Population balance modelling of particle flocculation with attention to aggregate restructuring and permeability

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Abstract

A population balance model based on a detailed literature review is used to describe coagulation and flocculation kinetics as well as the time evolution of aggregate size distribution in a turbulent shear flow simultaneously with the breakage and restructuring of aggregates. The fractal nature and permeability of the aggregates and their evolution with time are also part of the model. Restructuring is absent in coagulation with soluble salts, but is present in flocculation caused by large polyelectrolyte molecules; in the latter, aggregates never reach a steady-state size, but a size that decreases gradually through particle and polymer rearrangement. The model is tested against available experimental data for monodisperse polystyrene particles coagulated with hydrated aluminium sulphate at different shear rates, and precipitated calcium carbonate flocculated with a cationic polyelectrolyte of very high molecular weight at different flocculant dosages. The numerical solution of the model requires adjusting three parameters, i.e., maximum collision efficiency (αmax), critical force needed for the breakage of the aggregates (B) and rate of aggregate restructuring (γ), which are obtained from minimising the difference between experimental data and model predictions. The model studied for the two very different systems shows excellent agreement with experimental flocculation kinetics and a reasonably good fit for aggregate size distributions. The model is most sensitive to the fragmentation rate through parameter B, somewhat less to the collision efficiency through parameter αmax and little to γ. When the aggregates undergo restructuring, properties such as permeability, breakage rate and collision rate change considerably over time. When the aggregates are permeable, the collision frequency is significantly smaller than when they are impervious.

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1. Introduction

The separation of small particles from a liquid medium can be very complex and difficult to control; the issue is of great importance, because it is a fundamental stage in many industrial applications, for instance, in
mining, extracting oil, cellulose and paper production, water purification, wastewater treatment and industrial food preparation. Particularly in mining, the shortage of water strongly encourages recovering and recycling water from large thickeners. In recent times, this separation operation is as central as flotation, as thickeners cannot cope against increasing volumes of material, increasing amounts of fines in the feed ore to the plants and more saline waters; in some cases, the direct processing of seawater is involved. Sometimes, limitations in the thickeners force the drastic decision to stop plants from operating. For efficient separation, it is necessary to promote the aggregation of particles to form larger structures that can settle by gravitational effects [see for instance Refs. 1–6]. This can be stimulated in different ways, either by adding salts and small destabilising particles or by manipulating the pH of the medium; although, the more traditional method and usually the more effective one is to add a flocculant, that is, large macromolecules capable of adhering to suspended particles in order to form aggregates or flocs very quickly. Indeed, the characteristics of these aggregates and their size, structure and resistance to breakage directly determine the efficiency of the separation, including sedimentation speed, quality of the water recovered and rheological and mechanical properties of the resulting sediment [7]. For this reason, in recent years, the emphasis has been on directly studying flocculation by examining the characteristics of the aggregates with light-scattering techniques as a function of molecular weight, charge density and distribution of the flocculant, pH and temperature, flocculant dosage, shear velocity and so forth. [8–15]. At the same time, there have been several attempts to predict the behaviour of the aggregates through analytical models, particularly for automatic control and for reducing the experimental burden. These models usually make use of the classical equation of von Smoluchowski [16], which is based on population balance equations (PBEs) that describe the rate of irreversible aggregation. This equation is useful to describe aggregates that are dense and which density is preserved as in coagulation but not to describe aggregates that are irregular and loose as in the case of flocculation. Thus several authors have proposed modifications achieving considerable progress in the modeling of particle flocculation through heuristic methods with adjustable parameters that are ultimately responsible for reconciling experimental data with model [see for instance Ref. 17]. More recently, such physics of the aggregation problem has also been enriched. The irregular structure of the aggregates has been included through the fractal dimension, which is crucial, according to Thomas et al. [18], if the model is to represent a real system. Thus, some authors began to include the fractal dimension in the PBE [19–21]. However, most assume a fixed fractal dimension, meaning that the structure of the flocs is preserved throughout the process, which is not generally the case. In many cases, the measured flocculation kinetics show that particles are added to structures that increase in size until they reach a maximum, and then they decrease until they reach a stable size [4, 22–24]. According to Heath et al. [4], the reduction in floc size is caused by polymer degradation and consequent floc break up. However, experimental studies have indicated that it is also because of changes in structure, owing to the rearrangement of aggregates, particles and flocculant; therefore, considering a unique fractal dimension prevents the model from being representative of such behaviour. Selomulya et al. [25] successfully incorporated the restructuring in the PB by considering that the fractal dimension changes during flocculation. The introduction of more than one fractal dimension implies changes in the porosity of the aggregates. More recently, Antunes et al. [26] and Sang and Engelzos [27] correctly modelled flocculation kinetics curves by changing the fractal dimension, but failed to take into consideration the permeable nature of the aggregates. Although their results fit the experimental data well, the adjustable parameters are of limited value to other systems. Somasundaran and Runkana [28] have demonstrated that permeability affects the movement of the aggregates and thus the collision rate. According to these results, a permeability law in terms of the changing porosity of the aggregates, seems necessary. Ahmad et al. [29] considered the aggregates as a permeable structure, but use the fractal dimension with a constant value, thus ignoring the restructuring. Here, we develop a PBE-based model that takes into account both aggregate permeability and restructuring.

2. Model description

The PBE used here is that of Hounslow et al. [17] with particle grouping, as suggested by Spicer and Pratsinis [30], divided into sizes based on a geometric progression. The discrete form of the resulting balance, based on doubling the particle or aggregate volume ($V_i$) after each interval ($V_{i+1} = 2V_i$) describing the rate of change for number concentration, is:

\[
\frac{dN_i}{dt} = \sum_{j=1}^{\max_1} 2^{i-j} \alpha_{i-j} \beta_{i-1} N_{i-j} - N_i \sum_{j=1}^{\max_1} \alpha_{i-j} \beta_{i-1} N_j + \frac{1}{2} \sum_{j=1}^{\max_2} \alpha_{i-j} \beta_{i-1} N_j - S_i N_i
\]

(1)

where $N_i$ is the number of aggregates or flocs containing $2^i$–1 particles, whereas $N_i$, for the size interval $i = 1$, is the number concentration of primary particles, $s$ is the aggregate–breakage–restructuring time. The first two terms from the right-hand side of Eq. (1) account for the formation or growth of aggregates in the $i$–th size interval from the collisions of aggregates of smaller size ranges. The third and fourth terms represent the loss of aggregates in the $i$–th size interval by the aggregation of flocs from size interval of those from other size intervals. The fifth term accounts for the loss of aggregates in the $i$–th size interval through fragmentation, whereas the sixth term denotes the gain of aggregates in the $i$–th size interval by fragmentation of larger flocs. The super indexes, max 1 and max 2, respectively, represent limiting size intervals to which the fourth and sixth terms of Eq. (1) are to be evaluated. The expression by Hounslow et al. and Spicer and Pratsinis involves four functions that represent particulate systems; the functions are (i) collision efficiency ($\alpha_i$), (ii) collision frequency ($\beta_i$), (iii) fragmentation rate of flocs in the $i$–th interval ($S_i$) and (iv) breakage distribution function for the break up of aggregates in the $j$–th interval, which generates fragments of sizes that fall in the $i$–th interval ($S_i$). Detailed description and analysis of these functions are given by Elimelech and Gregory [31]. More recently, Selomulya et al. [25] and Bonanomi et al. [32] introduced a new function to account for the change in floc structure as flocculation progresses, which can be quantified through the variation in the fractal dimension of the flocs with time. All of the five functions come from heuristic rules, and the parameters involved are determined by solving Eq. (1) against experimental data. These parameters determine the predictive power of the model in Eq. (1). Details for discretising the PB and the “lumping” of size intervals can be found in previously published reports (see for instance Ref. [20]).

Next, these functions are described for general permeable particles or flocs that are fractal in nature and for which the fractal dimension evolves with time. Spherical aggregates, impermeable aggregates and fractal aggregates with constant fractal dimensions are particular cases.

2.1. Collision frequency

The overall collision frequency between two particles in the $i$–th and $j$–th intervals, which is due to the Brownian motion of the particles and aggregates, the shear rate applied to the system, and the sedimentation by gravity, can be written as

\[
\beta_{ij} = \beta_{ij}^{p} + \beta_{ij}^{n} + \beta_{ij}^{b}
\]

(2)

where $\beta_{ij}^{p}$ is the collision frequency for perikinetic aggregation of aggregates belonging to intervals $i$ and $j$, $\beta_{ij}^{n}$ is the collision frequency for orthokinetic aggregation of flocs belonging to intervals $i$ and $j$ when
the system is subject to an applied shear, and $\beta_{ij}^{\text{fl}}$ is the collision frequency by gravity. In addition to the fractal dimension of the aggregates, Veerapaneni and Wiersner [33] considered the permeability of such aggregates. This new condition demanded a modification of the expressions for the collision frequency based on rectilinear paths by adding two parameters, a correction factor for the drag force ($\Omega$) and an efficiency of accumulation of fluid ($\eta$). The collision frequency between irregular and permeable aggregates in the intervals $i$ and $j$ are thus given by Eqs. (3) to (5) for the perikinetic, orthokinetic, and sedimentation components respectively

$$\beta_{ij}^{\text{fl}} = \frac{2k_BT}{3\eta} \left( \frac{1}{\Delta R_{ci}} + \frac{1}{\Delta R_{cj}} \right) \left(R_{ci} + R_{cj}\right)$$  \hspace{1cm} (3)

$$\beta_{ij}^{\text{fl}} = 1.294G \left( \sqrt{\eta R_{ci}} + \sqrt{\eta R_{cj}} \right)^3$$ \hspace{1cm} (4)

$$\beta_{ij}^{\text{fl}} = \pi \left( \sqrt{\eta R_{ci}} + \sqrt{\eta R_{cj}} \right)^3 \left(u_i' - u_j' \right)$$ \hspace{1cm} (5)

where $R_c$ is the collision or effective capture radius of aggregates in the $i$-th interval, $G = \left(u_i/u_j\right)^{1/2}$ is an estimated spatially averaged turbulent shear with $\epsilon$ the average energy dissipation rate and $\nu$ the fluid kinematic viscosity [34,35], and $u_i'$ is the settling velocity of permeable aggregates in the $i$-th interval which can be determined by using the Stokes sedimentation velocity expression [36] or a modified Stokes expression useful for permeable aggregates [37]. Here, collision frequency by gravity sedimentation is neglected because $\rho_{\text{particle}} \approx \rho_{\text{water}}$ [38].

The prefactor in Eq.(4) becomes $4/3$ for laminar shear with $\nu$ and $G$ is the linear shear rate [16]. The limitation of considering aggregates as perfect solid spheres has been overcome by considering the fractal nature of the aggregates. Flesch et al. [20] proposed

$$R_{ci} = R_{0} \left( \frac{N_i}{C} \right)^{1/d_f}$$ \hspace{1cm} (6)

where $R_0$ and $N_i$ are the radius and number of primary particles in an aggregate of size in the $i$-th interval ($N_i = 2^{i-1}$) respectively, whereas $k_i$ is a proportionality constant related to the particle packing density, which is generally taken as 1 [39], and $d_f$ is the mass fractal dimension of the flocs, which is an indicator of the space occupied by the particles in a given aggregate and its value is between 1 (a line of particles) and 3 (a solid sphere). In Eq. (3), $\Omega$ is given by the ratio of the force exerted by the fluid on a permeable aggregate to the force exerted by the fluid on an impermeable sphere of equivalent size [40], and $\eta$ is given by the ratio of the flow moving through an aggregate to the total flow approaching the aggregate [41]. For values of $\Omega$ and $\eta$, we used available expressions [37]. Thus, $\Omega$ and $\eta$ are given by Eqs. (7) and (8), respectively:

$$\Omega = \frac{2\xi^2 \left( 1 - \tanh \frac{\xi}{\kappa} \right)}{2\xi^2 + 3 \left( 1 - \tanh \frac{\xi}{\kappa} \right)}$$ \hspace{1cm} (7)

$$\eta = 1 - \frac{d}{r} - \frac{c}{\xi^3}$$ \hspace{1cm} (8)

where

$$\xi = \frac{r}{\sqrt{K}} \quad d = \frac{3}{2} \xi^3 \left( 1 - \tanh \frac{\xi}{\kappa} \right), \quad c = - \frac{1}{7} \left[ \xi^6 + 6\xi^3 - \frac{\tanh \xi}{\kappa} \left( 3\xi^3 + 6\xi^5 \right) \right]$$ \hspace{1cm} (9)

$$J = 2\xi^2 + 3 - 3\tanh \frac{\xi}{\kappa}$$ \hspace{1cm} (9)

in which $r$ is the size of the aggregates and $K$ is the permeability of the aggregates that need to be evaluated. Li and Logan [42] found that the Brinkman and Happel permeability equations provide more realistic predictions of the properties of fractal aggregates than the Carmen–Kozeny equation. In this study, the Brinkman equation is used, that is:

$$K = \frac{d_p^{2}}{72} \left[ \frac{3}{1 - \phi} - \frac{\phi}{1 - \phi} \right]$$ \hspace{1cm} (10)

where $\phi$ is the porosity of the aggregates, which is constant for non-fractal aggregates and size-dependent for fractal aggregates. For fractal aggregates, the porosity and fractal dimension are related through [42]:

$$\phi = 1 - C \left( \frac{d_p}{d_f} \right)^{d_f - 3}$$ \hspace{1cm} (11)

where $C$ is a packing coefficient, assumed here to be 1, whereas $d_a$ and $d_p$ are the flocc and primary particle diameters, respectively. The porosity depends on the size of the aggregates if $D < 3$. For non-fractal aggregates, $D = 3$ and the porosity is constant. Viscous flow along fractal pore walls in thin films of small thickness governed by disjoining forces and capillarity [43–49] is another possibility, which we leave for future work.

2.2. Collision efficiency

The collision efficiency ($\alpha_{ij}$) represents the probability that two particles or flocs stay together after colliding. It is a complex function that depends on the surface properties of the particles, the hydrodynamic effects within the aggregates and the interaction forces between the particles; thus, determining its value is not easy. In some cases, it is assumed to be an adjustable parameter [50], but in other cases a constant value is simply assigned [51,52]; generally, either one can limit the predictive power of the model. Moreover, some researchers choose to include the interaction potential between the interacting particles [53], benefiting the physical content of the model; however, the resulting mathematical model prevents its resolution in a reasonable time. A practical alternative is to use mathematical models deduced heuristically; these models are characterised by their mathematical simplicity while incorporating some relevant physical characteristics of the process, and the physical flaws are hidden in adjustable parameters. Along this line, Kusters [54] developed a model using the trajectory analysis of Adler [55] to predict the approaching paths of porous flocs modelled as impermeable cores surrounded by permeable shells. The resulting semi-empirical function estimated that the collision efficiency was significantly lower when the size ratio of the colliding flocs was $\leq 0.1$, compared to when the flocs are of similar size. This core–shell model correctly predicted that the attachment probability would be notably reduced for larger and/or less permeable flocs. Selomulya et al. [25] adopted the following analogous empirical form for the collision efficiency model of Kusters; this form is also used here:

$$\alpha_{ij} = \left[ \exp \left( -x(1 - \frac{1}{j})^2 \right) \right]^{\alpha_{\text{max}}}_{\alpha_{\text{max}}}$$ \hspace{1cm} (12)

where $i$ and $j$ are the intervals to which the colliding flocs pertain. Higher values of $\alpha_{ij}$ are allowed for flocs of comparable sizes, that is, when $i = j$, and lower values are otherwise allowed. Values for $x$ and $y$ are used as fitting parameters and $\alpha_{\text{max}}$ is used to denote the upper limit of $\alpha_{ij}$, with $0 \leq \alpha_{\text{max}} \leq 1$. We use $x = y = 0.1$ [25,26] and consider $\alpha_{\text{max}}$ as an adjustable parameter, as others have done [26,56].
2.3. Fragmentation rate

The breakage of aggregates is mainly caused by hydrodynamic stress experienced in the aggregates. The fragmentation rate \( S_i \) of aggregates in the \( i \)-th interval is given by the semi-empirical relation [54]:

\[
S_i = \left( \frac{4}{5\pi} \right)^{1/2} \left( \frac{\gamma}{\nu} \right)^{1/2} \exp \left( -\frac{\epsilon_{\text{crit}}}{\epsilon} \right)
\]

where \( \epsilon_{\text{crit}} \) is the critical energy dissipation rate needed for the breakage of aggregates in the \( i \)-th interval, which can be estimated from the floc size through \( \epsilon_{\text{crit}} = B/R_{\text{CR}} \), a relationship observed experimentally [57, 58] and in simulations [59]. Clearly, larger aggregates break up more easily. The fragmentation rate increases with increasing shear rate \( \gamma \). \( B \) is a fitting parameter that represents the critical force needed for the breakage of aggregates and, according to Selomulya et al. [25], can be adjusted to allow fewer or more break ups at the \( i \)-th size interval for a given shear rate. Parameter \( B \) can also be selected to define the size interval in which fragmentation starts. Aggregates with lower fractal dimensions experience higher fragmentation rates.

2.4. Breakage distribution function

The breakage distribution function \( \Gamma_i \) describes the distribution of fragments in the \( i \)-th interval from the break up of aggregates in the \( j \)-th interval. There are several ways to define the breakage distribution function [51]. Here, we use a binary breakage function [60] that is easy to implement, requires no additional adjustment parameters and yet adequately predicts aggregate sizes:

\[
\Gamma_{ij} = V_i/V_j \text{ for } j = i + 1 \text{ and } \Gamma_{ij} = 0 \text{ for } j \neq i + 1
\]

where \( V_i = 2^i - 1 \) and \( V_j = 2^j \) and \( V_0 \) is the primary particle volume.

2.5. Restructuring

Particle flocs suffer restructuring during flocculation by aggregation, fragmentation, elongation and compaction [61,62]. Such restructuring is incorporated in Eq. (1) through the evolution of the fractal dimension [25,32], according to:

\[
\frac{d(d_f)}{dt} = \gamma (d_f \text{max} - d_f)
\]

where \( \gamma \) is a fitting parameter that represents a type of rate of aggregate restructuring and \( d_f \text{max} \) is the maximum fractal dimension.

3. Model solution

Here, the model was tested against the experimental data of Flesch et al. [20] and Antunes et al. [63]. Flesch et al. worked with monodisperse polystyrene particles coagulated with hydrated aluminium sulphate, whereas Antunes et al. used a cationic polyelectrolyte of very high molecular weight to flocculate particles of precipitated calcium carbonate. The flocculation kinetics curves obtained experimentally correspond to the time evolution of the volume mean size of the aggregates, \( d[4,3] \). However, the PBE of the model [Eq. (1)] describes the evolution of the number of particles in each size interval with time. To compare the experiments and model them, it is necessary to transform the aggregate number concentration in each size interval \( i \) to volume size, according to the definition:

\[
\left[ d[4,3] \right] = \sum_{i=1}^{i_{\text{max}}} N_iD_i^4/ \sum_{i=1}^{i_{\text{max}}} N_iD_i^3
\]

with

\[
D_i = \left( 2^{(i-1)/d_f} \right) d_0
\]

where \( d_0 \) corresponds to the mean diameter of the primary particles.

The PBE of the model [Eq. (1)] was solved numerically by the method of Bogacki and Shampine [64], which provides a result of third-order accuracy and an estimated error based on an embedded second-order formula, which is used to implement an adaptive step size. The maximum number of size intervals was 30, covering aggregates containing 1 to 2\(^{29} \) particles. Integrating Eq. (1) requires the value of the shear rate of the system \( \gamma \), the average primary particle size \( d_0 \), the number concentration of primary particles \( N_i \) and the fractal dimension of the aggregates at the beginning \( d_f \) and at the end of the process \( d_f \text{max} \) as inputs. The numerical solution of the model requires the adjustment of three parameters, \( \epsilon_{\text{crit}}, B \) and \( \gamma \), which are obtained from minimising the following objective function:

\[
\text{GoF} (\alpha_{\text{max}}, B, \gamma) = \sum_{i=0}^{i_{\text{max}}} d[4,3]_{\text{experimental}} - d[4,3]_{\text{model}}
\]

To solve Eq. (16), we use the Matlab function \texttt{fminsearch}, which uses the Nelder–Mead direct search to find the minimum of an unconstrained multivariate function. As a goodness of fit (GoF), we use [50]:

\[
\text{GoF} \% = 100 \frac{d[4,3]_{\text{error}}}{d[4,3]_{\text{total}}}
\]

with the standard error \( s_{\text{error}} \) determined from Eq. (19):

\[
s_{\text{error}} = \sqrt{\frac{\sum_{i=0}^{i_{\text{max}}} \left( d[4,3]_{\text{experimental}} - d[4,3]_{\text{model}} \right)^2}{n-f}}
\]

where \( n \) is the number of data values and \( n-f \) is the number of degrees of freedom; in the latter, \( f = 3 \) for a model with three parameters. With these definitions, a GoF of 90% or higher means that the proposed model is able to predict the flocculation kinetics.

Eq. (21) is used to calculate the restructuring parameter \( RP \), which we use as an indicator of the degree of restructuring. Antunes et al. [26] defines \( RP \) as:

\[
RP = \frac{d_f \text{max} - d_f \text{final}}{d_f \text{max}} \times 100\%
\]

where \( d_f \text{max} \) corresponds to the maximum floc size, typically in the early stage of flocculation, and \( d_f \text{final} \) corresponds to the final floc size at a steady state. \( d_f \text{max} \geq d_f \text{final} \). Finally, conservation of the total volume of particles or flocs was verified at all integration times; this ensures that the simulations are not sacrificing particle populations.

4. Results and discussion

Fig. 1 shows the effect of the shear rate on the flocculation kinetics of polystyrene particles with aluminium sulphate hydrate, as reported by Flesch et al. [20] in addition to the results from our model. The results of the aggregate size are from both coagulation, which is more significant at shorter times, and fragmentation, which is more significant after a certain time once the aggregates become larger. Polystyrene surfaces in water are not strictly neutral, because they bare negative residual charges, and thus coagulation at early times should not be expected to be important, owing to repulsive forces [65–67]. The aggregates grow initially for all three shear rates, but then smoothly reach a steady-state size. Increasing the shear rate increases both coagulation and
fragmentation; however, the latter increases faster, thus decreasing the steady-state size of the aggregates and the time for reaching it. This effect of shear on the flocculation dynamics of inorganic systems has been shown repeatedly in previously published reports. As can be seen in Fig. 1, the model correctly describes the experimental data at all stages of the flocculation process and all three shear rates. Table 1 shows the parameters fitted for each shear rate and the quality of the fits, which are always better than 87%. Flesch et al. also compared their experimental results with a PB model using a single parameter. Their model is in excellent agreement with their experimental results. More recently, Somasundaran et al. [7, 28] compared the experimental results of Flesch et al. with a very similar PBE model, except for a different collision frequency and a collision efficiency they set to unity from the outset. For these reasons, it is likely that their results are not as good as those of Flesch et al.; polystyrene particles become charged in water and, therefore, one should expect some repulsion between particles and, consequently, a collision efficiency less than unity. Our model with two parameters, for particles with time- and scale-invariant fractal dimensions, shows good agreement with the experimental data of Flesch et al. with a collision efficiency that is significantly less than 1 and for which the value decreases with the shear rate.

Results in Fig. 1 are for averaged aggregate size and it is important to compare the complete experimental steady-state aggregate size distribution with the distribution predicted by the model. Fig. 2 shows such a comparison for the three different shear rates. As expected, the experimental distribution narrows and shifts to smaller aggregate sizes for increasing shear rates. Predictions from the present model track the experimental unimodal size distribution very well and it is somewhat better than the model of Flesch et al., which predicts a bimodal distribution in all cases. These latter authors make a commendable effort towards finding the origin of the deviation by changing the binary breakage (which we use here) of several forms of the normal fragment size distribution; the predictions significantly improved for the distribution mode for the larger sizes, but the second mode for smaller particles continued to appear. The origin, however, according to our results, is the collision efficiency, which is clearly less than 1 in all of the cases studied. We also compare the experimental aggregate size distribution evolution with predictions from the model. Fig. 3 shows such comparison for $G = 50$ s$^{-1}$ and different flocculation times. Our results for simple binary breakage show somewhat better agreement with the unimodal experimental data than the model of Flesch et al. with a normal fragment size distribution. Our model captures the broadness of the distribution at all times, but particularly at longer times approaching the steady state.

Flocculation kinetics induced by high-molecular-weight polymers or surfactants are far different from the kinetics reported by Flesch et al.

<table>
<thead>
<tr>
<th>$G$ [s$^{-1}$]</th>
<th>$\alpha_{\text{max}}$ [dimensionless]</th>
<th>$B$ [m$^3$/s$^2$]</th>
<th>Gof [%]</th>
</tr>
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<tr>
<td>50</td>
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<td>87</td>
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<tr>
<td>100</td>
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<td>13.11</td>
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</table>
concentration: 6, 8 and 10 mg/g of PCC; shear rate: 312 s⁻¹ for 27 min

Fig. 3. Experimental (symbols) vs. calculated (continuous lines) time evolution of aggregate size distribution, corresponding to Fig. 1 at four different flocculation times, that is, 6, 8, 14 and 27 min for G = 50 s⁻¹. Experimental data were obtained from Flesch et al. [20].

Fig. 4. Experimental (symbols) vs. calculated (continuous lines) time evolution of the mean volume diameter of aggregates of precipitated calcium carbonate (PCC) with a high-molecular-weight polyacrylamide, as reported by Antunes et al. [63], and the results from our modelling, taking into account both flocc permeability and restructuring. All three dosages show that the aggregate size first increases, reaches a maximum and then decreases to a stationary size.

At short times, the flocculant has not reached the particles and, therefore, the only possible aggregation mechanism is coagulation, and the extent of it is limited by the repulsive forces exerted by the negative charges on the particle surfaces (zeta potential of primary particles is negative). This explains why the curves in Fig. 4 show a similar increase in the rate of aggregate size at extremely short times. At longer times, the flocculant reaches the particles and dominates the aggregation process over the fragmentation of the aggregates. The aggregates reach a maximum size, which depends on the flocculant dosage. In systems coagulated with salts (see Refs. [19,20] for examples), the maximum size is also the stationary size; however see Ref. [68] for a case out of this rule. According to Heath et al. [4,21,23] and Selomulya et al. [22], fragmentation is reversible in systems with coagulant salts, because the salts are soluble. Flocculation of particles with a high-molecular-weight polymer follows a different trend, unless flocculation occurs primarily through mechanisms of surface-charge neutralisation. Large polymeric flocculants mainly act by forming polymer bridges between two or more particles and by extensive polymer solvation.

Fig. 4 shows that the stationary size is considerably smaller than the maximum aggregate size for all three dosages. This is typical of aggregation mediated by mechanisms of polymer bridging: the gentle decrease in aggregate size upon extended shearing is attributed to polymer degradation and rearrangement of aggregates. Some authors have also invoked the compaction of aggregates; however, Heath et al. [4] discarded it, at least for the calcite–polymer system, because the setting rates they measured show a decrease with aggregate size [23]. Interestingly, the largest maximum and stationary aggregate sizes are obtained for a dosage that is considered the optimum dosage. Fig. 4 shows that the model used here also correctly describes the experimental data of Antunes et al. [26] for all three dosages, including the optimum dosage of 8 mg/g. Table 2 shows the parameters fitted for each flocculant dosage, the quality of the fits, which is always better than 93%, and the degree of restructuring, which is higher for the optimum dosage. Antunes et al. also compared...
their experimental results with a PB model using three parameters. Their model is in good agreement with their experimental flocculation kinetic curves for all three flocculant dosages and with their measured aggregate size distributions. Our model, also with three parameters, is an improvement over that of Antunes et al. as the key permeability of aggregates is included. Our results, as can be seen in Fig. 4, are in excellent agreement with their flocculation kinetic curves. The model can still be improved by adding surface forces in place of empirical functions for the collision efficiency, as has been done by Somasundaran and collaborators [7,28]. Good agreement has been found for particle systems flocculated with coagulant salts and polymer flocculants; however, thus far, the model appears to have been tested in systems showing only monotonous growth in the aggregate size.

The restructuring can be evaluated in terms of the fractal dimension of the aggregates, which is obtained from Eq. 15. For the data reported by Flesch et al. [20] the fractal dimension is constant throughout the aggregation process ($d_f = 2.05$), but increases for the data of Antunes et al. [63] (Fig. 6) justifying the maximum in the flocculation kinetics.

To appreciate the model to its full potential, we compared the experimental time evolution of the aggregate size distribution with predictions from the model, given that a good prediction of the flocculation kinetics in Fig. 4 is less revealing, because it only refers to the average size of the aggregates. Fig. 5 shows the comparison of the flocculant in Fig. 4 at concentration of 8 mg/g with that at two different flocculation times. The model captures the breadth of the distribution very well at all times, but particularly at longer times approaching the steady state.

Next, we present several predictions from the present model that we cannot compare with experimental data, because these are not available; however, the different predicted behaviours reveal important aspects of the aggregates, depending on their flocculation characteristics.

Fig. 7 shows that, when the structure of the aggregate remains unchanged, the fragmentation rate for aggregates of different sizes is not altered over time. However, according to Fig. 8, the behaviour is quite different when the aggregates suffer restructuring, because the fragmentation rate decreases as the flocculation process progresses. This latter result is totally expected, considering that aggregates with open and branched structures are more likely to break than aggregates that are tightly packed. Figs. 7 and 8 also show that the rate of breakage is greater for larger aggregates, as expected.

The permeability of aggregates depends on both porosity and characteristic pore length [70–73]. We currently use the Brinkman equation (Eq. (10)); therefore, the permeability depends exclusively on the porosity of the aggregates. For fractal aggregates, the porosity depends on the size of the aggregates (Eq. (11)) and so thus the permeability. For the system studied by Flesch et al. [20], the aggregate structure is the same for all shear rates and remains unchanged throughout the flocculation process; therefore, the model predicts that the permeability does not change with time or with shear rate (Fig. 9), but increases as the aggregate size increases. However, in the system studied by Antunes et al. [63], aggregates become less permeable as the flocculation process progresses (Fig. 10). This is attributed to a significant restructuring of the aggregates, which reduces the number of channels available for fluid flow. In many practical applications, high compaction and high corresponding densities of the aggregates are needed. Usher et al. and van Deventer et al. [61,62] have shown that densification of aggregates significantly changes the macroscopic characteristics of the suspensions, mainly because the drag force is reduced, which, in turn, increases the rate of sedimentation, thus improving the performance of the thickening processes. Changes in the gel point and mechanical properties such as compressive sediment yield stress are also important. Although, Gregory [74] indicates that, when the floc structure is very open (low fractal dimension), the permeability

<table>
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<th>Dosage [mg/g]</th>
<th>$\alpha_{\text{max}}$ [dimensionless]</th>
<th>$B$ [m$^3$/s$^2$]</th>
<th>$\gamma$ [min$^{-1}$]</th>
<th>GoF [%]</th>
<th>RP [%]</th>
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<tr>
<td>6</td>
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<td>7.5</td>
<td>93.5</td>
<td>31.9</td>
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<tr>
<td>10</td>
<td>0.28</td>
<td>70.4</td>
<td>7.98</td>
<td>93.4</td>
<td>29.3</td>
</tr>
</tbody>
</table>

Fig. 6. Predicted time evolution of the fractal dimension of aggregates for the precipitated calcium carbonate aggregates at three flocculant concentrations in Fig. 4. Data were obtained from Antunes et al. [63].

Fig. 5. Experimental (symbols) vs. calculated (continuous lines) time evolution of aggregate size distribution, corresponding to Fig. 4 at two different flocculation times, that is, 1.5 and 14 min for a flocculant concentration of 8 mg/g. Experimental data were obtained from Antunes et al. [63].

Fig. 7. Calculated fragmentation rates for the range of aggregate sizes reported by Flesch et al. [20] at $G = 100$ s$^{-1}$ and for three different flocculation times.
can be increased significantly and, in principle, reduce the drag and increase the sedimentation rate. When restructuring is absent, as in the case studied by Flesch et al. [20], the collision frequency factor does not change with time nor with shear rate, but increases with the size of aggregates, as shown in Fig. 11. For impermeable aggregates, the collision frequency is markedly lower than for permeable aggregates. In the presence of restructuring, as in the case studied by Antunes et al. [63], the frequency factor decreases with time and flocculant concentration, because aggregates become increasingly compact, as characterised by a higher fractal dimension, thereby reducing their collision radius, disfavouring the collision frequency, as shown in Fig. 12. The latter Fig. shows that the effect is much more pronounced in permeable aggregates. Porous aggregates lose permeability over time, becoming more compact and smaller so that the frequency of collisions decreases. These results prove that, in the modelling of flocculation induced by high-molecular-weight polymers, the structure and permeability of the aggregates should not be neglected.

Finally, Figs. 13 and 14 show the sensitivity of the model for the various parameters considered, both for the system studied by Flesch et al. [20] and that studied by Antunes et al. [63]. The Figs. show that the model is very sensitive to the fragmentation rate through parameter $B$. As this rate depends on the fractal and permeable nature of the aggregates, it is then mandatory to feed the model with accurate information regarding the fractal dimensions, at least at two points in the flocculation process, as well as with a permeability law that is a function of the porosity, but also of the characteristic pore length, which controls fluid flow through the aggregates. The model is somewhat less sensitive to the collision efficiency through parameter $\alpha_{\text{max}}$, particularly if the fractal nature of the aggregates is introduced. When modelling the results of Antunes et al. [63], we considered the time evolution of the fractal dimension, which alleviates the dependence on $\alpha_{\text{max}}$ simply because the size distribution of agglomerates at all times is best represented. It is not the same in the modelling of the data of Flesch et al. [20], as the sensitivity of the model is notably high with respect to the collision efficiency through parameter $\alpha_{\text{max}}$; this is because the fractal dimension of the system is assumed to be invariant, even if the applied shear is changed. The problems encountered by Flesch et al. to predict the evolution of the size distribution of the aggregates may lie in the assumption of a unique fractal dimension. In our attempt to model these data, we considered such fractal dimension as well as the permeable condition of the aggregates. The model remains heavily dependent on $\alpha_{\text{max}}$, although our predictions of the time evolution of the size of the agglomerates improve. Regarding parameter $\gamma$, the model is not very sensitive to the rate at which the maximum fractal dimension of the aggregates changes to the fractal dimension at the steady state, but it is sensitive to the difference between these two fractal dimensions. In ongoing work, we apply the present model to a number of other systems for which experimental data are available; the goal is to explore the existence of correlations and to anticipate the appropriate parameters for given systems.
we are using the present model to describe a number of other systems for which experimental data are available; we seek parameter values for a given system.

5. Conclusions

We described the coagulation and flocculation kinetics and the time evolution of the aggregate size distribution in turbulent shear flow simultaneously with the breakage and restructuring of aggregates using a population balance model. The fractal nature and permeability of the aggregates and its evolution with time were also included. The model was tested against previously published experimental data, showing excellent agreement with experimental flocculation kinetics and reasonably good agreement with the aggregate size distribution in cases with and without restructuring. The numerical solution of the model required the adjustment of three parameters: maximum collision efficiency ($\alpha_{\text{max}}$), critical force needed for the breakage of aggregates ($B$) and rate of aggregate restructuring ($\gamma$). The model was very sensitive to the fragmentation rate through parameter $B$, somewhat less sensitive to the collision efficiency through the parameter $\alpha_{\text{max}}$ and very little to $\gamma$. When the aggregates underwent restructuring, properties such as permeability, breakage rate and collision rate changed considerably over time. When the aggregates were permeable, the collision frequency was significantly smaller than when they were impervious. Currently, we are using the present model to describe a number of other systems for which experimental data are available; we seek parameter correlations with operational variables, which may be useful in anticipating the appropriate parameters for a given system.

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