Collision Frequencies of Fractal Aggregates with Small Particles by Differential Sedimentation

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Two groups of aggregates with fractal dimensions of 1.81 ± 0.09 and 2.33 ± 0.07 were generated by coagulation of latex microspheres (2.84 μm) in a jar test (paddle-mixing) device. The collision rates between these fractal aggregates (200–1000 μm) and small (1.48 μm) particles were measured for individual aggregates that had settled through a suspension of the small particles. Aggregate permeabilities calculated from measured settling velocities were 3 orders of magnitude greater than predicted by a permeability model based on a homogeneous distribution of primary particles within the aggregates. Collision efficiencies of small particles by settling aggregates were <0.2% based on the total volume of water swept out by an aggregate. Fluid collection efficiencies, collision frequencies, and particle capture efficiencies of the fractal aggregates decreased with the magnitude of fractal dimensions. A fractal permeability model was developed by modifying the Brinkman correlation to describe the permeability as a function of aggregate size. This model was used in conjunction with a filtration model to predict capture rates and capture efficiencies of small particles by settling fractal aggregates. Based on these experiments and models, it is argued that the high aggregate permeabilities and the low overall particle capture efficiencies of fractal aggregates can be explained by flow through macropores formed between large clusters within the aggregates.

Introduction
The capture of suspended small particles by fast-settling porous aggregates is of interest in the description of particle transport in natural waters as well as in water and wastewater treatment systems. As these aggregates fall, they may permit fluid to flow through their porous interior, and some small particles in the internal flow will collide with and attach to the aggregates. Previous models have shown that flow through the interior of highly porous aggregates will increase collision rates and therefore coagulation rates between the aggregates and small particles (1–3). However, two important components of these models have not been well established through experiments relative to the fractal properties of aggregates: models of the aggregate permeability during settling and the capture efficiency of suspended particles by the aggregate during fluid flow through the aggregate interior.

Experimental measurements have demonstrated that aggregates settle much faster than predicted by Stokes’ law (4–6), indicating that intra-aggregate flow reduces the drag for aggregates compared to that for the equivalent impermeable particles. These observations are consistent, however, with the settling velocities predicted using models based on the aggregates being composed of small spheres homogeneously distributed within the aggregates. These permeability models predict that aggregates would settle only slightly faster than predicted by Stokes’ law (6–8). Thus, the permeability correlations used in previous studies must underestimate aggregate permeabilities and intra-aggregate flow rates. The failure of these models to describe the aggregate permeability is likely due to the assumption of a uniform distribution of primary particles throughout an aggregate.

Substantial research indicates that aggregates produced by coagulation are fractal (9–11). Fractal aggregates have a heterogeneous mass distribution, a structure resulting from the coagulation of small and more densely packed clusters into larger and overall less dense aggregates (6). Macropores formed between these clusters within a fractal aggregate will permit greater interior flow through the aggregate, resulting in a faster settling velocity and much more suspended small particles flowing into the aggregate. Existing permeability models must be modified to incorporate this non-homogeneous (fractal) distribution of primary particles comprising the aggregate.

The second consideration for describing particle capture by a permeable aggregate is that not all small particles in the fluid flowing through the aggregate will be captured by the aggregate. In many previous studies, it was assumed that all particles entering the aggregate were completely scavenged, that is, the removal efficiency of suspended particles was unity (1, 3, 12). While this assumption is reasonable when the aggregate is densely packed or for large particles entering the aggregate, it is not necessarily true for small particles. Large pores within a fractal aggregate may permit many small particles to flow through the aggregate without colliding with the material that forms the aggregate. This small particle capture efficiency of the settling fractal aggregate has not been previously investigated.

In the present work, we report the first measurements of collision frequency functions between settling fractal aggregates (200–1000 μm) and small (1.48 μm) particles and the capture efficiencies of these small particles by the aggregates. By comparing measured aggregate settling velocities with those predicted by Stokes’ law, a fractal permeability correlation was derived. Using fractal mathematics and filtration theory, we proposed a fractal collision model to describe the capture of small particles by fast-settling fractal aggregates.

Methods

Experimental Section. Generation of Fractal Aggregates. The aggregates used in settling–coagulation experiments were produced using red dyed latex microspheres 2.85 μm in diameter with a density of 1.05 g cm⁻³ (Polysciences). Aggregation of red microspheres (−10⁻⁷ M⁻¹) was conducted in 200 mL of a 0.34 M (2.0%) NaCl solution in a jar test device (Model 7790-400, Phipps and Bird) using flat paddles (7.6 × 2.5 cm²) at 10 rpm, which produced an average shear rate of 6.2 s⁻¹. Four batches of aggregates (A1, A2, B1, and B2) were produced using two different conditions by adjusting the solution pH using acids and bases. For the generation of group A aggregates (batches A1 and A2), 0.1 mL of HCl (0.95 M) and 1 mL of buffer (pH = 2, Baxter, 7732-18-5) were first added into the solution, resulting in a stable pH of ~5. After...
16 h, 0.3 mL of NaOH (0.66 M) and 2.5 mL of buffer (pH = 10, Fisher, SO-B-115) were added to raise the solution pH to ∼8.5; aggregates were then rapidly formed and were collected after 4 h of coagulation. Group B aggregates (batches B1 and B2) were generated by adding 0.3 mL of NaOH (0.66 M) and 2 mL of buffer (pH = 10) into a solution, producing a stable pH of ∼8.5; aggregates were formed more slowly and were collected after 20 h. Due to the relative rates of coagulation under these conditions, aggregates in group A can be considered as being formed by fast coagulation relative to those in Group B.

Settling Column and Settling–Coagulation Experiments. Settling–coagulation experiments were performed in a glass settling column 3.15 cm in diameter, containing a narrow tube at the top to transfer aggregates into the column (total settling distance was 25 cm) and a retrieval well at the bottom to recover the aggregates. The column was similar to the settling column previously used (6) except that an additional plate 1.2 cm in height, called a screen plate, was inserted between the column and the retrieval well. This screen plate contained an open channel 3.2 cm in diameter and was intended to keep the bulk particle suspension in the column separated from the liquid in the retrieval well as described below. All three separate sections (column, screen, retrieval well) of the settling apparatus could be slipped on and off. The apparatus was designed so that when the column was moved to one side it remained filled. Silicon lubricating grease was used to seal all contacting surfaces to prevent leakages.

Three solutions were placed into the three separate sections before each experimental run. The column was filled with a 0.34 M NaCl solution containing 10^6 mL^{-1} of yellow-green (YG) fluorescent latex microspheres 1.48 μm in diameter with carboxylate surface groups (Polysciences). The solution had a pH of 8.5 and a density of 1.012 g cm^{-3} at room temperature (22–23 °C). The screen channel was filled with a pure 0.34 M NaCl solution (without YG beads), while the retrieval well was filled with a slightly denser (0.44 M) pure NaCl solution. These three sections were then carefully slipped together to form a single concentric tube. This arrangement of different solutions in different sections permitted aggregates that settled through the YG bead suspension to pass through a bead-free zone before settling into a solution kept free of YG beads in the retrieval well.

After the settling apparatus was completely assembled, individual aggregates generated from red beads in the Jar-test device were gently transferred into the top of the settling column using a rubber dropper bulb with a 1-mL pipet tip cut midway between its ends. To ensure that the water within the aggregate had exactly the same salinity and pH as the liquid in the settling column, the aggregate was transferred in series through three separate beakers filled with water identical to that placed in the column prior to being placed into the settling column. The time for the aggregate to traverse the 5-cm distance in the settling column at a depth of 19–24 cm below the release point was recorded to calculate the aggregate settling velocity, U. After the aggregate reached the bottom of the retrieval well, the column and the screen plate were slowly pushed to the side and removed, leaving the aggregate in the well for subsequent analysis. Aggregates that broke up during settling or any transfer step were discarded.

Aggregate Characterization. The cross-sectional area of an aggregate, A, was measured by placing the well base containing the aggregate on a microscope (Olympus BH-2) stand for sizing using an image analyzer (ScanArray II, Galai). Aggregate size was calculated as an equivalent diameter using

\[ d_{e} = (4A/d)^{1/2} \]

where \( A_{0} \) is the projected area of the aggregate. The number of YG fluorescent beads captured by the aggregate, \( P_{w} \), was then counted using the fluorescence microscope under blue light.

After sizing and counting, the aggregate was transferred into a container containing 4 mL of isotonic solution (Coulter) and sonicated for 2 h to completely breakup the aggregate. A Coulter particle counter (Multisizer II, Coulter) was used to measure the total solid volume of the red beads, \( V_{r} \), which composed the aggregate.

Collision Efficiency (α) between the Red and YG Beads. The method to measure \( \alpha \) between the red and YG beads was similar to that detailed in Jiang and Logan (13). Briefly, the experiment was conducted in the jar-test device at a mean shear rate of \( G = 20 s^{-1} \). The same NaCl solution used in the settling column was used to prepare a particle solution containing \( N_{r} = 3.6 \times 10^{5} mL^{-1} \) of red beads and \( N_{YG} = 5 \times 10^{6} mL^{-1} \) of YG beads. At various time intervals (t ≤ 90 min), a 2-mL sample was withdrawn and filtered through a 0.2-μm filter and viewed under a microscope using both white (for red beads) and blue (for YG beads) lights. Based on a rectilinear expression for the coagulation in turbulent shear (13, 14), \( \alpha \) between the red and YG beads was calculated from the change rate of the singular YG bead concentration using

\[ \ln \left( \frac{N_{YG}}{N_{YG(0)}} \right) = - \frac{1}{8} \left( d_{r} + d_{YG} \right) N_{r} \alpha \ \text{ct} \]

where \( d \) refers the diameter of respective beads and \( N_{YG(0)} \) is the initial YG bead concentration. This approach works because at a pH of 8.5 the YG beads are stable; it was verified in separate experiments that coagulation between YG beads could be neglected. In addition, by using a lower concentration of red beads (1/7th the concentration of YG beads), the coagulation rate of red beads with each other was much smaller than that between YG and red beads.

The rectilinear collision efficiency was determined as \( \alpha_{rec} = 0.0947 \). According to the numerical solutions provided by Han and Lawler (15), in these experimental conditions the curvilinear collision rate between the red and YG beads was only \( 0.4 \times \) the rectilinear prediction, or \( \alpha = \alpha_{rec} \times 0.4 = 0.237 \).

Theoretical Section. Collision Frequency Function for Permeable Fractal Aggregates. For a heterodisperse particle suspension, a Smoluchowski-type description of the kinetics of particle aggregation can be expressed in the discrete form (16) as

\[ \frac{dN_{r}}{dt} = \frac{1}{2} \sum_{i \neq j} \alpha(i,j)N_{i}N_{j} - N_{r} \sum_{i \neq j} \alpha(i,j) \beta(i,k)N_{i}N_{k} \]

where \( N_{r}, N_{v}, \) and \( N_{a} \) are the number concentrations of particles of size classes \( i, j, \) and \( k, \) respectively, \( \beta(i,j) \) and \( \beta(i,k) \) are collision frequency functions between particles of the size classes indicated, and \( \alpha(i,j) \) and \( \alpha(i,k) \) are corresponding collision efficiencies. Collisions can be generated by Brownian motion, shear, and differential sedimentation, but for large settling aggregates collisions produced by Brownian motion and shear can be neglected.

For a binary system composed of two sizes of particles, large aggregates of diameter \( d_{a} \) and small particles of diameter \( d_{s} \), the first term on the right-hand side of eq 2 can be dropped since there is no production of small particles. Initially, the rate of change in the small particle concentration, \( N_{p}, \) is

\[ \frac{dN_{p}}{dt} = -\alpha(a,p)\beta(a,p)N_{p} - \alpha(p,p)\beta(p,p)N_{a} \]

where a and p are subscripts referring to the aggregates and the smaller particles. The first term on the right-hand side of eq 3 describes the loss of the small particles by coagulation with the aggregates. The rate of these small particles captured by a single aggregate, \( R_{c} \), can thus be written as
Several models have been developed to describe the collision frequency function, \( \beta \), a function that is supposed to incorporate all physical factors affecting collisions between particles. In actuality, any inaccuracies in predicting \( \beta \) from a model are commonly included into \( \alpha \). In order to distinguish between these models, a subscript is added to \( \beta \) when it is predicted by the rectilinear (\( \beta_{\text{rec}} \)), curvilinear (\( \beta_{\text{cur}} \)), and fractal (\( \beta_{\text{fract}} \)) models, while \( \beta \) without a subscript indicates a measured collision function. Only collisions generated by differential sedimentation are considered below.

The collision frequency function between a large, fast-settling aggregate and much smaller, slow-settling particles according to the rectilinear model (17, 18) is

\[
\beta_{\text{rec}} = \frac{\pi}{4} d_p^2 U
\]

where \( U \) is the settling velocity of the aggregate, \( \beta_{\text{rec}} \) is therefore the rate that fluid approaches the settling aggregate of diameter \( d_p \) and \( \beta_{\text{rec}} N_p \) is the number of small particles that approach the aggregate per unit time.

The curvilinear collision model, in which hydrodynamic interactions and short-range forces between particles are taken into account, can be used to more accurately describe \( \beta \) for impermeable particles (15, 16). The collision frequency calculated using the curvilinear collision function, \( \beta_{\text{cur}} \), is smaller than the rectilinear collision kernel by a factor \( \alpha \), or

\[
\beta_{\text{cur}} = \alpha \beta_{\text{rec}}
\]

(6)

Based on Han and Lawler's numerical solution (15)

\[
e_{\text{cur}} = \exp[-3.4 + 0.62 \log(\gamma) + 1.2 \log(\gamma)] \quad (\text{for } \gamma < 0.01)
\]

(7)

where \( \lambda \) is \( d_p/d_a \), \( \gamma = 8A/(3\pi Ud_a^2) \), and \( A \) is the Hamaker constant, assumed here to be \( 4 \times 10^{-20} \), although Han and Lawler's results were not sensitive to the value of \( A \). This Hamaker constant is typical of particles in water (16) and is the same value used by Han and Lawler.

Flow through a highly porous fractal aggregate can significantly increase collision frequencies between the aggregate and suspended small particles as compared to those predicted by the curvilinear model. In order to derive a collision model for a fast-settling fractal aggregate, we introduce a fractal factor, \( e_{\text{fract}} \), to relate \( \beta_{\text{rec}} \) to \( \beta_{\text{fract}} \) as

\[
\beta_{\text{fract}} = e_{\text{fract}} \beta_{\text{rec}}
\]

(9)

The number of small particles contained in the fluid flowing through the aggregate interior per unit time is \( e_{\text{fract}} N_p \).

The fluid collection efficiency of an aggregate, \( e \), is calculated as the ratio of the interior flow passing through an aggregate to the flow approaching it. Not all particles in the fluid entering an aggregate will collide and attach to the aggregate. Defining \( e \), as the particle removal efficiency from the intra-aggregate flow, the rate of small particles captured by the aggregate can be written as

\[
R_c = e e_p \beta_{\text{rec}} N_p
\]

(9)

Combining eqs 4, 8, and 9, we obtain

\[
e_{\text{fract}} = \frac{e e_p}{\alpha}
\]

(10)

(10)

The ratio \( e/\alpha \) is actually the fraction of small particles in the flow passing through an aggregate that collides with the aggregate. Since \( \alpha \) is normally included in the filtration equation that will be used to calculate \( e_p \), \( \alpha^{-1} \) is included in eq 10 so that it will be removed from the general coagulation rate expression given in eq 4.

The overall small particle capture efficiency by a settling aggregate, \( E \), is calculated as the ratio of the particles captured by the aggregate to the total particles approaching it, or

\[
E = \frac{R_c}{(\beta_{\text{rec}} N_p)}
\]

Substituting eq 9 for \( R_c \) produces

\[
E = e e_p
\]

(11)

The fluid collection efficiency, \( e \), can be obtained from previous theoretical work describing the movement of the fluid around and through a porous aggregate as isothermal creeping flow of an incompressible, Newtonian fluid (19). When Brinkman's extension of Darcy's law is used to describe the interior flow, the fluid collection efficiency of the aggregate is given (8, 20) by

\[
e = \frac{q(1 - \tanh \xi)}{2\xi^2 + 3(1 - \tanh \xi)}
\]

(12)

where \( \xi = d_p/(2\sqrt{\nu}) \) and \( \nu \) is the permeability of the aggregate. In order to use eq 12 for fractal aggregates, a proper permeability correlation needs to be developed.

Fractal Aggregate Permeability. The permeability of a porous material is a function of porosity and the structure of the medium. Many models have been developed for calculating aggregate permeabilities. One of the most frequently used models for highly porous aggregates is the Brinkman model (21)

\[
x_{\text{Brinkman}} = \frac{d_p^3}{72} \left[ 3 + \frac{4}{1 - \epsilon} - 3 \sqrt{\frac{8}{1 - \epsilon} - 3} \right]
\]

(13)

where \( d_p \) is the diameter of primary particles within the aggregate and \( \epsilon \) is the porosity of the aggregate. Brinkman's model, like other permeability models, assumes a homogeneous distribution of primary particles throughout an aggregate. This assumption is not valid for fractal aggregates.

In order to incorporate the heterogeneous structure of fractal aggregates into an expression of aggregate permeability, eq 13 is modified by relating the pore distribution of a fractal aggregate to the aggregate size. The solid volume of a fractal aggregate, \( v_s \), is a function of its characteristic size, \( d_b \), according to

\[
v_s = cd_b^D
\]

(14)

where \( D \) is a fractal dimension and \( c \) is a coefficient that can also be a function of \( D \) (22). The porosity of the fractal aggregate, \( \epsilon \), is therefore

\[
\epsilon = 1 - \frac{6c}{\pi} d_b^{D-3}
\]

(15)

For a closely packed Euclidean structure \( D = 3 \), and the porosity everywhere in the aggregate is constant. In contrast, the primary particles within a fractal aggregate are not uniformly distributed. They are distributed according to a hierarchical structure such as the self-similar structure shown in Figure 1. At each decreasing hierarchical level, the parts of a fractal aggregate are composed of successively smaller units (clusters). The size of the largest clusters, defined here as the principal clusters that directly form the aggregate, is on average related to the size of the whole aggregate. We assume here a general power law relationship between the
sizes of the principal clusters, \( d_c \), and the aggregate \( d_a \) as

\[
d_a = sd_c^b
\]

where \( b \) and \( s \) are empirical coefficients.

Within fractal structures, such as the one shown in Figure 1 in two dimensions, there are increasingly larger gaps or pores formed by the clusters (9, 23). It is our hypothesis that the high permeability of an aggregate is produced by flow through the largest pores, or macropores, between the large (principal) clusters. Thus, the largest pores dictate the overall aggregate permeability, and flow within those clusters can be neglected. Replacing \( d_{cap} \) of the primary particles in eq 13 with \( d_c \) of the principal clusters (assumed to be impermeable), the permeability of a fractal aggregate becomes

\[
\kappa_{frac} = \frac{5^2 d_a^{2b}}{72} \left[ 3 + \frac{4}{1 - \epsilon} - 3 \sqrt{\frac{8}{1 - \epsilon} - 3} \right]
\]

(17)

According to this model, the permeability of a fractal aggregate is solely a function of its size, porosity, and distribution of the largest (principal) clusters within the aggregate. Using aggregate porosity calculated for each aggregate of size \( d_a \) from \( \epsilon = 1 - 6c/(\pi d_a^3) \) and aggregate permeability calculated from the settling velocity (see below), the coefficients \( b \) and \( s \) can be determined from a linearized form of eq 17

\[
\frac{1}{2} \log \left[ \frac{72k}{3 + \frac{4}{1 - \epsilon} - 3 \sqrt{\frac{8}{1 - \epsilon} - 3}} \right] = b \log (d_a) + \log (s)
\]

(18)

Small Particle Removal Efficiencies by Fractal Aggregates from the Interior Flow (\( \epsilon_{int} \)). There is no analytical solution of \( \epsilon_{int} \) for a fractal aggregate. In order to estimate \( \epsilon_{int} \) for a fractal aggregate, we modified a model describing particle filtration by a porous medium. According to the one-dimensional filtration equation of Yao et al. (24), the fraction of mono-sized small particles in the interior flow captured after flowing a distance \( L \), assumed here to be the aggregate diameter \( d_a \), is

\[
e_p = 1 - \exp \left( \frac{-3}{2} \frac{(1 - \epsilon)}{d_c} \alpha_{int} \sqrt{d_a} \right)
\]

(19)

where \( d_c \) is the diameter of the particles forming the porous medium, defined as the size of principal clusters, \( \eta \) is the single collector efficiency, and \( \alpha_{int} \) is the particle sticking coefficient between the material comprising the aggregate (red beads) and the particles (YG beads) in the fluid flowing through the aggregate. Since \( \alpha_{int} \) incorporates any inaccuracies in predicting collector efficiency, \( \alpha_{int} \) may be different from the \( \alpha \) measured in a coagulation test. Three particle transport processes (diffusion, interception, and sedimentation) regulate the collector efficiency \( \eta \). Detailed derivation and analytical solutions for the calculation of \( \eta \) and comparisons of this filtration model with experimental data are available elsewhere (25–27). Substituting eq 16 into eq 19 produces

\[
e_p = 1 - \exp \left( \frac{-3}{2s} \frac{(1 - \epsilon)}{d_a} \alpha_{int} \sqrt{d_a} \right)
\]

(20)

Combining eqs 5, 8, 10, 12, and 20, we obtain the expression for the collision frequency function between a fractal aggregate and small particles as

\[
\beta_{frac} = \frac{9 \pi \alpha_{int}^2 U \left(1 + \tanh \left( \frac{3}{2s} \frac{1 - \epsilon}{\epsilon} \right) \right)}{4 \alpha_{int} \left(2s^2 + 3 \left(1 - \tanh \left( \frac{3}{2s} \frac{1 - \epsilon}{\epsilon} \right) \right) \right)}
\]

(21)

The fractal collision model is based on our assumption that the rate of collisions between the aggregate and small particles occurring on the outer surface of the aggregate are negligible compared to that occurring within the aggregate interior. This assumption will be validated by demonstrating that the small particle capture efficiency of a settling aggregate is an order of magnitude higher than that expected from an analysis using a curvilinear model for an aggregate assumed to be an impermeable sphere.

Calculation of Model Parameters from the Experiments. The permeability of a fractal aggregate was calculated from its settling velocity. Flow through the aggregate interior increases the aggregate settling velocity as compared to the calculation from Stokes’ law since the interior flow reduces the aggregate drag. The ratio of the actual settling velocity of the aggregate \( (U) \) to the predicted Stokes’ settling velocity of an equivalent impermeable sphere \( (U_{imp}) \) is given (7, 28) by

\[
\frac{U}{U_{imp}} = \left( \frac{\pi}{\frac{3}{2s}} \right) \left( 1 - \tanh \left( \frac{3}{2s} \frac{1 - \epsilon}{\epsilon} \right) \right)
\]

(22)

Thus, measurement of \( U, d_a, \) and \( \epsilon \) for each aggregate results in a data set between these parameters and \( \beta \), and therefore for \( \kappa \), using eq 22. The fluid collection efficiency of the aggregate, \( \epsilon_{int} \), is calculated from eq 12.

Assuming that the rate of small particles captured by a falling aggregate, \( R_a \), described in eq 4 is constant over a short time \( t \), where \( t = H/U \) (the time for an aggregate to settle a distance \( H \) at the velocity \( U \)), the number of the particles captured by the falling aggregate is thus \( P_{t} = R_a t \) or

\[
P_{t} = \frac{\alpha_{int} H N_a}{U}
\]

(23)

In these experiments, the total height of YG bead suspension in the column was \( H = 25 \) cm, \( \alpha = 0.237 \), and a YG bead concentration of \( N_a = 10^8 \text{mL}^{-1} \). Thus, the collision frequency function \( (\text{cm}^2/\text{s}) \) between the aggregate and YG beads is calculated from eq 23 as

\[
\beta = 1.7 \times 10^{-7} P_{t} U
\]

(24)
The overall fractal dimension of aggregates in group A aggregates for the same reason (slope comparison, batches B1 and B2 aggregates were combined into "group B" previously, they were combined into "group A" aggregates, while fractal dimensions (slope comparison, condition were not significantly different in terms of their aggregates generated in four separate batches were successively recovered and analyzed. From the slopes of the regression lines, \( D_A = 1.81 \pm 0.09 \) for group A aggregates and \( D_B = 2.33 \pm 0.07 \) for group B aggregates.

During the settling of an aggregate from the top to the bottom of the settling column, the total number of YG beads approaching the aggregate is \( N = \left( \frac{7}{4} \right) d_H^2 N_p \). The overall small particle capture efficiency of the aggregate, \( E = P/a P_{ag} \), is therefore

\[
E = \frac{5 \times 10^{-5} P_c}{d_a^2} \tag{25}
\]

From eq 11, the removal efficiency of small particles by an aggregate from the intra-aggregate flow is \( E_p = E/e \) or

\[
e_p = \frac{5 \times 10^{-5} P_c}{e d_a^2} \tag{26}
\]

Results

Fractal Dimensions. A total of 210 latex microsphere aggregates generated in four separate batches were successfully recovered and analyzed. From the slopes of the regression lines in Figure 2, the fractal dimensions were \( 1.80 \pm 0.13 \) and \( 1.85 \pm 0.14 \) for the aggregates in batches A1 and A2, respectively, and \( 2.37 \pm 0.09 \) and \( 2.33 \pm 0.12 \) for the aggregates in batches B1 and B2, respectively. Batches A1 and A2 aggregates produced under the same coagulation condition were not significantly different in terms of their fractal dimensions (slope comparison, \( p > 0.79 \); 29). Therefore, they were combined into "group A" aggregates, while batches B1 and B2 aggregates were combined into "group B" aggregates for the same reason (slope comparison, \( p = 0.77 \)). The overall fractal dimension of aggregates in group A (\( D_A = 1.81 \pm 0.09 \)) was significantly (slope comparison, \( p < 10^{-5} \)) lower than that of aggregates in group B (\( D_B = 2.33 \pm 0.07 \)). The solid volume data indicate that aggregate porosities were generally greater than 92%. Aggregates in group A had higher porosities than those in group B, and the differences in the porosity between these two aggregate groups became larger as aggregates increased in size.

Permeabilities and Fluid Collection Efficiencies of Fractal Aggregates. The observed settling velocities of aggregates in both groups A and B were higher than predicted by Stokes' law for impermeable spheres of identical size and mass (Figure 3), an observation consistent with lower drag coefficients and higher permeabilities of fractal aggregates (6, 30). Group A aggregates on average had higher \( U/U_{imp} \) ratios (2.84 \pm 1.00) than group B aggregates (2.39 \pm 0.79) (t-test, \( p < 0.03 \)) (Figure 4), suggesting that aggregates with a lower fractal dimension had higher permeabilities than the similarly sized aggregates with a higher fractal dimension.

The \( U/U_{imp} \) ratios calculated from the original Brinkman’s permeability model assuming a uniform porosity within aggregates were close to unity and significantly lower than the measured data (Figure 4). The difference between theoretical and observed \( U/U_{imp} \) ratios indicates that the permeability correlations derived for a homogeneous distribution of primary particles in a porous medium incorrectly describe the permeability function of fractal aggregates.

Aggregate permeabilities were calculated using data in Figure 4 and eq 22, as shown in Figure 5. The permeabilities of the aggregates in group A increased with size more rapidly than those in group B (slope comparison, \( p < 0.01 \)). On average, group A aggregates had greater permeabilities, \( 2.7 \pm 2.5 \times 10^{-4} \) cm/s than group B aggregates, \( 2.0 \pm 1.6 \times 10^{-4} \) cm/s, although the permeability for a specific aggregate size varied widely. These permeabilities calculated from settling velocity data were nearly 3 orders of magnitude larger than those calculated using the original Brinkman permeability model.

Based on the permeabilities derived from settling velocities, the two empirical coefficients in eqs 17 and 18 were determined as \( b = 0.439 \pm 0.056 \) and \( s = 0.056 \pm 0.008 \), producing the fractal permeability function (cm/s) for an aggregate of size \( d_a \) (cm)

\[
\kappa = 4.4 \times 10^{-5} \left( \frac{d_a}{c} \right)^{0.88 \left( \frac{2 \pi d_a^{3-D}}{3c} - 3 \sqrt{\frac{4 \pi d_a^{3-D}}{3c} - 3} \right)}
\tag{27}
\]

The average size of the principal clusters within the aggregate is related to the aggregate size by \( d_c = 0.056 d_a^{0.44} \).
Using the permeability data and eq 12, fluid collection efficiencies of the aggregates, $e_f$, were determined to vary from 0.08 to 0.83 (Figure 6), indicating that a large fraction of the fluid approaching an aggregate flowed through the aggregate. On average, aggregates in group A had greater $e_f$ values (0.54 $\pm$ 0.14) than those in group B (0.46 $\pm$ 0.15) ($t$-test, $p < 0.01$).

Collision Frequency Functions. Group A aggregates ($D_A = 1.81$) captured more than twice the number of YG beads than equally-sized group B aggregates ($D_B = 2.33$) during settling tests (Figure 7a). As a result, group A aggregates had a greater collision frequency with YG beads than group B aggregates (Figure 7b). $\beta$ for the aggregates in group A increased with size more rapidly than that in group B based on a comparison of slopes ($p < 0.05$).

Collision frequency functions between aggregates and YG beads were 1 order of magnitude higher than predicted by the curvilinear collision model and 2 orders of magnitude lower than predicted by the rectilinear collision model for the aggregates of identical sizes and settling velocities (Figure 7b). The rectilinear model overestimates $\beta$ since it does not account for hydrodynamic interactions and short-range forces between approaching particles. In contrast, the curvilinear model underestimates $\beta$ since it does not include a mechanism for flow through the aggregate interior.

YG Bead Removals ($e_p$) and Overall YG Bead Capture Efficiencies ($E$) of Fractal Aggregates. Not all YG beads in the fluid flowing through the interior of a fractal aggregate successfully attached to the aggregate. In fact, $<1\%$ of the beads in the intra-aggregate flow were removed by the aggregates (Figure 8a). Group A aggregates generally had higher bead removal efficiencies, $e_p$, than group B aggregates.

In order to reconcile the measured particle removals with the interior flow through the aggregates calculated from the permeabilities derived from settling velocities, the filtration equation (eq 19) was used to estimate bead removal efficiencies, $e_p$. When the same collision efficiency of $\alpha = 0.237$ determined for red and YG beads in the shear coagulation experiment was used as the particle sticking coefficient, i.e., $\alpha_{filt} = 0.237$, the calculated bead removals were lower than those observed (Figure 8a). Flow through the aggregates can be reconciled with filtration theory by assuming a larger sticking coefficient of $\alpha = 3$ (Figure 8b). Previous studies have demonstrated that the filtration model underestimates the number of collisions occurring in porous media, and greater than unity sticking coefficients have been observed for completely destabilized particles (26, 31, 32).

Based on the total volume of water swept out by a settling aggregate (according to the rectilinear model), the overall bead capture efficiencies of the fractal aggregates, $E$, ranged from 0.00024 to 0.0017. Aggregates in group A had greater E values than those in group B (Figure 9). If $\alpha = 3$ was again used, the predictions based on the filtration model show much better agreement with the data.

Discussion

Measured collision frequencies between settling fractal aggregates and small microspheres were 1 order of magnitude greater than predicted by a curvilinear collision model that assumed the aggregates were impermeable spheres. The magnitude of the fractal dimension of aggregates had an inverse impact on the collision rates of the aggregates with small particles. The differences between the observed and predicted collision frequency functions, $\beta$ and $\beta_{out}$, likely resulted from the high aggregate permeability produced by a heterogeneous fractal distribution of primary particles within
calculated using Brinkman’s permeability model would be around \( k \approx 10^{-7} \) cm², approximately 3 orders of magnitude lower than those derived from the observed settling velocities. The predicted fluid collection efficiencies based on the homogeneous permeability model were around \( \eta_a \approx 0.04 \), about 2 orders of magnitude lower than experimental measurements.

Although greater permeabilities of fractal aggregates increased the collision frequencies between the aggregates and suspended particles, the observed \( \beta \) values were still 2 orders of magnitude lower than predicted by the rectilinear model. For YG beads in the intra-aggregate flow, \(<1\%\) of the beads was removed by the aggregates, suggesting that \(<4\%\) beads in the internal flow eventually collided with the aggregates (based on \( \alpha = 0.237 \)). Macropores can account for the higher settling velocities of fractal aggregates than those of impermeable spheres, but the large sizes of these pores mean that all small particles in the intra-aggregate flow would pass through the aggregate without contacting the clusters forming the aggregate.

It was assumed in many previous theoretical studies that all suspended particles in the fluid flowing through an impermeable aggregate would be captured by the aggregate, i.e., \( \eta_a = 1 \). Stolzenbach (2) used a simplified filtration equation to estimate the fraction of small particles scavenged by falling porous aggregates. However, his calculation based on a homogeneous distribution of primary particles within an aggregate produced \( \eta_a \approx 1 \) in most cases. These \( \eta_a \) values may be reasonable for large suspended particles or when the aggregates are densely packed, but they are inconsistent with the experimental data of \( \eta_a \approx 1 \) calculated in this study. Thus, using values of \( \eta_a = 1 \) for fractal aggregates would overestimate the small particle removal efficiencies.

To reconcile particle removal fractions with the intra-aggregate flow calculated from measured settling velocities, it was necessary to increase \( \alpha \) from 0.237 to 3. Theoretically, these two \( \alpha \) values should be equal since \( \alpha \) only indicates the success of attachment after collisions and not the context of those particle interactions. However, it is well known from experiments with porous media and completely destabilized suspended particles that the filtration model can underestimate collector efficiencies, \( \eta \) (31). To incorporate the inaccuracies in models of \( \eta \), \( \alpha \) values greater than unity have been used. For instance, Logan et al. (26) reported \( \alpha = 1.1 \) for experiments by others for destabilized latex microspheres and a quartz medium, and Martin et al. (32) measured maximum \( \alpha \) values in the range of 2–4 between quartz particles and bacteria in high ionic strength solutions.

Another factor that may have contributed to the underpredictions of bead removals by falling aggregates was that the principal clusters within an aggregate were treated as impermeable medium granules. Due to the hierarchical structure of fractal aggregates, principal clusters consist of smaller clusters that likely also have fluid to flow through their interiors. From both experimental measurements and theoretical predictions (Figure 8a,b), the small particle removal efficiency from the intra-aggregate flow increased as the aggregates decreased in size. Since the principal clusters within a fractal aggregate were many times smaller than the aggregate, these clusters might have greater particle removal efficiencies than the aggregate. Although the quantity of flow through the interior of the principal clusters might not significantly contribute to the overall permeability of an aggregate during settling, this flow could be important for filtration calculations.

In summary, fractal aggregates were considered to be composed of relatively large, dense clusters. The measured settling velocities that were much faster than predicted by a homogeneous permeability model could be explained by flow...
through macropores formed between these clusters within fractal aggregates. Fluid flowing through the aggregates significantly increased collision frequencies between the aggregates and suspended small particles, and these collision frequencies decreased with the magnitude of the fractal dimension. Large macropores within the fractal aggregates also allowed a majority of small particles in the interior fluid to flow through the aggregates without contacting the aggregates. Thus, <0.2% of small particles in the fluid presumably swept out by a settling aggregate was captured by the aggregate.

Acknowledgments
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Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>A_o</td>
<td>cross-sectional area of an aggregate</td>
</tr>
<tr>
<td>b</td>
<td>empirical constants defined in eq 16</td>
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<tr>
<td>c</td>
<td>constant defined in eq 14</td>
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<tr>
<td>D</td>
<td>fractal dimension</td>
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<tr>
<td>d</td>
<td>particle diameter</td>
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<tr>
<td>E</td>
<td>overall particle capture efficiency of an aggregate</td>
</tr>
<tr>
<td>( \theta_{cur} )</td>
<td>curvilinear reduction factor relative to the rectilinear collision kernel defined in eq 6</td>
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<td>( \epsilon_r )</td>
<td>fluid collection efficiency of an aggregate</td>
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<tr>
<td>( \theta_{frac} )</td>
<td>fractal collision kernel defined in eq 8</td>
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<tr>
<td>( \epsilon_p )</td>
<td>particle removal efficiency from intra-aggregate flow</td>
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<tr>
<td>G</td>
<td>mean shear rate</td>
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<tr>
<td>H</td>
<td>traveling distance of a settling aggregate</td>
</tr>
<tr>
<td>N</td>
<td>particle number concentration</td>
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<tr>
<td>P_o</td>
<td>number of small particles approaching an aggregate</td>
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<td>P_c</td>
<td>number of small particles captured by an aggregate</td>
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<tr>
<td>R_c</td>
<td>rate small particles are captured by an aggregate</td>
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<tr>
<td>s</td>
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</tr>
<tr>
<td>t</td>
<td>time</td>
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<tr>
<td>U</td>
<td>terminal settling velocity</td>
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<tr>
<td>( \nu_s )</td>
<td>solid volume of an aggregate</td>
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Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>( \alpha )</td>
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<td>( \alpha_{flit} )</td>
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<td>( \epsilon )</td>
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<td>( \eta )</td>
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<td>( \kappa )</td>
<td>permeability</td>
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<td>( \lambda )</td>
<td>size ratio of two approaching particles</td>
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<td>( \xi )</td>
<td>dimensionless permeability</td>
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Subscripts

<table>
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<tr>
<td>a</td>
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<td>characteristics of a pore in a porous medium</td>
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<td>primary particle</td>
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<td>red colored microspheres</td>
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<tr>
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<td>rectilinear collision model</td>
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<tr>
<td>YG</td>
<td>yellow-green colored microspheres</td>
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</table>

Literature Cited

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