \quad (\text{S4})$$

where $\Delta P/L$ is the pressure drop across a Hemispheres-in-cell unit; μ is the dynamic viscosity of the fluid; and $\gamma = (1 - \varepsilon)^{1/3}$. This pressure drop is approximately three times of that in the Happel sphere-in-cell model (3).

Similarly, we fitted our pressure drop with a Kozeny-Carman equation and found that the coefficient would be around 460, instead of 180 or 64 that have been reported by them (3). However, it should be noted that this is a maximum pressure drop in the unit cell, determined from the maximum and minimum pressures among all elements in the Hemispheres-in-cell mesh.

Drag forces and hydrodynamic retardation corrections

The force and torque balance requires correction for hydrodynamic retardation (expulsion of fluid between the approaching surface), which is based on classic literature (4-9). These corrections

were developed to account for influences on particle translation normal to surfaces, particle translation tangential to surfaces, and particle rotation on an axis tangential to the surface in response to simple shear flow under a laminar flow regime (low Reynolds number).

Correction of drag forces due to translational particle motion normal to the surface was implemented as follows. The normal drag force now becomes:

$$F_D^n = -\frac{6\pi\mu a_p u_n}{f_1} + 6\pi\mu a_p v_n f_2 \quad (\text{S5})$$

where F_D^n is the corrected drag force in the normal direction; u_n and v_n are the particle and fluid velocity in the normal direction, respectively; f_1 and f_2 are the universal hydrodynamic interaction functions, and their expressions are described in Johnson et al. (10). The first term on the right side is due to flow disturbance resulting from the motion of a spherical particle perpendicular to a collector surface under an applied force in an otherwise stationary fluid (4); the second term accounts for flow disturbance due to the presence of a stationary particle (7).

The balance of forces in the normal direction yields the following:

$$\left(m + \frac{2}{3}\pi a_p^3 \rho_f\right) \frac{du_n}{dt} = F_n^{GRP} - \frac{6\pi\mu a_p u_n}{f_1} + 6\pi\mu a_p v_n f_2 \quad (\text{S6})$$

where m is the particle mass; $F_n^{GRP} = F_G^n + F_L + F_{EDL} + F_{vdW} + F_B^n$, that is, F_n^{GRP} is the sum of all forces acting in the normal direction, including gravitational force (F_G^n), shear lift (F_L), electrostatic double layer (F_{EDL}), van der Waals (F_{vdW}), and Brownian forces (F_B^n). After a series of mathematical manipulations, one obtains:

$$u_n^\tau = \frac{\left(m + \frac{2}{3}\pi a_p^3 \rho_f\right) u_n^{\tau-1} + \left(F_n^{GRP} + 6\pi\mu a_p v_n f_2\right) \Delta t}{\left(m + \frac{2}{3}\pi a_p^3 \rho_f + \frac{6\pi\mu a_p}{f_1} \Delta t\right)} \quad (S7)$$

where Δt is the time step.

Correction of drag forces and torques due to particle translation tangential to the surface, and particle rotation on an axis tangential to the surface, is implemented as follows. The tangential drag force is:

$$F_D^t = 6\pi\mu a_p u_t F_t^{tr*} + 6\pi\mu a_p^2 \Omega F_t^{r*} + 6\pi\mu a_p (h + a_p) S F_t^{s*} \quad (S8)$$

where F_D^t is the corrected drag force in the tangential direction; the terms on the right represent the flow disturbance due to particle translation, rotation and shear flow, respectively, along the tangential dimension; Ω is the angular velocity; S is the shear rate; and h is the separation distance between the particle and the collector (5, 6, 8, 9).

The balance of torques acting on an axis tangential to the surface is:

$$0 = 8\pi\mu a_p^2 u_t T_y^{tr*} + 8\pi\mu a_p^3 \Omega T_y^{r*} + 4\pi\mu a_p^3 S T_y^{s*} \quad (S9)$$

where the subscript y refers to the axis of rotation (orthogonal to the tangential direction); the three terms on the right hand side account for the torque due to particle translation, rotation (y direction), and shear flow, respectively (5, 6, 8, 9). Re-arranging the torque balance yields:

$$\Omega = -\frac{\frac{1}{a_p} u_t T_y^{tr*} + \frac{1}{2} S T_y^{s*}}{T_y^{r*}} \quad (S10)$$

By defining:

$$f_3 = \frac{\frac{a_p}{2h} T_y^{s*} F_t^{r*} - F_t^{s*} T_y^{r*}}{F_t^{tr*} T_y^{r*} - F_t^{r*} T_y^{tr*}} \quad (\text{S11})$$

and

$$f_4 = \frac{T_y^{r*}}{T_y^{tr*} F_t^{r*} - F_t^{tr*} T_y^{tr*}} \quad (\text{S12})$$

and subsequently substituting Ω , f_3 , and f_4 into the tangential force balance one obtains:

$$\left(m + \frac{2}{3} \pi a_p^3 \rho_f \right) \frac{du_t}{dt} = F_t^{GRP} - \frac{1}{f_4} 6\pi\mu a_p u_t + \frac{f_3}{f_4} 6\pi\mu a_p v_t \quad (\text{S13})$$

where $F_t^{GRP} = F_G^t + F_B^t$ and $v_t = (h+a_p)S$. After additional mathematical manipulations, one

obtains:

$$u_t^\tau = \frac{\left(m + \frac{2}{3} \pi a_p^3 \rho_f \right) u_t^{\tau-1} + \left(F_t^{GRP} + \frac{f_3}{f_4} 6\pi\mu a_p v_t \right) \Delta t}{m + \frac{2}{3} \pi a_p^3 \rho_f + \frac{1}{f_4} 6\pi\mu a_p \Delta t} \quad (\text{S14})$$

Again, f_3 and f_4 are the universal hydrodynamic interaction functions, and the corresponding

expressions are described in Johnson et al. (10).

Retarded Brownian forces

The Brownian force (F_B) is modeled as a Gaussian white noise process (11-13):

$$F_B = \Re \sqrt{\frac{2\xi kT}{\Delta t}} \quad (\text{S15})$$

where $\Re$ is a Gaussian random number with zero mean and unit variance; k is the Boltzmann

constant; T is the absolute temperature; and ξ is the friction coefficient, the magnitude of which

depends on particle-surface separation distance. In the normal direction (4):

$$\xi \approx \frac{6\pi\mu a_p}{f_1} \quad (\text{S16})$$

In the tangential direction (14):

$$\xi \approx \frac{6\pi\mu a_p}{f_4} \quad (\text{S17})$$

Adaptive time steps

Two opposing constraints arising from simulation of Brownian motion and colloid-surface interaction forces must be considered in implementing the adaptive time steps. To approximate Brownian motions as a series of uncorrelated random movements (eq S15), the time step employed in the trajectory simulations should be much greater than the particle momentum relaxation time (MRT) (15-18), which is m/ξ , ξ being the friction coefficient, as described above. On the other hand, the time step should be sufficiently small such that all forces acting on the particle can be treated as constants during a time step (trajectory step) in implementing the Langevin equation (eq 2 in the Manuscript). This is especially challenging at small separation distances (<1000 nm), where colloidal interaction forces (F_{EDL} and F_{vdW}) change drastically with separation distance. Time steps that are too large will allow the colloid to move “through” an energy barrier (under unfavorable conditions) by not recognizing the full extent of repulsion corresponding to that segment of the trajectory. The lower limit of the range of Δt values between these two constraints is set by the MRT. The MRT values corresponding to our simulated particle sizes are given in Table S1. However, the MRT decreases at small separation distances as a result of increased friction near the surface relative to the bulk solution (e.g. eq S16). To evaluate the

effect of time step on deposition, simulations were run for three different particle sizes over a range of time step values (Figure S2). The simulated values of collector efficiency (η) were unaffected by time step within 1-1000 MRT. Based on these results, for the remaining simulations, we set the lower limit of Δt equal to 10 MRT and allow Δt to increase up to 1000 MRT.

Correlation equation development

A correlation equation was developed to distribute the results of numerical simulations using the Hemispheres-in-cell model under favorable conditions (absent an energy barrier). This correlation equation was regressed to mechanistic simulations of particle trajectories with all processes (i.e. diffusion, sedimentation, and interception) and forces (Table 2 in the Manuscript) operating simultaneously. The strategy to derive this equation is briefly described below, which is similar to that described in Tufenkji and Elimelech (19); however, with the advantage that the Lagrangian approach allows simple elimination of the Brownian force.

- η_I . The contribution of interception to the collector efficiency, η_I , was determined by eliminating the Brownian force (setting it equal to zero) and by eliminating the gravitational force (simulating neutrally-buoyant particles).
- η_G . The contribution of gravitational settling to the collector efficiency, η_G , was determined by difference between simulations with only Brownian force eliminated ($\eta_I + \eta_G$) versus simulations with both Brownian and gravitational forces eliminated (η_I).

Hence, $\eta_G = (\eta_I + \eta_G) - \eta_I$.

- **η_D** . The contribution of Brownian motion to the collector efficiency, η_D , was determined via the difference between the deposition rate with no processes eliminated versus that with diffusion eliminated; i.e., $\eta_D = (\eta_I + \eta_G + \eta_D) - (\eta_I + \eta_G)$.

The overall collector efficiency (η) was summed from the contributions of all three components, i.e. $\eta = \eta_I + \eta_G + \eta_D$.

Deposition rate coefficient

The relationship between the deposition rate coefficient (k_f) and the collector efficiency (η) for the Hemispheres-in-cell model was developed following the analyses of Logan et al. (20) and Nelson and Ginn (16). The particle accumulation rate on the unit collector surface ($k_f C_0 \varepsilon$) is determined as follows

$$k_f C_0 \varepsilon = r_s \beta N_c^* \quad (\text{S18})$$

where C_0 is the particle concentration in the volumetric fluid; ε is the porosity; r_s is the rate at which particles strike the collector; β is the adhesion efficiency; and N_c^* is the number of unit collectors per control volume. The rate at which particles strike the collector (r_s) is described by

$$r_s = \tilde{\eta} U C_0 A \quad (\text{S19})$$

where $\tilde{\eta}$ is the collision efficiency; U is the approach velocity; and A is the projected area of collector including the fluid shell in the Hemispheres-in-cell geometry. Unlike the Happel sphere-in-cell geometry where $A = \pi b^2$, for the Hemispheres-in-cell geometry,

$$A = \pi b^2 - 2 \left[b^2 \cos^{-1} \left(\frac{a_c}{b} \right) - a_s \sqrt{b^2 - (b - a_c)^2} \right] \quad (\text{S20})$$

Upon using the relationship (eq S1) for the Hemispheres-in-cell geometry, one obtains

$$A = \left[\frac{\pi(3-\varepsilon)}{3-3\varepsilon} - \frac{2(3-\varepsilon)}{3-3\varepsilon} \cos^{-1} \left(\frac{3-3\varepsilon}{3-\varepsilon} \right)^{1/2} + 2 \sqrt{2 \left(\frac{3-\varepsilon}{3-3\varepsilon} \right)^{1/2} - 1} \right] \frac{d_c^2}{4}, \quad (\text{S21})$$

where d_c is the collector diameter.

Like the Happel sphere-in-cell model, the Hemispheres-in-cell model also has non-physical geometry; meaning that these unit collectors cannot be stacked to construct a porous medium.

However, the collectors each have a known volume; hence, the number of collectors corresponding to a volume of porous media can be determined. The number of the Hemispheres-in-cell unit collectors per control volume is thus given by

$$N_c^* = \frac{1-\varepsilon}{\frac{4}{3} \pi a_c^3} = \frac{1-\varepsilon}{\frac{\pi d_c^3}{6}}. \quad (\text{S22})$$

Substituting the above expressions for r_s and N_c^* into the expression for $k_f C_0 \varepsilon$ and recognizing that

$U = v_p \varepsilon$, where v_p is the average pore water velocity in the unit collector, and also $\eta = \tilde{\eta} \beta$ in the

absence of an energy barrier to deposition, one obtains

$$k_f = \frac{3(1-\varepsilon)}{2d_c} \eta v_p \left[\frac{3-\varepsilon}{3-3\varepsilon} - \frac{2(3-\varepsilon)}{\pi(3-3\varepsilon)} \cos^{-1} \left(\frac{3-3\varepsilon}{3-\varepsilon} \right)^{1/2} + \frac{2}{\pi} \sqrt{2 \left(\frac{3-\varepsilon}{3-3\varepsilon} \right)^{1/2} - 1} \right]. \quad (\text{S23})$$

Variability in simulated η values

Variability in the simulated values of η decreases with increasing numbers of simulated trajectories. In [Figure S4](#), duplicate simulations involving equivalent numbers of trajectories (4000)

are shown for the conditions corresponding to panel (a) in [Figure 2 of the manuscript](#) ($\varepsilon = 0.37$, average pore water velocity = 4 m/day). The narrow error bars show the range in the duplicate simulations.

Literature Cited

1. Wakiya, S. Slow Motion in Shear Flow of a Doublet of Two Spheres in Contact. *J. Phys. Soc. Japan* **1971**, *31*(5), 1581-1587.
2. Rajagopalan, R.; Tien, C. Trajectory analysis of deep-bed filtration with the sphere-in-cell porous media model. *AIChE J.* **1976**, *22*(3), 523-533.
3. Tien, C.; Ramarao, B. V. *Granular Filtration of Aerosols and Hydrosols*; Elsevier: Oxford, 2007.
4. Brenner, H. The slow motion of a sphere through a viscous fluid towards a plane surface. *Chem. Eng. Sci.* **1961**, *16*, 242-251.
5. Goldman, A. J.; Cox, R. G.; Brenner, H. Slow viscous motion of a sphere parallel to a plane wall - I Motion through a quiescent fluid. *Chem. Eng. Sci.* **1967**, *22*, 637-651.
6. Goldman, A. J.; Cox, R. G.; Brenner, H. Slow viscous motion of a sphere parallel to a plane wall - II Couette flow. *Chem. Eng. Sci.* **1967**, *22*, 653-660.
7. Goren, S. I.; O'Neill, M. E. On the hydrodynamic resistance to a particle of a dilute suspension when in the neighborhood of a large obstacle. *Chem. Eng. Sci.* **1971**, *26*(3), 325-338.
8. Spielman, L. A., Particle capture from low-speed laminar flows. *Annual Rev. Fluid Mech.*

1977, 9, 297-319.

9. Spielman, L. A.; Cukor, P. M. Deposition of non-Brownian particles under colloidal forces. *J. Colloid Interface Sci.* **1973**, 43(1), 51-65.
10. Johnson, W. P.; Li, X.; Yal, G. Colloid retention in porous media: Mechanistic confirmation of wedging and retention in zones of flow stagnation. *Environ. Sci. Technol.* **2007**, 41(4), 1279-1287.
11. Li, A.; Ahmadi, G. Dispersion and deposition of spherical particles from point sources in a turbulent channel flow. *Aero. Sci. Technol.* **1992**, 16(4), 209-226.
12. Ounis, H.; Ahmadi, G.; McLaughlin, J. B. Brownian diffusion of submicrometer particles in the viscous sublayer. *J. Colloid Interface Sci.* **1991**, 143(1), 266-277.
13. Kubo, R. The fluctuation-dissipation theorem. *Rep. Prog. Phys.* **1966**, 29, 255-284.
14. Adamczyk, Z.; Dabros, T.; Czarnecki, J.; van de Ven, T. G. M. Particle transfer to solid surfaces. *Adv. Colloid Interface Sci.* **1983**, 19(3), 183-252.
15. Ermak, D. L.; McCammon, J. A. Brownian dynamics with hydrodynamic interactions. *J. Chem. Phys.* **1978**, 69(4), 1352-60.
16. Nelson, K. E.; Ginn, T. R. Colloid filtration theory and the Happel sphere-in-cell model revisited with direct numerical simulation of colloids. *Langmuir* **2005**, 21(6), 2173-2184.
17. Chandrasekhar, S. Stochastic problems in physics and astronomy. *Rev. Modern Phys.* **1943**, 15(1), 1-89.
18. Uhlenbeck, G. E.; Ornstein, L. S. On the theory of the Brownian motion. *Phys. Rev.* **1930**, 36,

823-841.

19. Tufenkji, N.; Elimelech, M. Correlation equation for predicting single-collector efficiency in physicochemical filtration in saturated porous media. *Environ. Sci. Technol.* **2004**, *38*(2), 529-536.
20. Logan, B. E.; Jewett, D. G.; Arnold, R. G.; Bouwer, E. J.; O'Melia, C. R. Clarification of clean-bed filtration models. *J. Environ. Eng.* **1995**, *121*(12), 869-873.
21. Tong, M.; Johnson, W. P. Excess colloid retention in porous media as a function of colloid size, fluid velocity, and grain angularity. *Environ. Sci. Technol.* **2006**, *40*(24), 7725-7731.
22. Tufenkji, N.; Elimelech, M. Breakdown of colloid filtration theory: Role of the secondary energy minimum and surface charge heterogeneities. *Langmuir* **2005**, *21*(3), 841-852.
23. Li, X.; Lin, C.-L.; Miller, I. D.; Johnson, W. P. Pore-scale observation of microsphere deposition at grain-to-grain contacts over assemblage-scale porous media domains using x-ray micro-tomography. *Environ. Sci. Technol.* **2006**, *40*(12), 3762-3768.

TABLE S1. Particle Momentum Relaxation Times (MRT)

d_p (μm)	MRT (μs)	d_p (μm)	MRT (μs)	d_p (μm)	MRT (μs)
0.04	9.40E-05	1	0.059	5	1.468
0.1	5.87E-04	1.2	0.085	6	2.114
0.2	0.002	1.6	0.150	7	2.878
0.4	0.009	2	0.235	8	3.759

0.6	0.021	3	0.529	9	4.757
0.8	0.038	4	0.940	10	5.873

TABLE S2. Predicted Versus Observed Deposition Rate Coefficients Under Favorable Conditions (Absent Energy Barriers)

particle diameter (μm)	average pore water velocity (m/day)	observed			
		k_f (h^{-1})	k_f (HS) (h^{-1})	k_f (RT) (h^{-1})	k_f (TE) (h^{-1})
0.1 ^a	2		23.9	23.4	14.9
	4	10.0	29.2	29.5	18.2
	8	20.0	35.7	37.2	22.1
0.2 ^a	2		13.8	14.8	8.6
	4	8.0	16.9	18.6	10.5
	8	14.5	20.7	23.5	12.8
0.32 ^b	19.38	9.8	36.5	44.4	22.5
0.5 ^a	2	3.7	6.8	8.1	4.2
	4	6.5	8.3	10.2	5.1
	8	7.0	10.1	12.8	6.3
	2 ^d	6.0	5.9	7.3	3.7
	4 ^d	10.0	7.3	9.1	4.5
	8 ^d	14.0	8.9	11.5	5.5
0.93 ^a	2	1.9	4.2	5.3	2.5
	4	4.0	4.8	6.5	3.1
	8	5.0	5.9	8.2	3.8
2 ^a	2	2.5	3.0	4.9	2.5
	4	4.1	3.6	5.6	2.8
	8	6.5	4.3	6.7	3.4
3 ^b	19.38	4.7	13.5	19.6	13.0
36 ^c	3.6	835	376	476	391
36 ^c	3.6 ^d	742	441	639	464
36 ^c	9 ^d	2711	480	683	522

^aData from Tong and Johnson (21); ^bData from Tufenkji and Elimelech (22) and the observed k_f values were calculated from C/C_0 ; ^cData from Li et al. (23) and the k_f values are now in h^{-1} unit; ^dIn quartz sand; all the other experiments were conducted using glass beads.

(a)

(b)

FIGURE S1. (a) Schematic of velocity vectors on the outer fluid boundary for a part of the Hemispheres-in-cell model after compression; the compression was performed by linear

re-distribution of flow from the Happel $\pi/2$ radian arc (e.g. abc) to a lesser length arc between the planes $x = 0$ and $x = a_c$ (e.g. arc ab). (b) Representative example of the velocity vectors on the outer fluid boundary for the Hemispheres-in-cell model generated from Star-ccm+.

FIGURE S2. Simulated collector efficiencies (η) at various time steps using three representative particle sizes under favorable conditions. The other parameters were listed in Table 1 in the Manuscript. The values of η remained relatively unaffected when time step was set within the range of 1-1000 MRT.

FIGURE S3. Representative flow streamlines around the grain to grain contact in the Hemispheres-in-cell model. The upper velocity bar refers to flow lines at symmetry plane $x = a_c$ and the lower velocity bar refers to flow lines at plane $y = 0$.

FIGURE S4. Simulated and predicted collector efficiencies as a function of particle size for $\varepsilon = 0.37$ and average pore water velocity = 4 m/day. Error bars show range of η values from duplicate

simulations involving 4000 trajectories.