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Stochastic Modeling of Kaolinite Transport through a Sand Filter

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ABSTRACT

Accurately modeling the transport of clay particles through coarse-grained porous media is essential to engineering applications ranging from filtration and drainage, groundwater flow modeling, to contaminant transport. However, predicting the retention and clogging behavior of clay particles within a coarse-grained soil matrix is extremely challenging because clay particles can aggregate and form clusters with a variety of fabrics depending on the prevailing geochemistry of the pore fluid (i.e., pH and ionic strength). The work performed in this study developed a stochastic model to investigate the uncertainty of clay particle transport in porous media using random sampling at given grain size distribution to account for inherent uncertainty of the size of clay clusters being transported. Results demonstrated that the model proposed in this work can evaluate upper and lower boundaries of retention profiles of clay particles in a sand medium at given mean and standard deviation of grain size distributions. In addition, the deterministic approach (using median sizes of sand and clay particles in the simulation) underestimated of the mass of retained particles at small size ratios of clay particle size/sand particle size when compared to the stochastic prediction, which would result in nonconservative design.

Keywords: stochastic; clay particle; grain size distribution; random sampling; retention profile;

1. Introduction

Physical clogging of soil filters is significant in the long-term performance of geotechnical and geoenvironmental infrastructure and is especially critical due to the complexity in predicting the reduction in pore space and conductivity caused by clogging. If the size of the pore can be predicted, then prediction of hydraulic conductivity, using existing equations/theories such as Kozeny Carman equation (Chapuis and Aubertin 2003; Choo et al. 2018) and particle dynamics in cylindrical tubes (Reddi et al. 2005; Happel and Brenner 2012; Won and Burns 2017) is relatively straight forward. In order to predict the clogging behavior and the reduction of hydraulic conductivity, the transport/retention behavior of particles in porous media should be studied. To date, much of the work in modeling the retention behavior of soil particles have focused on the dispersed state, rather than clusters of particles; however, when the clogging material is clay particles, aggregation and flocculation can have significant impacts on the retention behavior of clay particles because of increase in their size due to the aggregation. Therefore, it is necessary to accurately model the retention behavior of clay particles under a variety of geochemical conditions and states of aggregation in order to fully understand clogging phenomena.

Clay minerals are commonly encountered natural colloidal particles, and the prediction of retention of clays in a sand filter is complex because of the sensitivity of clay particles to pore solution chemistry (Jang and Santamarina 2016). In addition to the typical factors that can impact particle retention (i.e., degree of saturation, ionic strength, flow rate, and surface roughness of the filtration media) (Saiers and Lenhart 2003; Torkzaban et al. 2007; Torkzaban et al. 2015; Bradford et al. 2015), the polydispersity (i.e., multi-sizes) of clay clusters, must also be taken into account to fully predict transport behavior. The relative size of transporting colloidal

particles versus the filter sand particles is one of the key factors controlling retention profiles and breakthrough curves. Because different size ratios impact not only straining phenomena due to variations in geometry, but also the interaction energy between the clays and the sand (Bradford et al. 2011), the aggregated and/or flocculated structure of the transporting clays can have significant control on clogging of the filter (or bed) material.

Using monodispersed particles in a particle transport experiment and median grain size (d_{50}) of sand in the particle transport model is appropriate to represent the semi-monodispersed particle (e.g., pathogenic bacteria), but may not be valid for the transport of polydispersed particles such as clays, which are present in nature with highly variable sizes. The coefficient of uniformity (C_u , measure of the range of grain sizes) for the sand particles and clay particles can frequently be as high as ten in natural systems (Mitchell and Soga 2005), which implies that d_{50} is not a sufficient descriptor of grain size and the polydispersed characteristics of both the clay and the filtration medium (sand or gravel) should be considered in the transport/retention of clay particles. Additionally, clay particles aggregate into four different types of fabric formations as a function of solution chemistry (i.e., pH and ionic strength): edge-to-face particle association, edge-to-edge particle association, face-to-face particle association, and combined face-to-face and edge-to-face association (Palomino and Santamarina 2005). Determining the precise size of a clay cluster is challenging, particularly under the condition of geochemical perturbations, which in turn leads to complexity in predicting particle transport through the subsurface. Therefore, a stochastic model is needed to account for the uncertainty of the sizes of transporting clay clusters and polydispersed characteristics of clay particles and sand.

To date, a number of stochastic models have been documented, which mathematically describe random physical properties of porous media and colloids including pore size

distribution, pore length, and flow characteristics of porous media (Cortis et al. 2004; Berkowitz et al. 2006; Cortis 2007; Boano et al. 2007; Bedrikovetsky 2008), chemical heterogeneity (Tufenkji et al. 2003), and attachment rate coefficient (Bradford and Toride 2007). However, no stochastic model is available for modeling the effect of size variability of sand and clay particles on the transport of clay particles through a sand filter with addressing attachment, detachment, and straining: mainly mechanisms for colloid transport in saturated porous media (Bradford et al. 2003).

This study investigated the inherent uncertainty of clay particle retention profiles in a sand filter medium with variability in the size of both the sand and the clay particles. Sizes of clay and sand were determined using Metropolis-Hastings sampling and Latin Hypercube sampling at given distributions. Experimental grain size distributions of clay and sand were fitted to the best lognormal distribution (least square fit), and the sampled clay and sand were then used in the numerical calculations. The calculation was first performed based on the lab scale experimentally determined grain size distribution and experimental conditions, followed by a sensitivity analysis.

2. Mathematical model

2.1 Particles transport in saturated porous media

The governing equations for advection-dispersion including attachment, detachment, and straining mechanisms for particle transport in saturated porous media are expressed as (Bradford et al. 2003):

$$\frac{\partial(nC)}{\partial t} = -U \frac{\partial C}{\partial z} + \frac{\partial}{\partial z} \left(nD \frac{\partial C}{\partial z} \right) - nk_{att}\psi_{att}C + \rho_b k_{det}S_{att} - nk_{str}\psi_{str}C \quad (1)$$

$$\rho_b \frac{\partial S}{\partial t} = nk_{att}\psi_{att}C - \rho_b k_{det}S_{att} + nk_{str}\psi_{str}C \quad (2)$$

where n (-) is porosity, C (ML^{-3}) is the particle concentration in aqueous phase, t (T) is time, U (LT^{-1}) is the Darcy velocity, z (L) is the depth, D (L^2T^{-1}) is the dispersion coefficient, k_{att} (T^{-1}), k_{det} (T^{-1}) and k_{str} (T^{-1}) are the attachment, detachment, and straining coefficients respectively, ψ_{att} (-) and ψ_{str} (-) are the attachment and straining functions, ρ_b (ML^{-3}) is the bulk density, and S , S_{att} , and S_{str} (MM^{-1}) is the solid phase concentration of total retained particles, attached particles, and strained particles respectively. Note that n is set equal to the volumetric water content (θ_w) in this work, assuming that all particles in the aqueous phase are accessible to the water.

Available sites for particle attachment on the surface of the sand may decrease over time as attached particles block access to the surface, and most of the particle straining will take place at the surface layer of the filter medium, due to the pore size restriction. To account for these two mechanisms in Eq. (1), ψ_{att} (Treumann et al. 2014; Sun et al. 2015) and ψ_{str} (Bradford et al. 2003) may be written as:

$$\psi_{att}(r_c, r_s) = 1 - \frac{S_{att}}{S_{max}(r_c, r_s)} \quad (3)$$

$$\psi_{str} = \left(\frac{d_{s50} + z}{d_{s50}} \right)^{-\beta} \quad (4)$$

where S_{max} (MM^{-1}) is the maximum mass of particles that can be attached to the unit mass of sand, d_{s50} (L) is the median size of sand, and β (-) is a fitting parameter ($\beta = 0.43$ (Bradford et al. 2003)). From a geometrical standpoint, S_{max} at given r_c and r_s may be expressed assuming that the shapes of the sand and clay particles (or clusters) are spherical (Won and Burns 2017):

$$S_{max}(r_c, r_s) = \left(\frac{r_c^3 G_s^c}{r_s^3 G_s^s} \right) \cdot \left(\frac{1}{1 + e_c} \right) \cdot \left(\frac{N_{max}^2 - 8N_{max}}{4} \right) \quad (5)$$

where r_c (L) and r_s (L) are the radius of clay particle (or cluster) and sand respectively, G_s^c (-) and G_s^s (-) are specific gravity values of clay and sand respectively, e_c (-) is the void ratio of clay cluster to account for the void in aggregated clay particles, N_{max} (-) is the maximum number of clay particles or clusters that can contact the sand surface in the two-dimensional domain, calculated by the sine law. In addition, the empirical expression of k_{str} (T^{-1}) at given r_c and r_s used in this work is expressed as (Bradford et al. 2003):

$$k_{str}(r_c, r_s) = 4.495 \left(\frac{r_c}{r_s} \right)^{1.42} \quad (6)$$

2.2 DLVO and k_{att} calculation

The attachment coefficient, k_{att} , presented in Eq. (1) can be obtained by calculating the Derjaguin-Landau-Verwey-Overbeek (DLVO) interaction energy combined with colloid filtration theory (Bradford et al. 2011). Note that non-DLVO forces such as Born repulsion or hydration forces were not considered in this calculation. Under the condition of $r_s \gg r_c$, the total interaction energy (G) between the clay particles and sand can be expressed as (Israelachvili 2011):

$$G(r_c) = G_{DL}(r_c) + G_{VDW}(r_c) = (r_c Z \exp(-\kappa H)) + (-A_{swc} r_c / 6H) \quad (7)$$

where G_{DL} (ML^2T^{-2}) and G_{VDW} (ML^2T^{-2}) are interaction energies attributed to double layer repulsion and van der Waals attraction respectively, Z (ML^2T^{-3}) is an interaction constant that is a function of surface potential of the sand and clay, κ (L^{-1}) is a reverse of Debye length as a function of ionic concentration and valence, H (L) is the separation distance, and A_{swc} (ML^2T^{-2})

is the Hamaker constant in sand-water-clay system calculated by the refractive indices and dielectric constants of those three materials.

Particles can attach to the primary minimum when the secondary minimum energy is relatively low, and the energy barrier is sufficiently low for particles to overcome it. To account for the attachment at both the primary and secondary minimums, the following was used (Shen et al. 2007):

$$\alpha(r_c) = \alpha_{pri}(r_c) + \alpha_{sec}(r_c) = 1 - \int_{\frac{\sqrt{\Delta\Phi(r_c)}}{\sqrt{\Delta\Phi_{sec}(r_c)}}}^{\sqrt{\Delta\Phi(r_c)}} \frac{4}{\pi^{0.5}} x^2 \exp(-x^2) dx \quad (8)$$

where $\alpha_{pri}(-)$ and $\alpha_{sec}(-)$ is the attachment efficiency attributed to the primary minimum and the secondary minimums, $\Delta\Phi(-)$ is a sum of Φ_{max} and Φ_{sec} (Φ_{max} is maximum interaction energy at the energy barrier and Φ_{sec} is interaction energy at the secondary minimum, Φ_{max} and Φ_{sec} are interaction energies normalized by kT , where k ($ML^2T^{-2}K^{-1}$) denotes the Boltzmann constant, and T (K) denotes the absolute temperature), and $x^2(-)$ is the dimensionless kinetic energy of particles. In colloid filtration theory, k_{att} at given r_c and r_s is estimated as (Raychoudhury et al. 2014):

$$k_{att}(r_c, r_s) = \frac{3(1 - \theta_w)}{2d_{s50}} \alpha(r_c) \eta_0(r_c, r_s) v_s \quad (9)$$

where $\alpha(-)$ is the attachment efficiency, $\eta_0(-)$ is the single-collector collision efficiency obtained by a sum of collision efficiencies of particles associated with diffusion, interception, and gravitational effects (Rajagopalan and Tien 1976; Tufenkji and Elimelech 2004), and v_s (LT^{-1}) is the average seepage velocity. The value of η_0 in this study was obtained by the correlation equation proposed by Tufenkji and Elimelech (Tufenkji and Elimelech 2004). Employing Eqs. (8)

and (9) provides an analytical calculation of k_{att} in Eq. (1) as a function of r_s and r_c (η_0 is a function of r_s and r_c , and $\Delta\Phi$ is a function of r_c).

2.3 Sampling procedure from grain size distribution of sand and clay

Two sampling techniques were implemented to sample clay particles and sand at given lognormal distributions: the Metropolis-Hastings algorithm (Metropolis et al. 1953), which was used to implement Markov chain Monte Carlo analysis, and the Latin Hypercube Sampling (LHCS) method originally proposed by McKay et al. (1979). These two methods were chosen to compare the fit generated by sampling algorithms based on fundamentally different approaches. For the sampling, a fit of the lognormal cumulative distribution function (CDF) to the experimental grain size distribution curves using least squares yielded the target lognormal distributions. Experimental grain size distributions were determined by hydrometer testing (ASTM D422) for clay particles (Georgia kaolinite), and by sieve analysis (ASTM C136) for sand particles (ASTM 20/30 sand).

A key mathematical expression of the Metropolis-Hastings algorithm is given as:

$$u < \Gamma(x_s, x^*) = \min\left\{1, \frac{p(x^*)}{p(x_s)}\right\} \quad (10)$$

where s is an integer between 1 and $N-1$, u is a random number generated from 0 to 1, $p(x)$ is the probability at target CDF corresponding to the value x , x_s is the value of s^{th} sampling, x^* is the random number generated based on the proposal function (q) at given x_s ($q(x^* | x_s)$ is a normal distribution centered at x_s). If the condition in Eq. (10) is satisfied, x_{s+1} is equal to x^* , otherwise, $x_{s+1} = x_s$ with the continuous iteration of the algorithm until s reaches the given sampling size (N).

In contrast, the LHCS method is a technique fundamentally different from the common Monte Carlo method because it provides a constraint for evaluating evenly distributed samples at the target CDF, even at relatively small N . The mathematical formulation of constraint in the LHCS method is given as:

$$P_m = \left(\frac{1}{N}\right)u_m + \left(\frac{m-1}{N}\right) \quad (11)$$

where m is an integer between 1 and N , u_m is the random number generated from 0 to 1 in each m , P_m is the random probability value at target CDF for the m^{th} interval located between $1/N$ and $(m-1)/N$. Generated random P_m values in Eq. (11), which ensure evenly distributed sampling values in target CDF, were used to evaluate samples from the inverse CDF (F^{-1}):

$$x_m = F^{-1}(P_m) \quad (12)$$

For the Metropolis-Hastings algorithm, it potentially generates identical values successively if selected x^* fails to satisfy the condition in Eq. (10), while each sampled value is unique in the LHCS method and well distributed throughout the target CDF regardless of N . Therefore, the LHCS method is a more efficient method to describe grain size distributions than Metropolis-Hastings sampling, particularly under low N (Fig. 1). Nevertheless, Metropolis-Hastings sampling was also used in this work to account for the inherent uncertainty of sizes of clay particles during transport. This is especially important because the sizes of clay clusters may not follow the original grain size distribution when chemical conditions change or at high hydrodynamic forces, which can increase or decrease the effective size of the clay cluster. The randomness of Metropolis-Hastings sampling at given CDF provides an implementation of the transport simulation using random sizes of clay particles or clay clusters in a reasonable range

(Fig. 1). Sampling in this work was performed within the 95% confidence interval of corresponding normal PDF for the target lognormal PDF in order to avoid physically unacceptable size ratios between sand and clay (i.e., $r_c/r_s > 1$ can occur for sampling without the confidence interval).

2.4 Numerical procedure

The Picard iteration (Celia et al. 1990; Huang et al. 1998) was used in each time step to solve Eq. (1) numerically (forward in time and centered in space). This provided iterations until 0.1 % accuracy for C in all discretized depths was reached. If the assumed blocking theory was valid in particle attachment (Eq. (3)), i.e., the attachment between particles and attached particles on the sand is neglected primarily due to identical surface charge characteristics of the particle and the sand, then sampled r_c and r_s at given N_{rc} and N_{rs} (N_{rc} and N_{rs} here indicate the sampling size for r_c and r_s) may be applied independently to calculate concentration $C_{ij}(z,t)$, where i and j indicate i^{th} sampled r_c and j^{th} sampled r_s respectively. To account for the independent calculation for any sampled r_c or r_s , a uniform distribution for the probability of r_c or r_s was used. This uniform distribution is valid because the target CDF is from the mass-based grain size distribution. Hence, total inlet mass-based concentration of particles at any given time ($C_0(t)$) can be decomposed to the inlet boundary concentration of particles for i^{th} r_c and j^{th} r_s ($C_{0ij}(t)$):

$$C_{0ij}(t) = C_0(t)p(r_c)p(r_s) = C_0(t)\frac{1}{N_{rc}}\frac{1}{N_{rs}} \quad (13)$$

Using a backward Euler method, Eq. (1) can be rewritten as:

$$n^{q+1} \frac{C_{ij}^{q+1} - C_{ij}^q}{\Delta t} = -U \frac{\partial C_{ij}^{q+1}}{\partial z} + \frac{\partial}{\partial z} \left(n^{q+1} D_{ij} \frac{\partial C_{ij}^{q+1}}{\partial z} \right) - n^{q+1} (k_{att})_{ij} \psi_{att}^{q+1} C_{ij}^{q+1} + \rho_b (k_{det})_{ij} (S_{att})_{ij}^{q+1} - n^{q+1} (k_{str})_{ij} (\psi_{str})_j C_{ij}^{q+1} \quad (14)$$

Note that the U and the ρ_b are independent of the sampled r_c or r_s because all simulations were under constant flow rate and ρ_b are only dependent on n if G_s^s is constant. The attachment coefficients, k_{att} and k_{str} , can both be expressed as a function of r_c and r_s (Eqs. (6) and (9)). η_0 in Eq. (9) was determined from r_c and r_s , which led to k_{att} values as a function of r_c and r_s (details in (Tufenkji and Elimelech 2004) for the η_0 calculation), and ψ_{str} is expressed here as a function of the sampled diameter of sand d_s ($d_s = 2 \times r_s$) to replace d_{s50} in Eq. (4). In addition, dispersivity in the transverse direction can be neglected when water flows in one direction, the dispersion coefficient D_{ij} can be expressed as:

$$D_{ij} = \tau D_{m(i)} + \alpha_{L(ij)} v_s \quad (15)$$

where τ is the tortuosity factor ($= n^{m-1}$, derived from Archie's equation (Sahimi 1993; Boudreau 1996), n is porosity and $m = 1.3$ for unconsolidated sand (Archie 1942)) (-), D_m is molecular diffusion coefficient ($= kT / (6\pi\mu r_c)$), described by Stokes-Einstein equation, μ is the dynamic viscosity of water ($ML^{-1}T^{-1}$), and r_m is the atomic radius (cm)), α_L is the longitudinal dispersivity (L), and v_s is the seepage velocity ($L T^{-1}$). α_L was calculated using the expression in Delgado (2007), which is a function of D_m and Peclet number (see detail in Delgado (2007)).

The ψ_{att} and n in Eq. (14) was globally updated every time step without reflecting the number of sampled r_c and r_s (note that ψ_{att} and n is expressed as ψ_{att}^{q+1} and n^{q+1} in Eq. (14) respectively without i and j) because polydispersed particles are transporting at the same time. In addition, porosity n was updated globally for the calculation in next time step:

$$n(z,t) = \frac{n_0 G_c - G_s(1 - n_0) \sum_i \sum_j ((S_{str}(z,t))_{ij} + (S_{att}(z,t))_{ij})}{G_c} \quad (16)$$

where G_c (-) and G_s (-) are the specific gravity values of clay and sand respectively, and n_0 (-) is the initial porosity of sand medium. Note that r_{c50} and r_{s50} were adopted for the S_{max} calculation in Eq. (5) herein to be consistent with taking ψ_{att} as a global function.

η_0 in Eq. (9) is defined as the ratio between the rate of colloid successful collision with a single grain and the rate of approach advective colloid flux to the projected area of the grain (Yao et al. 1971; Rajagopalan and Tien 1976). Therefore, it is physically unrealistic that the single collector collision is larger than 1 (the rate of colloids collision should be equal to or smaller than the rate of colloid flux). However, η_0 is occasionally larger than 1 based on the calculation of relatively high r_c / r_s ratio. Hence, any η_0 larger than 1 caused by the high size ratio was set equal to 1. In addition, $(k_{det})_{ij}$ was assumed to $0.05 \times (k_{att})_{ij}$ for all simulations implemented in this work. Coefficients for attachment and straining $((k_{att})_{ij}$ and $(k_{str})_{ij})$ can then be determined as a function of grain size (sand and clay or clay cluster) (Fig. 2), with the numerical procedure summarized in Fig. 3. The visualization of filtration of clay particles in deterministic approach and stochastic approach at relatively low size ratio (close to dispersed state) is also illustrated in Fig. 4.

2.5 Experimental procedure

The results of two cases from soil column experiments performed using Georgia kaolinite as the clay colloidal medium and ASTM 20/30 as the sand medium were compared to the numerical results as presented in Fig. 5. The column experiments were performed as follows: 10 pore volumes (PV) of kaolinite suspension at concentration of $1 \times 10^{-3} \text{ g / cm}^3$ was injected into the sand column (30.48 cm long). A constant Darcy velocity of $U = 7.3 \times 10^{-2} \text{ cm / s}$ was applied

using a peristaltic pump at the top of the column, and the inflow suspension was stirred continuously using a magnetic stirrer during the injection to prevent the kaolinite particles or clusters from settling. After injection, the amount of retained kaolinite particles was evaluated by sampling the retained mass of kaolinite in each 2.54 cm layer of sand (see details for the experimental procedure in Won and Burns (2017)). In the column test presented in Fig. 5, CaCl_2 was used as the background electrolyte. Possible errors of the column experiments would be the pulsation effect (pulsation energy generated by the peristaltic pump) and preferential flow at the interface between sand and the rigid wall.

To accurately sample r_c and r_s within the experimental conditions, target CDFs for sand and clay were obtained based on the results of sieve analysis for the ASTM 20/30 sand and the hydrometer test for kaolinite particles and clusters. Because a highly uniform sized sand was used in the experiment, the median grain size of the sand was used as the representative diameter in the simulation (i.e., $N_{rs} = 1$).

3. Results and discussion

3.1 Simulated retention profile compared to experimental results

To demonstrate the validity of the outlined model quantitatively, the simulated retention profile was compared with the experimental retention profile obtained through the soil column experiments. Prediction of the retention profiles using the sampled r_c from the lognormal-fit (target CDF) with $\text{IS} = 3 \times 10^{-1}$ and 3×10^{-3} M (clay particles were in the flocculated state) was comparable to the experimentally observed retention profile (Fig. 5). The discrepancy between these two simulated retention profiles is attributed to an increase in the k_{att} and k_{str} values as the size ratio increased (Fig. 2); that is, the smaller sizes of kaolinite cluster at $\text{IS} = 3 \times 10^{-1}$ M led to

a decrease in straining and increase in attachment because of smaller size ratio and larger attraction energy. This resulted in a less exponential retention profile at $IS = 3 \times 10^{-1}$ M in experimental and modeled retention profiles. These results demonstrate that the solution geochemistry and aggregation behavior of clay particles must be included to properly predict retention profiles of clay within sand filtration media, which is especially important because small changes in the retention profile of the clay particles can have significant impact on the hydraulic conductivity of the soil. Clearly, predicting the retention profile of clay particles is challenging, particularly under heterogeneous solution chemistry or changing geochemical conditions (e.g., de-icing salt runoff in winter conditions) due significant changes in the size of clay clusters that form during transport. To investigate the uncertainty of the retention profiles, further simulations were performed up to 10 PV of injection under $C_0 = 1$ g / L.

3.2 Uncertainty of the retention profile using the Metropolis-Hastings algorithm

The uncertainty of the retention profile caused by random sizes of clay particle clusters was investigated, using the radius of the clay clusters (r_c) sampled by the Metropolis-Hastings algorithm at the given target CDF. To consider the randomness of the sampled r_c in the simulation, N_{rc} was fixed to 100 in order to use the random nature of the Metropolis-Hastings algorithm (Fig. 1). The low number for N_{rc} here was because a larger number of N_{rc} ($> 10^4$) led to the more complete representation of the target CDF by sampled r_c , which meant that the Metropolis-Hastings sampling and the LHCS method showed similar results for large N_{rc} . In Metropolis-Hastings sampling, the starting point of sampling was fixed to μ_c to avoid the burn-in period and have equal probabilities of jumping in $r_c < \exp(\mu_c)$ and $r_c > \exp(\mu_c)$ in the first iteration of the sampling. One hundred sets of simulations were performed with $N_{rc} = 100$, which satisfied the median value of r_{c50} equal to target CDF.

The frequency of r_{c50} in each set of sampling with $N_{rc} = 100$ using Metropolis-Hastings algorithm is shown in Fig. 6. In seventy-five sets, r_{c50} was less than $0.6 \mu\text{m}$, while in twenty-five sets, r_{c50} was larger than $0.6 \mu\text{m}$. In the extreme case, r_{c50} used in one particular simulation ranged between $5 \mu\text{m}$ and $6 \mu\text{m}$ and r_{c50} values in three sets were larger than $2 \mu\text{m}$. Consequently, sampled r_c with large r_{c50} resulted in high mass retention profiles (Fig. 7). The large r_{c50} values in the simulation for particle transport reflected the uncertainty of r_c in the retention behavior. The maximum retention profile in Fig. 7 (when $5 \mu\text{m} < r_{c50} < 6 \mu\text{m}$, Fig. 6) can significantly overestimate the retention profile at a given CDF, but 99 % of the whisker lines in each depth indicated that large uncertainty still existed for prediction of the retention of clay particles (see stochastic in Fig. 7 for the range of possible retention profiles at given conditions). Moreover, the shapes of box plots in each discretized space were at least qualitatively consistent with the histogram (Fig. 6), which implies that the distribution of stochastic retention profiles follows the shape of grain size distribution of clay particles (Fig. 5).

In addition, the retention profile evaluated by the deterministic approach (i.e., $N_{rc} = N_{rs} = 1$, Fig. 7) was much lower than the mean or median retention profile. Median cluster size $[r_{c50}]$ (Fig. 6) was used in the deterministic calculation, indicating that the deterministic approach may potentially underestimate the retention profile, particularly when kaolinite particles aggregate and form clusters. The variation of the deterministic retention profile and the median or mean retention profile was less significant as C_u of the clay particles decreased (discussed in the sensitivity analysis, next section).

3.3 Sensitivity analysis

As mentioned earlier, the C_u of a soil can range from 1 (uniformly graded particle size) to higher than 10 (well-graded particle size). Setting $\sigma_c \approx 1.52$ ($\mu_c \approx -0.93$) for the target CDF (Fig.

7) corresponds to $C_u \approx 10$, which represents a well-graded soil. Therefore, in order to investigate the effect of grain size distribution shape on the retention profile at constant μ_c (i.e., constant r_{c50}), a sensitivity analysis was performed with σ_c (or σ_s) = 1.5, 1.4, 1.2, 1.0, 0.5 and 0.1, which corresponded to $C_u = 10, 8.57, 6.3, 4.64, 2.15$ and 1.16 (ranging from soils that are well-graded to almost perfectly uniform). The LHCS method was utilized as the sampling technique for all simulations in the sensitivity analysis in order to represent grain size distributions effectively for sand and clay at the relatively small sampling size (Fig. 1).

The simulated retention profiles and breakthrough curves according to the σ_c under identical r_{c50} and r_{s50} ($\sigma_s = 0$) demonstrate the importance of grain size distribution on particle retention (Fig. 8 and Fig. 9). Because the LHCS method provided $r_{c50} = \exp(\mu_c)$, regardless of the sampling size, in contrast to the randomness of sampling in the Metropolis-Hastings algorithm (Fig. 6), the LHCS method ensured the reproducibility of the retention profiles and the breakthrough curves under a particular σ_c . Retention profiles and breakthrough curves approached the deterministic values as σ_c decreased. In other words, as the grain size distribution of the clay particles was more well graded, the deterministic retention profile was more underestimated (nonconservative) and the deterministic breakthrough curve was more overestimated. The inconsistency of the retention profiles and breakthrough curves according to σ_c revealed that the grain size distribution of clay particles must be considered an important factor for the transport/retention behavior of clay particles in porous media. For example, the overestimation of the breakthrough curve by the deterministic approach (Fig. 9) may result in the overestimated transport of contaminants that are favorably adsorbed by clay particles because there will be more particle retention than predicted. Likewise, the underestimation of the

retention profile by the deterministic approach led to the underestimation of the reduction of hydraulic conductivity in the sand medium.

The variation of the retention profiles or breakthrough curves between the deterministic and the stochastic approaches would be altered according to the r_{c50} / r_{s50} ratio and the polydispersity of particles and sand. The retention profiles and the breakthrough curves presented (Fig. 8 and Fig. 9) were performed with $r_{c50} / r_{s50} \sim 0.001$ and $N_{rs} = 1$, which cannot fully represent various r_{c50} / r_{s50} ratios and the polydispersity of sand; consequently, the retention profiles were also evaluated under three sampling conditions: 1) $N_{rc} = 1$ and $N_{rs} = 10^3$, 2) $N_{rc} = 10^3$ and $N_{rs} = 1$, and 3) $N_{rc} = 10^2$ and $N_{rs} = 10^2$. In order to investigate the variation of the amount of retained particles, the total amount of retained particles in all discretized depths (S_{sum}) in six r_{c50} / r_{s50} ratios were normalized by S_{sum} in the corresponding ratio in the deterministic approach (Fig. 10). The LHCS method was employed here with $u_m = 0.5$ in Eq. (11) for the reproducibility of results, and both σ_c and σ_s were equal to 1 in all simulations.

The trend of normalized S_{sum} according to the r_{c50} / r_{s50} ratio in the three sampling conditions was comparable. In addition, values of normalized S_{sum} were larger than 1 in the three sampling conditions for all r_{c50} / r_{s50} ratios except $r_{c50} / r_{s50} > 5.6 \times 10^{-3}$ in $N_{rc} = 10^3$, $N_{rs} = 1$ and $N_{rc} = 10^2$, $N_{rs} = 10^2$. Most of the particles were retained at high r_{c50} / r_{s50} ratio in both the deterministic and stochastic approaches, leading to less difference under relatively high r_{c50} / r_{s50} ratio. Therefore, the deterministic approach significantly underestimated the amount of retained particles, particularly under low r_{c50} / r_{s50} ratio (Fig. 10). Additionally, the result demonstrated that the underestimation of normalized S_{sum} in the deterministic approach was most significant when $N_{rc} = N_{rs} = 100$. This indicated that the polydispersed characteristics of clay and sand should be reflected in the analysis instead of reflecting the characteristics of only one material.

Note that the values of normalized S_{sum} for $N_{rc} = 10^2$ and $N_{rs} = 10^2$ were underestimated for $r_{c50} / r_{s50} \geq 0.0056$ because of the applied restriction in the simulation (Fig. 10): any sampled r_s smaller than 10 times of maximum sampled r_c was set equal to 10 times of maximum sampled r_c .

The limitation of the model used in this work was the failure to calculate k_{det} in Eq. (1) analytically and the assumption of $k_{\text{det}} = 0.05k_{\text{att}}$ in all simulations. In addition, the shape of clay particles or clusters and sand were approximated as spherical and the numerical calculation implemented in this work may not be valid if clay particles continue to aggregate or disperse during transport/retention.

4. Conclusion

This study explored the inherent uncertainty in clay particle transport/retention in a sand medium by developing a stochastic model for interaction between clay particles and a sand filter medium. Two sampling techniques were used to reflect the polydispersed characteristics of the particles and the sands, and they provided a plausible range of retention profiles and accurate estimation of grain size distributions. Comparison between the resulting retention profiles that were evaluated using the deterministic and stochastic sizes for sand and clay revealed that the retention profile with only median sizes of sand and clay was significantly underestimated when the grain size distribution of sand and clay were more well graded. This effect was more noticeable under relatively small r_{c50} / r_{s50} ratio, which represented a well-dispersed clay particle system (i.e., less aggregation of clay particles). In addition, the high uncertainty of the retention profile under random sampling of r_c at a given target CDF implied that a wide range of retention profiles may result if the aggregated sizes of clay particles were not modeled. Therefore, the

stochastic approach used in this work can be beneficial to account more realistically for the transport of polydispersed particles such as clay.

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Figure captions

Fig. 1. Sampling under $N = 50$ using the Metropolis-Hastings algorithm and the LHCS method at the target lognormal CDF from the clay colloids grain size distribution, where μ and σ are mean and standard deviation of log-normally fitted target CDF, r_{c50} is the median value of sampled r_c , and R^2 is the coefficient of determination between the CDF and the experimental grain size distribution. The experimental grain size distribution was obtained by hydrometer test using Georgia kaolinite in a solution of ionic strength $= 3 \times 10^{-3}$ M (CaCl_2). Unexpectedly high r_{c50} was observed in this sampling for Metropolis-Hastings algorithm due to the relatively small N , while r_{c50} evaluated by LHCS method was almost identical to the r_{c50} in the lognormal CDF and well distributed to the target CDF, even under small N .

Fig. 2. Example calculation of k_{att} and k_{str} as a function of r_c and r_s when $N_{rc} = N_{rs} = 1000$. Both k_{att} and k_{str} nonlinearly increase as r_c / r_s ratio decreases. The target lognormal PDFs used in the calculation were $\mu_s = 5.17$, $\sigma_s = 0.34$, $\mu_c = -0.93$, and $\sigma_c = 1.52$ (μ and σ indicate mean and standard deviation of normal PDF corresponding to the target lognormal PDF, subscript s = sand, c = clay), $r_{c50} \approx 0.47 \mu\text{m}$, and $r_{s50} \approx 181.27 \mu\text{m}$. The Metropolis-Hastings algorithm was used for sampling.

Fig. 3. Numerical procedure of the stochastic model proposed in this work.

Fig. 4. A schematic drawing of the filtration of monodispersed versus polydispersed clay particles in a sand medium at relatively low size ratio. A deterministic approach significantly underestimates the amount of retained clay particles at low size ratio (refer to Fig. 10).

Fig. 5. (a) Experimental grain size distributions and corresponding target CDFs and (b) Observed and simulated retention profiles. Metropolis-Hastings algorithm used here with $N_{rc} = 10^4$ and $N_{rs} = 1$, and $r_{s50} = 360 \mu\text{m}$, $U = 7.3 \times 10^{-2} \text{ cm / s}$, $n_0 = 0.365$.

Fig. 6. The histogram of r_{c50} in 100 sets of random sampling using the Metropolis-Hastings algorithm when $N_{rc} = 100$. The median value of r_{c50} ($\text{Med}[r_{c50}]$) was almost equal to the median value of the target CDF (Fig. inside), which indicates that the combination of 100 sets of sampling was well distributed to the target CDF without biased toward the one direction.

Fig. 7. Maximum, minimum, and mean of simulated retention profile along with the box plot and retention profile from deterministic r_c and r_s (i.e. $N_{rc} = N_{rs} = 1$) with respect to 100 sets of sampled r_c (Fig. 5). The edges of the boxes correspond to 25% and 75% coverage, and the central line in the boxes represents the median value of retained particles in each discretized spatial point. The whisker line of each box plot indicates 99 % coverage for a distribution in each depth.

Fig. 8. Simulated retention profiles according to the different σ_c (or C_u) under constant μ_c and μ_s (i.e. r_{c50} and r_{s50}). LHCS method was used here with $N_{rc} = 1000$ and $N_{rs} = 1$ ($r_s = 360 \mu\text{m}$). Note the deterministic approach underestimated retention, which may underestimate hydraulic conductivity reduction.

Fig. 9. Simulated breakthrough curves according to the different σ_c (or C_u) under constant μ_c and μ_s . Note the deterministic approach underestimated the mass retention, which can result in over prediction of clay particle transport.

Fig. 10. Normalized S_{sum} according to r_{c50} / r_{s50} ratios under three different simulated conditions.

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(a) Metropolis-Hastings algorithm

(b) LHCS method

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