Settling and coagulating behaviour of fractal aggregates

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Abstract
Sedimentation of fractal aggregates (200-1000 µm) and their coagulation with suspended small particles (1.5 µm) were investigated through both theoretical analysis and experimental measurement. The settling velocities of the aggregates were nearly 3 times faster than calculated using Stokes’ law. Attachments of small particles on the aggregates were found to be 1 order of magnitude higher than predicted by a curvilinear collision model and 2 orders of magnitude lower than predicted by the rectilinear model. It is suggested that the internal flow through large pores within fractal aggregates likely contributed to the faster settling velocities and enhanced coagulation between the aggregates and suspended particles. The predictions for the interior flow rates and settling velocities of aggregates can be largely improved using a new fractal structure model in which aggregates are built directly from large clusters instead of the primary particles.

Keywords
Aggregates; coagulation; fractal; particles; permeability; settling velocity

Introduction
Large porous aggregates play an important role in regulating the transport and removal of particulate pollutants in natural waters as well as in water and wastewater treatment systems. As these aggregates fall, for example, they may permit fluid to flow through their interior, and some small particles in the internal flow will be captured by the aggregates. Current coagulation models, including the rectilinear model and curvilinear model, cannot be used to accurately predict coagulation rates between permeable aggregates and suspended particles. The intra-aggregate flow has not been properly included in the description of sedimentation of large aggregates and their coagulation with other particles (Stolzenbach, 1993; Veerapaneni and Wiesner, 1996; Li and Logan, 1997).

The permeability models used in the previous studies for porous aggregates assume a uniform distribution of small spheres within an aggregate. Based on these models, it was predicted that aggregates would settle only slightly faster than calculated by Stokes’ law (Sutherland and Tan, 1970; Chellam and Wiesner, 1993; Lee et al., 1996), a prediction inconsistent with many experimental observations (Li and Ganczarczyk, 1988; Johnson et al., 1996). The existing permeability models likely underestimate the aggregate permeability and thus, the significance of internal flow through aggregates, particularly large aggregates, cannot been established.

Substantial research indicates that aggregates formed by coagulation are fractal (Meakin, 1988; Jiang and Logan, 1991; Gregory, 1997). Unlike Euclidean objects with a constant porosity, fractal aggregates decrease in porosity as their size increases. More importantly, fractal aggregates have a hierarchical mass distribution, a structure resulting from the coagulation of small and more densely packed clusters into larger and overall less dense aggregates (Rogak and Flagan, 1990; Johnson et al., 1996; Li and Logan, 1997). Large pores formed between these clusters will permit greater interior flow through the aggregates, affecting significantly their settling and coagulating behaviour. In the present study, the permeability nature and settling velocity of a fractal aggregate as well as coagulation between a settling aggregate and small particles were investigated through both theoretical analysis and experimental measurement.
Methods

Theoretical

Fractal Aggregates. Aggregates are assumed to be self-similar fractals that can be characterised by a single fractal dimension. The number of primary particles within an aggregate, \( N_p \), scales with its size, \( d_a \), according (Rogak and Flagan, 1990) to

\[
N_p = C \left( \frac{d_a}{d_p} \right)^D
\]

where \( D \) is a fractal dimension, \( C \) is a packing coefficient and \( d_p \) the size of primary particles.

The porosity of the aggregate in terms of the primary particles, \( \varepsilon_p \), can be written as

\[
\varepsilon_p = 1 - C \left( \frac{d_a}{d_p} \right)^{D-3}
\]

Fluid Collection Efficiency. Aggregates produced by coagulation are highly porous and maybe permeable. The internal permeation of an aggregate is indicated directly by its fluid collection efficiency, \( \eta \), defined as the ratio of the interior flow passing through the aggregate to the flow approaching it. When Brinkman’s extension of Darcy’s law is used to describe the interior flow, the fluid collection efficiency of the aggregate is given (Chellam and Wiesner, 1993; Li and Logan, 1997) by

\[
\eta = \frac{9(\xi - \tanh \xi)}{2\xi^3 + 3(\xi - \tanh \xi)}
\]

where \( \xi = d_a/(2\kappa^{1/2}) \), \( \kappa \) is the hydraulic permeability of the porous aggregate.

Brinkman Permeability Model. A number of models have been developed for calculating the permeability of an aggregate composed of spherical primary particles. One of the frequently used models for highly porous media including aggregates is the Brinkman permeability equation (Lee et al., 1996, Li and Logan, 1997):

\[
\kappa = \frac{d_p^2}{72} \left( 3 + \frac{3}{1 - \varepsilon_p} - 3 \sqrt[3]{\frac{8}{1 - \varepsilon_p}} - 3 \right)
\]

\( \xi \) for Aggregates with a Homogeneous Distribution of Primary Particles. Existing permeability models are based on a structure model assuming that the primary particles are distributed homogeneously throughout an aggregate. Substituting equation (2) for \( \varepsilon_p \) in equation (4), the \( \xi \) factor for an aggregate can be derived as

\[
\xi_p = 4.2 \left( \frac{d_a}{d_p} \right)^3 \left[ 3 + 4 \left( \frac{d_a}{d_p} \right)^{3-D} - 3 \left( \frac{d_a}{d_p} \right)^3 - 3 \right]^{-1/2}
\]

Equation (5) indicates that the size and fractal dimension of an aggregate mainly determine its \( \xi \) factor. It should be noted that this permeability correlation is established for the aggregates with a uniform distribution of primary particles, although the decrease in porosity with size for fractal aggregates has been included in the model.

\( \xi \) for Aggregates Constructed with Principal Clusters. The most important feature of fractal aggregates is that the primary particles within an aggregate are not homogeneously distributed. They are distributed according to a hierarchical structure. At each decreasing hierarchical level in a self-similar configuration, parts of an aggregate are composed of successively smaller units (clusters), and a large cluster can be viewed as a collection of the same amount of sub-clusters with the same general shape (Rogak and Flagan, 1990). The
largest clusters that directly form the aggregate are defined here as the principal clusters. Assuming that an aggregate has \( n \) principal clusters, from equation (1), one can write

\[
\alpha = c \left( \frac{d_a}{d_c} \right)^D
\]

where \( d_c \) is the size of principal clusters of the aggregate, and \( n \) is named as a grouping factor.

There are increasingly larger gaps or pores formed by the clusters as the aggregates increase in size. The permeability of an aggregate is likely produced by flow through the largest pores, or macropores, between the principal clusters. It is argued that the macropores dictate the overall aggregate permeability. In terms of its principal clusters, the aggregate porosity becomes \( \varepsilon_c = 1 - c \left( \frac{d_a}{d_c} \right)^{D-3} \). Incorporating equation (6) for \( \frac{d_a}{d_c} \) yields

\[
\varepsilon_c = 1 - c \left( \frac{n}{c} \right)^{D-3}
\]

Replacing \( d_p \) of the primary particles in equation (4) with \( d_c \) of the principal clusters, as well as \( \varepsilon_p \) in terms of the primary particles with \( \varepsilon_c \) in terms of the principal clusters, the \( \xi \) value of an aggregate becomes

\[
\xi_c = 4.2 \left( \frac{n}{c} \right)^{D} \left[ 3 + 4 \left( \frac{n}{c} \right)^{3-D} - 3 \left( \frac{n}{c} \right)^{3-D} - 3 \right]^{-1/2}
\]

The items related with primary particles disappeared in the new expression (8) when the concept of principal clusters is introduced. The \( \xi \) factor does not change with the size of aggregates; instead, it is a function of the fractal dimension and the grouping factor of aggregates.

**Experimental**

*Generation of Fractal Aggregates.* The aggregates were produced using red-dyed latex microspheres with a diameter \( d_p = 2.85 \) (m and a density of 1.05 g/cm\(^3\) (Polysciences). Aggregation of these red particles was conducted in a 0.34 M (2\%) NaCl solution in a jar-test device using flat paddles at 10 rpm. By adjusting coagulation conditions such as the solution pH, a number of batches of aggregates with different fractal dimensions were produced.

*Settling-Coagulation Experiments (Figure 1).* Settling-coagulation experiments were performed in a glass settling column 3.15 cm in diameter. The settling apparatus had three separate sections, column, screen plate and retrieval well base (total settling distance was \( H = 25 \) cm), that could be slipped on and off as described in detail in Li and Logan (1997). The column was filled with a 0.34 M NaCl solution containing \( n_p = 10^6 / ml \) of yellow-green (YG) fluorescent latex beads 1.48 (m in diameter. Individual aggregates generated from red microspheres in the jar-test device were gently transferred into the settling column. The velocity, \( U \), for an aggregate settling in the column was measured. After the aggregate reached the bottom of the retrieval well, the column was slowly pushed to the side, leaving the aggregate with attached YG beads in the well for the subsequent analysis.

**Figure 1** Schematic representation of experimental procedures
Aggregate Characterisation. The characterisation of each recovered aggregate included the following: measuring its size, $d_a$, using an image analysis system and counting the number of YG fluorescent beads captured by the aggregate, $N_m$, under a microscope; measuring the total volume of the red microspheres, $v_s$, that formed the aggregate using a Coulter particle counter (MultisizerII, Coulter) after breaking up the aggregate with an ultrasonic device.

Calculation of Model Parameters from the Experiments. According to fractal geometry, $v_s \sim d_a^D$, the $D$ for a group of aggregates can be determined from a linear regression of $\log(v_s)$ vs. $\log(d_a)$.

Flow through the interior of a porous aggregate reduces the drag of the aggregate, resulting in a greater settling velocity than that predicted for identical but impermeable particles. The permeable characteristics $(\xi)$ of an aggregate can be identified from the ratio between its actual settling velocity, $U$, and that calculated by Stokes’ law, $U_s$, according (Johnson et al., 1996) to

$$U = \frac{\xi}{\xi - \tanh \xi} + \frac{3}{2\xi^2}$$

(9)

Based on the rectilinear collision model, the total number of YG beads approaching an aggregate during its settling through the YG bead solution in the column is $P = \frac{\pi}{4} d_a^2 H n_p$, where $H=25$ cm and $n_p=10^6$ ml$^{-1}$. Thus, the total attachment of YG beads on the aggregate predicted by the rectilinear model is

$$N_{rec} = \frac{\pi}{4} \alpha d_a^2 H n_p$$

(10)

where $\alpha$ is the collision efficiency factor between the red and YG microspheres and it was experimentally determined that (=0.237 as previously described by Li and Logan (1997).

The curvilinear collision models can be used to more accurately describe the coagulation rates between impermeable particles. The total attachment of YG beads on the aggregate predicted by the curvilinear model is smaller than the rectilinear prediction by a factor $e_{cur}$ or

$$N_{cur} = \frac{\pi}{4} e_{cur} \alpha d_a^2 H n_p$$

(11)

Calculation for the factor $e_{cur}$ can be found elsewhere (Han and Lawler, 1992; Li and Logan, 1997).

Results and discussion
Settling Velocities and Permeabilities of Fractal Aggregates
Two groups of aggregates were generated with fractal dimensions of $D_A=1.81\pm0.09$ and $D_B=2.33\pm0.07$. Aggregates settled on average 2-3 times faster than calculated using Stokes’ law (Fig. 2), an observation consistent with lower drag coefficients and higher internal permeation of fractal aggregates. Group A aggregates on average had higher $U/U_s$ ratios (2.84±1.00) than group B aggregates (2.39±0.79), suggesting that aggregates with a lower fractal dimension had higher permeabilities and would experience lower drag forces than the similarly sized aggregates with a higher fractal dimension.

Using the $\xi$ factors derived from the settling velocity ratios, $U/U_s$, the fluid collection efficiencies of the aggregates can be calculated using equation (3) (Figure 3). The fluid collection efficiencies varied from 0.08 to 0.83, indicating that a large fraction of the fluid approaching an aggregate flowed through the aggregate. On average, aggregates in group A had greater $\eta$ values (0.54±0.14) than those in group B (0.46±0.15). The fluid collection
Efficiencies predicted from the original Brinkman equation in terms of the primary particles were significantly lower than the measured data and actually could be neglected. Although the fractal dimension had been incorporated in the computations, the permeability model used was still based on the same assumption that an aggregate is a porous object with a uniform distribution of small spheres.

Fractal aggregates should be constructed directly from the principal clusters of primary particles. Based on this fractal structure model, the $\xi$ factor is no longer a function of the size and the fluid collection efficiencies of aggregates can be predicted using the modified Brinkman permeability model in terms of the principal clusters. A packing factor of $c=0.1$, which gives a reasonable and constant porosity of 0.9 for non-fractal aggregates with $D=3$, was used for the computations. It can be demonstrated that the $\xi$ value in equation (8) is not sensitive to the grouping factor when $n$ is greater than 15. Thus, a grouping factor of $n=25$ was employed in the present study. The predictions of $\eta$ obtained using this modified method were largely improved as they were much close to the experimental observations (Figure 3). Thus, the new permeability model based on the fractal structure of principal clusters can properly estimate the aggregate permeability to a great extent and is able to reveal the significance of internal flow through large aggregates.

**Coagulation of Small Particles with Fractal Aggregates**

Group A aggregates with a lower fractal dimension captured more than twice the number of YG beads than equally-sized group B aggregates with a higher fractal dimension during the settling tests (Figure 4). The measured attachments of small particles on the settling aggregates were 1 order of magnitude higher than predicted by the curvilinear collision model and 2 orders of magnitude lower than predicted by the rectilinear model for the aggregates of identical sizes. The rectilinear model overestimates coagulation rates between the aggregates and YG beads since it does not account for hydrodynamic interactions and short-range forces between approaching particles. In contrast, the curvilinear model underestimates the coagulation rates since it does not include a mechanism for flow through the aggregate interior.

The differences between the observed attachments of small particles on the aggregates and those predicted by the curvilinear model likely resulted from the high aggregate permeability produced by a heterogeneous fractal distribution of particle clusters within the aggregates. However, not all YG beads in the fluid flowing through a fractal aggregate successfully attached to the aggregate. In fact, $<1\%$ of the beads in the intra-aggregate flow were captured by the aggregates. Macropores can account for the faster settling velocities and higher fluid collection efficiencies of fractal aggregates, but the large sizes of these pores mean that most small particles in the internal flow would pass through the aggregates without contacting the clusters forming the aggregates.
Conclusions

Fractal aggregates settled on average 2 to 3 times faster than calculated using Stokes’ law, suggesting great internal flow through the aggregates. The attachments of small particles on the settling fractal aggregates were 1 order of magnitude higher than predicted by a curvilinear model and 2 orders of magnitude lower than predicted by the rectilinear collision model, and the coagulation rates decreased with the fractal dimension of aggregates. It was argued that flow through large pores formed between principal clusters within fractal aggregates contributed to greater aggregate permeabilities, faster settling velocities and enhanced coagulation between aggregates and suspended particles. Using a new fractal aggregate structure model in which aggregates are constructed directly from principal clusters, the description of internal permeation of large aggregates can be significantly improved.

References