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REVIEW PAPER

FLOCCULATION MODELLING: A REVIEW

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Abstract—The modelling of the flocculation process is reviewed. Recent developments in this area are discussed with reference to the classical analytical expression of Smoluchowski defining collision frequency and originally published in 1917. The constraints imposed by six principal assumptions made by Smoluchowski are considered individually, with the key models that have been developed to address specific limitations discussed in detail. These assumptions comprise: (1) all particle collisions lead to attachment, (2) fluid motion is limited to laminar shear, (3) particles are monodispersed (i.e. all of them are the same size), (4) no breakage of flocs occurs, (5) all particles are spherical in shape and remain so after collision and (6) collisions take place only between two particles. The discussion incorporates an examination of particle dynamics (i.e. rectilinearity vs curvilinearity), particle surface chemistry (van der Waals attraction and electrostatic repulsion), mixing parameters (mixing intensity and the Camp number) and the key floc growth parameter of fractal dimension D. In doing so limitations of modernised theories are identified. It is concluded that constraints imposed on the interpretation of models based on microscopic aspects of the system, pertaining mainly to those phenomena presiding at the particle:solution interface, severely restrict their application in real systems. The more recent microscopic approach based on characterisation of the system through determination of the fractal dimension as a function of time offers the opportunity of a simpler yet more representative modelling, but nonethe-less, currently relies on empirical measurement using fairly sophisticated experimental techniques.

Key words—flocculation, coagulation, modelling, fractal, particles

NOMENCLATURE

a = radius of primary particle, L
D = fractal dimension
d_i = diameter of particle i, L
k = Boltzmann constant ($M\,L^2\,T^{-2}\,K^{-1}$)
$\mathbf{G}$ = local root-mean-square velocity gradient (T^{-1})
$\mathbf{G}^*$ = global root-mean-square velocity gradient (T^{-1})
n_i = concentrations of particles of size i (L^{-3})
N_t = total concentration of particles at time t (L^{-3})
$n_v(t)$ = concentration of particles of volume v at time t (L^{-3})
T = absolute temperature (K)
v = particle volume (L^3)
α = collision efficiency
$\beta(i, j)$ = rate of collision between particles of size i and j ($L^3\,T^{-1}$)
ε = local rate of energy dissipation ($L^2\,T^{-3}$)
ε^* = global rate of energy dissipation ($L^2\,T^{-3}$)
ϕ = solid fraction of particles
j = total volume of aggregates (L^3)
y = self-similar size distribution function
κ = aggregate permeability (L^2)
λ = Kolmogorov microscale (L)
μ = viscosity of water ($M\,L^{-1}\,T^{-1}$)

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INTRODUCTION

The mathematical representation of flocculation, i.e. the process whereby destabilised suspended particles are aggregated, has conventionally been based on considering the process as two discrete steps: transport and attachment. The transport step, leading to the collision of two particles, is achieved by virtue of local variations in fluid/particle velocities arising through (a) the random thermal "Brownian" motion of the particles (*perikinetic* flocculation), (b) imposed velocity gradients from mixing (*orthokinetic* flocculation) and (c) differences in the settling velocities of individual particles (*differential sedimentation*). Attachment is then contingent upon a number of short range forces largely pertaining to the nature of the surfaces themselves.

The two precepts are most succinctly expressed mathematically as a rate of *successful* collision

between particles of size i and j:

$$\text{rate of flocculation} = \alpha\beta(i, j)n_i n_j, \qquad (1)$$

where α is the collision efficiency, $\beta(i, j)$ is the collision frequency between particles of size i and j, and n_i, n_j are the particle concentrations for particles of size i and j, respectively.

The collision frequency β is a function of the mode of flocculation, i.e. perikinetic, orthokinetic or differential sedimentation. The collision efficiency, α (taking values from 0 to 1), is a function of the degree of particle destabilisation: the greater the degree of destabilisation, the greater the value of α. Thus, in effect, β is a measure of the transport efficiency leading to collisions, whilst α represents the percentage of those collisions leading to attachment.

Nearly all flocculation models are based upon this one fundamental equation. The values of the parameters α and β are dependent upon a large number of factors ranging from the nature of the particles to the method of destabilisation and the prevailing flow regime during flocculation. Much of the research in flocculation modelling has been directed at establishing equations and specific values for these two parameters. It is important, however, not to forget the importance of the terms n_i and n_j in the equation, as the overall rate always increases with particle concentration.

The interpretation of α and β given above implies that the two parameters are independent of one another. However, there is a second interpretation of α and β which makes the distinction between them less clear cut. One could consider α, besides allowing for the degree of particle destabilisation, to be an experimental correction factor compensating for weaknesses in the theoretical representation of β, such that values for α are no longer confined to be between 0 and 1.

CLASSICAL EXPRESSIONS

The first major attempt at modelling the flocculation process was made by Smoluchowski (1917). Since the equations in Smoluchowski's model have formed the core of almost all subsequent research into flocculation modelling, subsequent developments can be considered with specific reference to each of the assumptions made by Smoluchowski.

The basic equation developed by Smoluchowski is given by

$$\frac{\mathrm{d}n_k}{\mathrm{d}t} = \tfrac{1}{2}\sum_{i+j=k}\beta(i, j)n_i n_j - \sum_{i=1}^{\infty}\beta\,(i, k)n_i n_k. \qquad (2)$$

Subscripts i, j and k represent discrete particle sizes. The first term on the right hand side defines the increase in particles of size k by flocculation of two particles whose total volume is equal to the volume of a particle of size k. The second term on the right hand side describes the loss of particles of size k by virtue of their aggregation with other particle sizes. The factor of one half in front of the first term on the right hand side ensures that over the summation the same collision is not counted twice. The overall equation thus defines the rate of change in the number concentration of particles of size k.

By presenting an equation such as equation 2 for each value of k, Smoluchowski constructed a series of differential equations that described the whole of the flocculation process. These equations are non-linear and solutions to them are not immediate. To render the differential equations more manageable Smoluchowski made a number of simplifying assumptions.

1. The collision efficiency factor, α, is unity for all collisions.
2. Fluid motion undergoes laminar shear.
3. The particles are monodispersed (i.e. all of the same size).
4. No breakage of flocs occurs.
5. All particles are spherical in shape and remain so after collision.
6. Collisions involve only two particles.

Based on these assumptions, Smoluchowski developed the following analytical expressions for the collision frequency for both perikinetic and orthokinetic flocculation:

$$\beta_{\text{perikinetic}} = (2kT/3\mu)(1/d_i + 1/d_j)(d_i + d_j), \qquad (3)$$

$$\beta_{\text{orthokinetic}} = (1/6)(\mathrm{d}u/\mathrm{d}y)(d_i + d_j)^3, \qquad (4)$$

where k is Boltzmann's constant, T is the absolute temperature of the fluid, μ is the fluid viscosity, and $\mathrm{d}u/\mathrm{d}y$ is the velocity gradient of the fluid. Smoluchowski produced solutions to the set of differential equations for both perikinetic and orthokinetic flocculation, the solution for orthokinetic flocculation being

$$N_t = N_0\exp(4/\pi)(\mathrm{d}u/\mathrm{d}y)\phi t, \qquad (5)$$

where, N_t is the total particle count at time t, N_0 is the initial particle count and ϕ is the volume fraction of the particles, which is assumed to be constant and given by $(4/3)\pi a^3 N_0$, a being the particle radius.

Camp and Stein (1943) extended Smoluchowski's equation for orthokinetic flocculation by substituting the fluid shear velocity, $\mathrm{d}u/\mathrm{d}y$, with the authors' definition of the fluid's root-mean-square velocity gradient, $\mathbf{G}$:

$$\beta(i, j) = (\boldsymbol{G}/6)(d_i + d_j)^3. \qquad (6)$$

The same authors found the collision frequency for differential sedimentation to be given by

$$\beta(i, j) = (g\pi/72\mu)(\rho_\mathrm{p} - \rho_\mathrm{l})(d_i + d_j)^3|d_i - d_j|, \qquad (7)$$

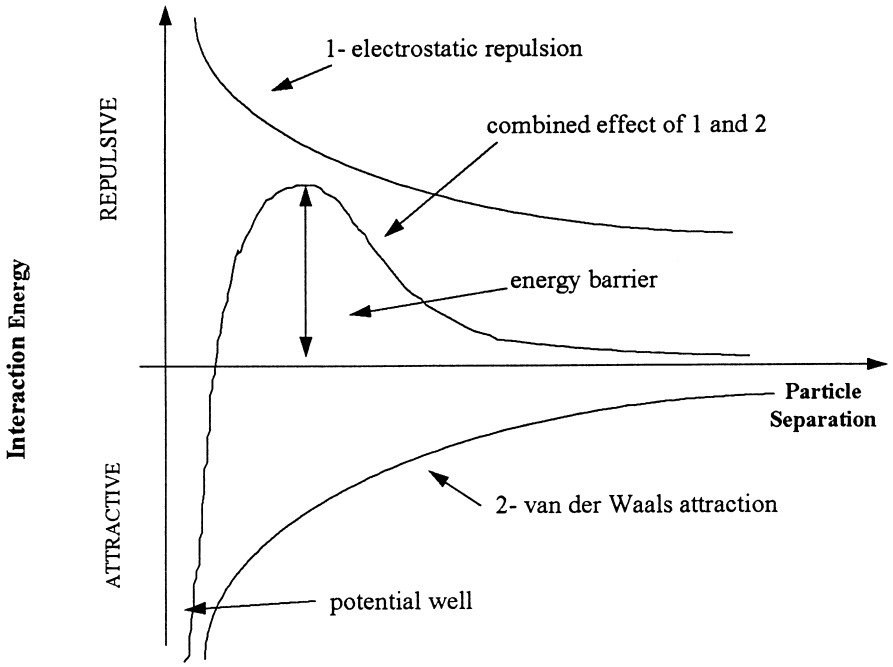

Fig. 1. Representation of DLVO theory.

where g is the gravity constant and ρ_p and ρ_l the particle and fluid densities, respectively.

Whilst the classical approach leads to analytical expressions to define the coagulation process, their pertinence to real systems is significantly constrained by the assumptions 1–6 above. In the following sections, the validity of each of the assumptions listed is considered in turn

MODERNISED EXPRESSIONS

The collosion efficiency factor, α, is unity for all collisions

Effects of short-range forces. In Smoluchowski's original paper, it was assumed that all collisions lead to attachment, thereby ignoring the effect of all short-range forces such as electrostatic repulsion, van der Waals or hydrodynamic forces. The combined effect of electrostatic repulsion and van der Waals attraction between two particles is described by the DLVO theory (Deryaguin and Landau, 1941; Verwey and Overbeek, 1948). This theory assumes that the effect of two forces is additive, and the results can be displayed in the form of a potential energy diagram shown in Fig. 1.

The main points of interest in Fig. 1 are:

1. the height of the energy barrier and
2. the low potential well at very small distances.

Figure 1 suggests that although it is energetically favourable for particles to come into close contact, a large energy barrier must first be overcome. The role of a coagulant is to lower the energy barrier by reducing the electrostatic repulsion and hence making it easier for the particles to come into close contact with one another. The lower the energy barrier, the closer to unity α becomes. Fuchs (1934) published a method of analysing the potential energy diagrams to calculate the value α.

A large body of literature devoted to the incorporation of surface forces into the coagulation transport equations has appeared since DLVO theory was first established, and a comprehensive critique of these papers is beyond the scope of this review. Readers interested in the current understanding of colloidal forces should refer to Kihira and Matijevic (1992) for a comprehensive review of recent work in this field.

Effects of hydrodynamic interactions. Early classical models are all based on the assumption that interparticle interactions are negligible until the point of contact, whereupon adhesion takes place with 100% efficiency. However, in reality the hydrodynamic forces impact significantly upon colliding particles. As particles collide, the fluid in the diminishing space between them is squeezed out. This motion of the fluid causes the particles to rotate relative to one another, such that they deviate from the linear path assumed in the classical approach. Consequently, the classical approach to flocculation modelling is described as *rectilinear*. The alternative is known as the *curvilinear* approach, whereby the hydrodynamic force causes the approaching particles to rotate slightly around one another. The corrections made to α through the consideration of hydrodynamic forces can be more accurately interpreted as modifi-

cations to the collision frequency functions and are discussed below.

The sizes of particles involved in collisions has a significant affect on the values of the various flocculation rates. Over different size ranges different flocculation mechanisms become dominant. In wastewater treatment, particle sizes can range from under 1 μm up 1000 μm, especially if metal hydroxides are precipitated.

Rectilinear Models

The rectilinear approach essentially assumes the fluid to have no influence upon the flocculation process other than bulk drag effects. In calculating collision frequencies between two particles — one fixed at 2 μm and the other varying from 1–1000 μm — based upon the rectilinear approach, Han and Lawler (1992) observed that:

1. perikinetic flocculation dominated when the secondary particle was less than 1 μm,
2. differential sedimentation dominated when the secondary particle was greater than 10 μm,
3. for both orthokinetic flocculation and differential sedimentation the collision frequency was a strong function of particle size, dominated by the diameter of the larger of the two particles.

The authors extended the analysis to compare collision between all pairs of particles with sizes in the range 1–1000 μm. For a set value of **G**, the authors found perikinetic flocculation to be the dominant mechanism only when both particles were small, whilst differential sedimentation was dominant only when one particle was quite large and the other was significantly smaller. In all other cases orthokinetic flocculation was the dominant mechanism. Hence, according to the rectilinear model of flocculation, orthokinetic flocculation is of paramount importance.

Curvilinear Models

Curvilinear models have been presented by a number of authors: Han and Lawler (1991) developed the equations for differential sedimentation, Han (1989) developed them for perikinetic flocculation and Adler (1981b) for orthokinetic flocculation.

Adler (1981b) was the first to apply the theory of hydrodynamic interactions to heterodispersed systems. The author showed, using equations based on laminar flow conditions, that in the presence of a combination of hydrodynamic, electrostatic and van der Waals forces, collision frequencies were highest when colliding particles were of the same size. The author indicated that the hitherto lack of consideration of hydrodynamic interactions had led to an overestimation of flocculation collision frequencies. Lawler (1993) calculated the collision efficiencies for various size ratios of colliding particles taking account of hydrodynamic forces. The results showed that the curvilinear model, compared to the rectilinear model, predicted orders of magnitude of collisions frequencies around 0.5 less for perikinetic flocculation, between 2 and 3 less for differential sedimentation and around 5 less for orthokinetic flocculation. More specifically, the results showed that collisions between particles that are greatly different in size are quite unlikely to occur by orthokinetic flocculation.

Numerical expressions approximating the correction factors for converting the rectilinear model to the curvilinear model are presented by Han and Lawler (1992). The numerical expressions are essentially functions of

1. the size ratio of the colliding particles and
2. the ratio of hydrodynamic shear forces to van der Waals forces between colliding particles.

Han and Lawler (1992) compared collisions between all pairs of particles with sizes in the range 1–1000 μm based on a curvilinear rather than a rectilinear approach. Compared to the rectilinear mode the regions in which perikinetic flocculation and differential sedimentation were dominant were both significantly expanded, whilst the region in which orthokinetic flocculation was dominant was commensurately reduced. In fact, orthokinetic flocculation only dominated for similarly-sized colliding particles.

Three important conclusions arise from the developments of curvilinear models:

1. orthokinetic flocculation is far less important in the curvilinear model than in the rectilinear model,
2. the curvilinear model predicts a much lower collision frequency than the rectilinear model, although the reduction is less when the particles are of a similar size, and
3. orthokinetic flocculation is no longer seen as being directly proportional of **G**, as predicted by Camp and Stein (1943).

The third of these observations is of particular interest. Han and Lawler (1992) concluded that designers could build flocculation units with the minimum **G** required to keep particles in suspension.

Current developments in the modelling of the hydrodynamic forces between colliding particles are developing in two areas, both of which pertain to a more realistic definition of aggregate structure (Section 2.5). The first area is concerned with the drag upon the aggregates, whilst the second, and related, area is associated with the paths the aggregates take as they approach one another.

In the first area, Veerapaneni and Wiesner (1996) calculated the flow and associated drag on a sphere with nonuniform porosity, whilst Li and Logan (1997a) modified the permeability expression of

Brinkman (1947) to take account of nonuniform porosity. Wu and Lee (1998) calculated the drag on a porous floc moving at a Reynolds number greater than one. The authors discovered that at sufficiently high porosity values, the drag coefficient remained inversely proportional to the Reynolds number up to Reynolds numbers as high as 40. In other words, according to Wu and Lee (1998), the Stokes' regime for the drag upon a porous aggregate extends substantially further than that for a solid sphere.

In the second area Kusters *et al.* (1997) used the results of Adler (1981a) regarding the flow through porous particles to calculate the collision efficiency between uniformly porous aggregate. These results applied only when the ratio of the radii of the colliding particles was less than 0.1. The authors found that above a critical limit of the dimensionless radius (defined as the $R/\sqrt{\kappa}$, where R is the aggregate radius and κ is the aggregate permeability) the collision efficiency became zero. Kusters *et al.* (1997) also presented values for the collision efficiency between uniformly porous flocs when the ratio of their radii was close to unity. The authors approximated the path along which porous particles approached one another by adopting the results of Adler (1981b), who calculated the paths for solid spheres. This approach, when incorporated into the basic flocculation equations by Kusters *et al.* (1997), produced a marked improvement in the accuracy of model predictions.

Fluid motion undergoes laminar shear

Laminar flow. The two extremes of flow that can be considered are laminar and turbulent which, for the sake of simplicity, can be associated with ordered and chaotic flow regimes, respectively. A key property of laminar flow is that knowledge of the flow at a given point in a fluid allows one to calculate the flow in a small region around that point. In mathematical terms, if two points in space, P and P', (see Fig. 2) are separated by a small vector R, then the difference in the flow between the two points is given as:

$$\mathrm{d}\boldsymbol{U} = \boldsymbol{U}(P') - \boldsymbol{U}(P) = \boldsymbol{R} \cdot \mathbf{A}, \tag{8}$$

where $\boldsymbol{U}$ represents velocity and $\mathbf{A}$ is relative velocity gradient tensor. In effect, for a fixed line in space $\mathbf{A}$ allows one to calculate how velocity changes along that line.

It is possible therefore in laminar flow regimes to calculate the relative velocity between particles. At first sight it might appear that particles collide by virtue of their relative velocity as characterised by $\mathbf{A}$. However, this is an oversimplification, because $\mathbf{A}$ incorporates particle rotation. The relative velocity between two points can be decomposed into two components: shear and rotation. The rotational element of the relative velocity does not contribute to the rate of collisions because during rotation particles remain at the same distance apart. It is thus only the shear component that leads to collisions between particles. The relative shear velocity between two points is characterised by the *strain-rate tensor*, $\mathbf{S}$, defined as:

$$\mathbf{S} = 1/2(\mathbf{A} + \mathbf{A}^{\boldsymbol{T}}), \tag{9}$$

where the superscript $\boldsymbol{T}$ stands for the transpose. Substituting $\mathbf{A}$ with $\mathbf{S}$ in equation 8 yields the relative shear velocity between points P and P'.

There are two generic types of strain: *pure-shear strain* and *pure-normal strain*. In pure-normal strain, the velocity in the direction of one of the principle coordinates, i.e. x, y or z, is a function of that coordinate only, whereas in pure-shear strain it is a function of the other two coordinates only. Smoluchowski (1917) in his original formulation of the flocculation equations assumed that the flow underwent pure-shear strain, i.e. laminar flow. In fact, the flow was a simplified two-dimensional form of pure-shear strain with only one component of the relative velocity considered. Based on this simplified flow, Smoluchowski deduced that the rate of orthokinetic flocculation was proportional to the velocity gradient, $\mathrm{d}u/\mathrm{d}y$.

Camp and Stein (1943) attempted to further develop Smoluchowski's approach so that three-dimensional fluid motion could be taken into consideration. They defined a term $\mathbf{G}$, the local root-mean-square velocity gradient for a small local element of fluid undergoing strain, and linked $\mathbf{G}$ with the local rate of energy dissipation, ε:

$$\mathbf{G} = (\varepsilon/\nu)^{1/2}, \tag{10}$$

where ν is the kinematic viscosity of water. In addition, the authors moved from the local scale to the global scale by defining $\mathbf{G}^*$, the global root-mean-square velocity gradient for a flocculating system:

$$\mathbf{G}^* = (\varepsilon^*/\nu)^{1/2}, \tag{11}$$

where ε^* is the average energy dissipation for the

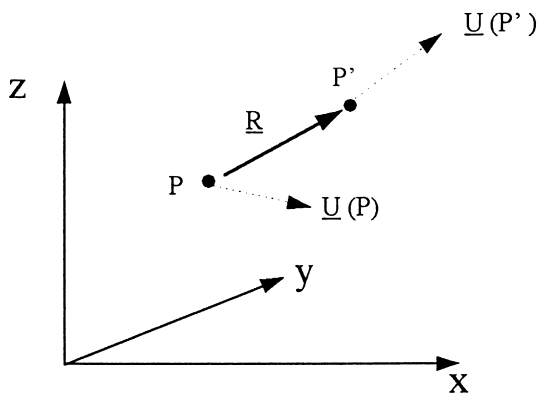

Fig. 2. Calculation of relative velocity between points P and P′.

whole flocculating system. Camp and Stein assumed that Smoluchowski's du/dy could be replaced by **G** for linear flow regimes and by **G*** in turbulent flow regimes.

Kramer and Clark (1997) identified two errors in Camp and Stein's work. Firstly, the method by which Camp and Stein moved from 2-D to 3-D flow ignored the contribution made by the pure-normal strain component of the rate-strain tensor, and consequently they incorrectly associated **G** with ε. In practice, this error has little serious effect, since few real-life flocculation units operate with laminar flow. The second error however has more immediate consequences regarding flocculation modelling. This error involved assuming that **G*** was a representative measure of the fluid dynamics within a flocculator. Kramer and Clark (1997) argued that the variations in the local root-mean-square velocity gradients within the tank meant that Camp and Stein had overestimated their global root-mean-square velocity gradient. In fact, the greater the local variations, i.e. the more turbulent the flow, greater the magnitude of the error.

Kramer and Clark attempted to extend the 2-D flow used by Smoluchowski to 3-D flow avoiding the error made by Camp and Stein. Assuming that the flow for a small fluid element could be described in laminar terms, the authors diagonalised **S** and deduced the rate of flocculation was proportional to $a_{\max}$, the maximum magnitude of the elements of the diagonalised tensor. The physical significance of diagonalising the strain-rate tensor is that for any small element of fluid experiencing shear, the axes can be configured in such away that the element undergoes pure-normal strain only. By focusing on relative strain rates rather than relative velocity gradients as carried out by Camp and Stein, Kramer and Clark (1997) gave a rigorous analysis of the rate of collision in laminar flow. The ideas of Kramer and Clark have not been extended from laminar to turbulent flow.

Turbulent flow. In overall terms, turbulence is still a poorly understood phenomenon. However, one model of turbulence that has been successfully adopted in flocculation modelling is the *isotropic model*. This model describes turbulence as a cascade of eddies of diminishing size. Energy applied to a fluid during mixing is primarily used for the formation of large eddies. These large eddies accomplish most of the momentum transport but only a small amount of energy dissipation. Energy is transferred via a series of eddies of decreasing size until a certain size of eddy is reached where all the energy is dissipated by viscous forces. The length scale of the eddy where energy dissipation by viscous forces dominates is called the *Kolmogorov microscale*, defined as

$$\lambda = (\nu^3/\varepsilon)^{1/4}, \tag{12}$$

where λ is the Kolmogorov microscale, ν is viscosity and ε is the rate of energy dissipation.

Based on the cascade model, Casson and Lawler (1990) put forward a proposal that in turbulent conditions, collisions between particles are promoted by eddies of a size similar to those of the colliding particles. They developed the orthokinetic collision frequency function by applying different values for **G** to different pairs of colliding particles. The developed model was in good agreement with experimental data. The authors concluded that the smaller particles were far more likely to collide with one another than with larger particles. This is identical to the conclusions from the curvilinear approach discussed above. The authors also stated that energy expended during mixing in the creation of large eddies could be ineffectual.

A similar conclusion was reached by Han and Lawler (1992) on studying the effect of hydrodynamic retardation upon the collision constants in the Smoluchowski equations. The authors concluded that because the hydrodynamic retardation effect was so pronounced for orthokinetic collisions, the actual contribution of orthokinetic flocculation to the overall flocculation process was minimal. As such, mixing simply provided a means of suspending the particles to keep the particle number count high enough for collisions to occur.

Kramer and Clark (1997) highlighted the fact that the local root-mean-square velocity gradient varies from one point to another within a tank. Consequently, as an aggregate is swept around a tank the root-mean-square velocity gradient to which it is exposed will vary. Kusters *et al.* (1991) determined experimentally that the time averaged value of the root-mean-squared velocity gradient to which an aggregate is exposed does not differ significantly from the definition of Camp and Stein (1943) of the global root-mean-square velocity gradient, **G***. However, it is important to note that an aggregate can be exposed, if only for an instance, to an significantly higher value of **G** than the global root-mean-square velocity gradient. In a flocculator stirred with an impeller these high values of **G** will occur close to the tip of the impeller. It is probable that breakage occurs in these regions of high shear intensity rather than in the more quiescent areas way from the impeller.

The particles are monodispersed

Parameters derived from classical theory. Because of the complex nature of the flocculation equations and difficulties encountered in their rigorous solution the assumption originally made by Smoluchowski (1917) of a monodispersed suspension has persisted. The incorporation of mixing intensity **G** and collision efficiency α into equation 5 yields:

$$N_t = N_0 \exp\{-(4/\pi)\mathbf{G}t\alpha\phi\}. \quad (13)$$

Based on this equation and assuming α and ϕ to be constant for a given system, some authors have concluded that the dimensionless quantity $\mathbf{G}t$, known as the *Camp number*, should be a prime design parameter for flocculation units in water treatment. Tambo (1965) and his various coworkers (Tambo and Ogasawara, 1970; Tambo and Watanabe, 1979; Tambo, 1991) proposed that it is the nondimensional product $\mathbf{G}t\phi$ that determines the progress of flocculation, rather than $\mathbf{G}t$. O'Melia (1972) suggested that for wastewater treatment, the dimensionless product $\mathbf{G}t\phi\alpha$ could be considered as a design parameter, adding that for successful flocculation it would probably be of the order 0.1.

The lack of progress in dealing with the flocculation equations for heterodispersed systems has kept attention focused upon parameters such as $\mathbf{G}t$, $\mathbf{G}t\phi$ and $\mathbf{G}t\phi\alpha$. These parameters are essentially associated with a very simplified form of the flocculation equations which would explain the lack of consensus in the literature regarding their true influence in flocculation. For example, Harris *et al.* (1966) observed the extent of the aggregation and floc formation to be a function of both $\mathbf{G}t\phi$ *and* size distribution. As not all of these parameters are within the control of plant operators they are of limited use in plant design.

Gregory (1981) modelled the flocculation of a destabilised, monodispersed colloid in laminar tube flow. The local variations in $\mathbf{G}$ and t experienced by particles entering the tube at different radial positions were accounted for, and predicted flocculation rates agreed well with experimental results. However, flocculation models based on the series of monodispersed assumptions, as applied by the author, are only applicable during the initial stages of flocculation before larger aggregates become involved in the collisions.

Effects in heterodispersed systems

Arithmetic and Geometric Series

A distribution of particle sizes in a heterodispersity can be described mathematically by either a discrete or continuous function. With a discrete size distribution, successive particle sizes are defined so as to fit some form of mathematical series, typically an *arithmetic* series, e.g. {1, 2, 3, 4,...}. Using arithmetic series becomes increasingly inefficient in terms of finding numerical solutions to the flocculation equations as the range of particle sizes under investigation increases. To overcome this problem Stratton *et al.* (1994) defined particle class sizes so that they formed a *geometric* series, namely {1, 2, 4, 8, 16,...}. This geometric series provided less detailed information than the arithmetic series {1, 2, 3, 4,...}. However, by calculating the change in concentrations for *classes* of particle size, i.e. {1–2, 2–4, 4–8,...}, rather than for each *individual* particle size, the authors were able to reduce the number of differential equations required to characterise the flocculation kinetics over a given range of particle sizes. In the study of breakage kinetics carried out by Calabrese *et al.* (1992), the lack of detail offered by geometric series meant that they could not adequately define particle sizes. Instead, the authors used a number of interlaced *Fibonacci* series, in which the value of any term is the sum of the two previous terms.

Continuous Functions and Self Similarity

An alternative way to describe size distributions is in the form of continuous mathematical functions. For example, the exponential size distribution is defined as

$$n(x) = A \exp(-Bx) \quad (14)$$

where A and B are constants, x is the particles size and $n(x)$ is the particle concentration. Based on a continuous size distribution, the flocculation equations become partial integro-differential rather than pure differential.

The usual way of representing a size distribution curve is to plot $n_v(t)$ against v. For a system of aggregating particles, the shape of this graph will change with time (assuming an equilibrium was not established). However, Schumann (1940) observed that the plot of $n_v(t)\varphi/N_t$ against vN/φ did not change shape or develop with time once a sufficient period of time had elapsed since the onset of flocculation. This was an example of *self-similarity*. A flocculating system is said to be self similar if some normalised form of its size distribution becomes independent of time once a sufficient period of time since the onset of flocculation has elapsed. Where a system displays self-similarity the complexities associated with individual collisions lead to predictable and repeatable patterns for the overall size distribution.

The fundamental assumption made by Swift and Friedlander (1964) in their investigation of self-similarity was that the particle size distribution took the form

$$n_v(t) = \frac{N_t^2}{\varphi}\psi\left(\frac{N_t v}{\varphi}\right), \quad (15)$$

where ψ is the self-similar size distribution. This equation reveals that whilst n changes with both size and time, ψ *does not change with time*. The main advantage of being able to represent the size distribution in terms of an equation such as equation 15, is that it reduces the number of variables required to describe the size distribution. It also makes it easier to make comparisons between different size distributions.

For a given flocculating system, regardless of whether the size distribution can be put in the form of equation 15, whether it is then a solution to the actual flocculation equations depends entirely upon the mathematical form of the collision frequencies. Pulvermacher and Ruckenstein (1974) calculated some of the necessary conditions that the collision frequencies would have to satisfy for equation 15 to represent a solution to the flocculation equations. Swift and Friedlander (1964) proved that equation 15 was indeed a particular solution to the flocculation equations for both perikinetic and orthokinetic flocculation.

In the situations where equation 15 is a solution, two hypotheses have been put forward.

1. The solution represents the long-term, or asymptotic, behaviour of the system.
2. The form of the self-similar size distribution is independent of the initial size distribution.

Although neither hypothesis has been proved mathematically, they are supported by a body of experimental work (Swift and Friedlander, 1964; Hidy and Lilly, 1965; Lai *et al.*, 1972). Some mathematical support was presented by Rosen (1984), who investigated the subject of flocculation from a statistical point of view. The author was able to provide good approximations of the self-similar size distributions for perikinetic flocculation *without* having to assume a particular form for the initial particle size distribution.

The more recent work on self-similarity has focused on systems with both fragmentation and flocculation (Family *et al.*, 1986; Sorensen *et al.*, 1987; Meakin and Ernst, 1988; Elminyawi *et al.*, 1991). Although complex in nature, the general results of the work can be summarised as:

1. Two different self-similarity distributions apply during aggregation: one at the start when flocculation dominates and another later on as the system approaches equilibrium. However, the size of the error incurred by assuming just one form of the self-similar size distribution (similar to equation 15) is small enough to be of no major concern.
2. At equilibrium, the value of the average particle size is a function of the collision frequencies and the breakage frequencies.

To predict the actual shape of a self-similarity size distribution demands detailed knowledge of both collision and breakage frequencies. Such information is not always readily available in real-life applications, such as wastewater treatment, but such systems may none-the-less display self-similarity. For example, Delichatsios and Probstein (1974) used the phenomenon of self-similarity to assist in the calculation of collision efficiencies for the flocculation of latex particles in turbulent flow. Koh *et al.* (1986) observed self-similarity in the upper range of the particle size distribution during orthokinetic flocculation of scheelite (an important ore of tungsten). Spicer and Pratsinis (1996a) reported self-similarity, with respect to mixing intensity, for polystyrene particles destabilised by aluminium sulphate. The authors analysed the self-similar size distributions and were able to make inferences about the strength of the polystyrene flocs. Spicer and Pratsinis (1996b) attributed the nature of this self-similarity to the particular breakage mechanism that occurred during mixing.

No breakage of flocs occurs

The importance of break-up phenomena. One of the assumptions of the original Smoluchowski model is that flocs do not break once formed. However, as demonstrated by Spicer and Pratsinis (1996b), it is the balance of the opposing phenomena of aggregation and break-up that determine the floc size and mass distributions. Early computer simulations by Fair and Gemmell (1964) identified the importance of breakage in modelling flocculation and the large effect different break-up assumptions can have on the predictions of flocculation models. Costas *et al.* (1995) simulated particle aggregation and fragmentation based on a series of simplified *kernels* (the mathematical term for kinetic rate constants in the Smoluchowski equations). In all simulations the initial particle distribution was monodispersed. Results illustrated the significant effects different assumptions about break-up mechanisms can have both on initial rates of reaction and eventual steady-state concentrations.

There is very little fundamental understanding of the factors affecting the strength of aggregates or their mode of breakage under stress, and most work has been of an empirical nature. It is generally accepted (Mühle, 1993) that the breakage mechanism in turbulent flow depends upon a floc's size relative to the Kolmogorov microscale. For flocs smaller than the Kolmogorov microscale, viscous forces predominate and *erode* the surface of the floc. On the other hand, for flocs larger than the Kolmogorov microscale, deformation or *fracture* may occur as a result of fluctuating dynamic pressure. These ideas imply that floc strength is proportional to floc size. However, recent experimental work by Yeung and Pelton (1996) has suggested that rather than strength being related to floc size, it is related to floc compactness. The authors found that more compact flocs were more likely to undergo erosions whereas less compact flocs were more likely to undergo fracture.

Relationship with **G**. Ritchie (1955) first pointed out a connection between break-up phenomena and the value of **G**. The author found an empirical relationship between applied **G** and maximum floc size and indicated the existence of a critical value of **G** for a particular system, above which flocculation

performance would be reduced. A similar effect was observed by Tambo and Hozumi (1979), who proposed the following relationship between maximum floc size and mixing intensity:

$$\text{max. floc size} = C(\mathbf{G})^{-x}, \tag{16}$$

where C and x are constants. Parker *et al.* (1972) calculated theoretical values for C and x for different break-up mechanisms (erosion and fracture) for particles larger or smaller than the Kolmogorov microscale. By assuming that erosion of a given particle to be caused by eddies similar in size that particle, the authors also developed a rate equation for particle erosion. It was proposed that particle erosion was proportional to $\mathbf{G}^2$ for the viscous subrange and $\mathbf{G}^4$ for the inertial subrange (i.e. smaller or larger than the Kolmogorov microscale).

Mühle and Domasch (1990) developed equation 16 to take account of floc strength and primary particle size as well as mixing intensity. These variables were assigned different exponents depending upon the ratio of floc size to the Kolmogorov microscale. As a result, the equation allowed for both floc erosion and floc fracture.

Peng and Williams (1993) proposed a breakage model setting the rate of breakage proportional to floc size. The rate constants associated with this model were found to be increasing functions of **G**. Similarly, Spicer and Pratsinis (1996b) proposed a breakage model where the rate terms this time were explicitly assumed to be functions of both floc size and **G**. Over a range of **G** values (25–150 s^{-1}) experimental results revealed that the rate of breakage was proportional to $\mathbf{G}^{1.6}$.

A quantitative treatment of floc break-up rate as part of the overall kinetic model of flocculation in turbulent mixing was developed by Argaman and Kaufman (1970), and resulted in a working expression for flocculation in continuous flow stirred tank reactors. The model is shown below for "m" CSTRs in series:

$$\frac{N_0}{N_t} = \frac{\left(K_F G t\right)^m}{1 + K_B G^2 t \sum_{i=0}^{m-1} \left(1 + K_F G t\right)^i}, \tag{17}$$

where K_B and K_F are the floc break-up and floc formation constants, respectively. One of the immediate conclusions of this equation is that the Camp number, $\mathbf{G}t$, is not sufficient in itself to categorise the flocculation process because it does not take into account the floc break-up phenomenon.

In some flocculation modelling, breakage is accounted for by setting an upper limit on floc size (Wiesner, 1992; Dharmappa *et al.*, 1994). This approach leads to a maximum in the computed floc size distribution, the value of which depends on the assumed mode of breakage.

All particles are spherical in shape and remain so after collision

Smoluchowski (1917) assumed that solid, spherical particles coalesce to reform perfectly spherical and solid particles. Early verifications of Smoluchowski's equations were based upon fine vapour dispersions where this assumption was perfectly valid. In reality however, particles in the majority of flocculating systems do not coalesce on contact. This is particularly true for water and wastewater systems where flocs are difficult to characterise because of their highly irregular and disordered nature. In a search for a convenient method of characterising water and wastewater aggregates, Li and Ganczarczyk (1989) recognised that they were *fractal* objects. One of the most important properties of fractal aggregates is that their porosity is a function of aggregate size; porosity increases with increasing floc size. Mathematically, this statement is written as

$$\varepsilon = 1 - S^* \mathrm{R}^{D-3}, \tag{18}$$

where ε is the floc porosity, D its *fractal dimension* and S a system-specific constant. The fractal dimension, which defines the relationship between particle size and density, takes values between 1 and 3. In general, the lower the fractal dimension then the more "open" the aggregate structure. If $D = 3$, then the porosity is constant and consequently density is independent of size. In effect, Smoluchowski's equations contain the implicit assumption that the fractal dimension is 3. However, for the majority of flocs in natural systems D is less than 3. When this is the case density will decrease with increasing particle size.

There are two important consequences for flocculation modelling when the fractal dimension is less than 3. Firstly, although mass is conserved when two particles collide, since density is no longer constant volume is not conserved; the volume of the resultant floc is greater than the combined volume of the two colliding particles. This in turn has implications for the rates of particle collision, since collision frequencies and collision efficiencies are functions of particle size. Expressed mathematically, when two particles of radius a_i and a_j collide then $a_{i,j}$, the radius the resultant floc, is defined as

$$a_{i,j}^D = a_i^D + a_j^D. \tag{19}$$

When D is equal to three, equation 19 is equivalent to a statement of volume conservation. Wiesner (1992) published a mathematical model based on equation 19. This model showed that systems with a lower fractal dimension display a more rapid increase in floc size during flocculation.

Secondly, flocs with a low fractal dimension allow fluid to flow though them. This phenomenon is known as *advection*. The degree of advection is characterised by η, the *fluid collection efficiency*,

defined as the ratio of volume of fluid flowing through a floc to the volume of fluid approaching a floc. η thus takes values between 0 for a totally impermeable floc and 1 for a totally porous floc. In effect, the rectilinear approach assumes flocs are totally porous whereas the curvilinear approach assumes flocs are totally impermeable. Neither of these two cases is strictly true for fractal flocs, which have a fluid collection efficiency factor lying *between* 0 and 1. Consequently, particles approach one another along semicurved paths; a compromise between the straight paths assumed in rectilinear modelling and the curved paths assumed in curvilinear modelling. Chellam and Wiesner (1993) demonstrated theoretically that η was correlated to fractal dimension and that the degree of advection became significant when the fractal dimension was less than 2. Where advection is significant, the rectilinear approach overpredicts the rate of collision, whilst the curvilinear approach underpredicts the rate of collision. This effect has been demonstrated for differential sedimentation flocculation (Li and Logan, 1997a) and orthokinetic flocculation in turbulent conditions (Li and Logan, 1997b).

Although it is known that for fractal flocs the rate of collision lies somewhere between the two extremes predicted by curvilinear and rectilinear modelling there is currently no theoretical basis to predict what the value should be. Veerapaneni and Wiesner (1996) proposed incorporating the fluid collection efficiency into collision frequency functions to *approximate* for the effect of advection. For orthokinetic flocculation, the authors proposed

$$\beta(i, j) = (\mathbf{G}/6)(d_i\sqrt{\eta_i} + d_j\sqrt{\eta_j})^3. \qquad (20)$$

Li and Logan (1997b) identified a correlation between fractal dimension and collision frequency for flocculation in turbulent flow conditions

$$\beta \sim \mathbf{G}^{(1-D/3)}. \qquad (21)$$

The factors that affect the magnitude of the floc fractal dimension are complex and not dealt within this review. However, it can be generally observed that, all other things being equal, systems with a higher collision efficiency will tend to form flocs with a lower fractal dimension, leading to dominance of rectilinearity over curvilinearity.

Collisions involve only two particles

The conventional kinetic approach to flocculation modelling discussed so far essentially relies upon the calculation of collision frequencies and collision efficiencies based on the knowledge of particle velocities and surface potentials. The validity of this approach is questionable when systems become concentrated such that collisions between more than two particles are likely.

An alternative approach to modelling flocculation is the *thermodynamic theory* of coagulation. In this approach, coagulation is seen as a "phase-separation" process: the stabilised colloid represents the dispersed phase and the destabilised/aggregated colloid represents the solid phase. This approach gives insight into floc structure but does not provide any information on the rate of coagulation. Rajagopalan (1993) applied thermodynamic theory to a colloidal dispersion represented by an idealised potential–separation graph, typical of van der Waals attraction between two neutral spheres. Interestingly, the phase diagrams attained for colloids modelled as adhesive hard spheres (i.e. zero attraction at all separation distances but infinite attraction once touching) were extremely close to the phase diagrams for the colloids modelled with short range attractive forces. Analysis of the constructed phase diagrams allows one to calculate the required degree of destabilisation to promote flocculation.

Summary

The collision efficiency term cannot be expected to provide a comprehensive account of the interparticle forces involved in flocculation. Substantial developments have been made in defining the influence of van der Waals attraction and hydrodynamic forces. In particular, the inclusion of hydrodynamic forces had lead to a marked reduction in both the expected rates of flocculation and the significance of mixing intensity.

Although substantial theoretical errors have been identified in the work of Camp and Stein (1943), their root-mean-square velocity gradient, **G**, has remained a key design factor in terms of flocculation modelling. The complexities of turbulent flow have hindered any major improvements upon the work of Camp and Stein, although it is generally accepted that previous work has overestimated the importance of **G**.

It is not feasible to construct and solve flocculation equations for each individual particle size if the range of interest covers more than two orders of magnitude. Instead particles can be grouped into classes to expedite solution of the flocculation equations. For flocculating systems under certain circumstances the particle size distribution displays predictable patterns that are independent of time and initial particle size distribution. This phenomenon is called self-similarity.

Uncertainty still exists as to the general nature of floc break-up, although it is accepted that the mechanism plays a major role in determining the overall size distribution during flocculation.

Particles are now recognised as fractal rather than solid objects. Consequently their density decreases with increasing size. This has lead to a reassessment of the validity of both the curvilinear and rectilinear models of flocculation. It is now accepted that the real situation lies somewhere between these two models.

Table 1. Mathematical models of flocculation applied to real systems. (O = orthokinetic flocculation, P = perikinetic flocculation, DS = differential sedimentation)

Reference	Breakage	Mechanism	Uniform density	Hydro-dynamic correction	Collision frequency	Material	Model success	Model weakness
Hudson (1965)	Ignored	DS	yes	no	Variable	River water		Errors in equations
Delichatsios and Probstein (1974)	Ignored	O	yes	no	1	Latex	Model within 12% of theoretical values.	Unable to extend results further than 10 s after initial flocculation
Gregory (1981)	Ignored	O	yes	yes	Variable	Latex	Matched general trend for total particle count	Over predicted rate of flocculation
Wiesner (1992)	Max size equal to Kolmogorov scale	O, P, DS	no	no	1	Ferric hydroxide	Successfully predicted volume fraction greater than 1 μm	Unable to successfully model size distribution
Dharmappa *et al.* (1994)	Max size $\sim G^{1/2}$	O, P, DS	no	no	0.2–0.4	Kaolin	Demonstrated that flocculation improvements were more sensitive to mixing time than mixing intensity	No comparison with experimental evidence provided.
Bhaskar *et al.* (1993)	Max size	O	yes	no	1	Mineral acid casein curd	Demonstrated that the Camp number characterises the early degree of flocculation	No experimental evidence provided to support experimental technique
Spicer and Pratsinis (1996b)	Various discrete models	O	yes	no	1	Polystyrene	Predicted final mean particle size	Unable to correctly predict initial rate of flocculation

There have been a number of attempts by researchers to model actual flocculation systems, each of which address some of the identified constraints in the original Smoluchowski equations, with varying degrees of success. Table 1 summarises some of these models and the assumptions contained within them.

APPLICATION TO REAL SYSTEMS

Microscopic approach

A number of shortcomings of the modified coagulation theory can be identified when applied to real systems.

1. The chemical nature of the surface of natural water-borne particles affects processes such as precipitation, destabilisation and surface adsorption. However, surface chemical effects are either ignored or dealt with in a simplistic manner in the flocculation models. Consequently, the correlation between the chemical nature of primary sewage particles, for example, and the interparticle colloidal forces becomes complex and obscure. The situation is further complicated by the presence of a matrix of soluble chemicals in primary sewage, such as alkalinity, hardness, phosphate and humic compounds. The interactions between these chemicals, the coagulant and the primary sewage particles are poorly understood.
2. Neither the rectilinear or curvilinear approach is entirely applicable to the flocculation of flocs. Ignoring the hydrodynamic affects, as in the rectilinear approach, is clearly incorrect. On the other hand, the assumption made in the curvilinear approach that fluid only flows around rather than through a floc is also an oversimplification. In reality, because flocs are porous, as water squeezes out of the gap in between approaching particles some water will escape by flowing through the particles. The actual situation for wastewater particles thus lies somewhere between the two extremes.
3. One of the underlying assumptions of the flocculation equations is that only binary collisions take place. This assumption may be true in dilute systems encountered in drinking water treatment, but in concentrated wastewaters such as primary sewage there is an increased likelihood of multibodied collisions.

Two important conclusions can be drawn from these considerations. Firstly, experimental results based on idealised particle suspensions are unlikely to be representative of the behaviour of real systems. Secondly, focusing on the microscopic behaviour of real particles in an attempt to deduce correlations between process parameters (e.g. mixing intensity, coagulant dosage) and flocculation kinetics (i.e. collision efficiencies) would be extremely difficult.

Macroscopic approach

Rather than either concentrating on *microscopic* phenomena such as individual collisions or relying entirely on empirical measurements, a compromise approach would be to focus on *macroscopic* measures of flocculation. One such macroscopic measure is the *fractal dimension*, D, of the flocs formed during the flocculation process. For flocs with a fractal dimension D and of length L, the mass of the floc is proportional to L^D. The value of the fractal dimension has a number of important consequences regarding flocculation. Since the fractal dimension partly defines the relationship between mass, porosity and size it affects the following:

1. the degree of advection through a floc,
2. the proportion of water contained within a floc,
3. the settling velocity of a floc,
4. the rate of collision of a floc and
5. the strength of a floc.

From the above list it is clear that knowledge of the fractal dimension is required to make a successful attempt at modelling flocculation. The parameter has important consequences in terms of water and wastewater treatment. Flocs with lower fractal dimension, besides settling more slowly, also contain a larger proportion of water. This leads to sludges that are both bulky and expensive to dewater. The balance between improving flocculation kinetics and producing flocs with high fractal dimension requires further investigation. It is important to optimise wastewater treatment with respect to both solids removal *and* sludge treatment costs. The ultimate success of using fractal dimensions to characterise the flocculation process will depend on whether or not relationships found between the fractal dimensions and operating parameters for one sewage for one source apply to generic water types from different sources.

CONCLUSION AND FUTURE DEVELOPMENTS

Considering the significant developments that have occurred since the publication of the original paper of Smoluchowski (1917), flocculation modelling could be described as an established field of research. The vast majority of papers published in this area consider the microscopic aspects of the system, namely surface chemistry and the particle interations which result from this. However, successful application of these models is largely limited to idealised, artificial systems — such as suspensions of uniform latex spheres — due to constraints imposed by the requirement for surface homogeneity. In real systems, which are invariably both physically and chemically heterogenious, the correlation

between simulated to experimental data has been poor.

More recent research has been directed at macroscopic parameters pertaining to floc growth, and in particular the transient fractal dimension. Whilst less rigorous that the microscopic approach, the modelling of the particle fractal dimension ultimately permits the characterisation of the behaviour of any system with reference to a single parameter. On the other hand, this parameter can at present only be determined empirically through fairly sophisticated modern techniques for particle characterisation. The application of flocculation modelling to complex matrices such as municipal wastewater thus requires a renewed effort in experimental work, based on techniques such as on-line particle size analysis and image analysis technology, to provide the opportunity to look in detail at both particle structure and flocculation kinetics. Having said this, experimental developments in this area have thus far tended to be focused on model systems (Jiang and Logan, 1996; Smoczynski and Wardzynska, 1996). The current level of understanding of the factors affecting fractal dimension in real life flocculating systems is thus low, though the area is developing rapidly.

Future methods for taking account of the hydrodynamic forces between approaching aggregates must account for (a) nonuniformity of their porosity, (b) nonsphericity and (c) Reynolds number greater than one. Moreover, the interaction between colloidal forces, e.g. van der Waals attraction, and hydrodynamic forces must also be taken into consideration. Although all of these aspects have already been dealt with within the literature, this has been carried out in isolation from one another. As yet, no single model has comprehensibly tackled all the issues associated with the collisions between fractal aggregates.

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