Coagulation and Fragmentation: The Variation of Shear Rate and the Time Lag for Attainment of Steady State

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The dynamic behavior and the attainment of steady state by a flocculating suspension in a stirred tank are evaluated using a population balance model. At long times, shear-induced coagulation and fragmentation reach a steady state, resulting in a particle size distribution (PSD) that is invariant (self-preserving) with respect to shear. The geometric standard deviations, \( \sigma_g \), of the self-preserving number or volume PSDs are 2.22 or 1.79, respectively, for the employed coagulation and fragmentation rates of flocculation. The time required to reach a steady-state PSD (time lag) is determined as a function of a dimensionless group comprised of the relative rates of coagulation and fragmentation. The effect of the omnipresent variable shear rate in stirred tanks during shear-induced flocculation is investigated through a sinusoidal function of the spatially averaged velocity gradient. Increasing the amplitude of the shear rate fluctuation decreases the steady-state mass mean floc size, the maximum \( \sigma_g \), and the time lag for attainment of steady state. The asymptotic (self-preserving) \( \sigma_g \) is not affected by the shear rate amplitude provided that > 99% of the primary particles have grown to larger sizes.

Introduction

Many industrial processes involve coagulation and fragmentation of the suspended phase in stirred tanks. Examples include polymerization (Blatz and Tobolsky, 1945), liquid–liquid dispersion (Coulaloglou and Tavlarides, 1977), emulsification (Danov et al., 1994), and flocculation (Lu and Spielman, 1985). An important design and control parameter in these processes is the size distribution of the suspended particles. In most practical systems, a steady state or equilibrium is reached between coagulation and fragmentation after a certain time (time lag) and the particle size distribution (PSD) no longer changes. This time lag determines the process requirements (i.e., batch time, power input, etc.) of a flocculation process.

Experimental studies have shown that the spatially averaged shear rate varies significantly throughout a stirred tank (Cutter, 1966; Sprow, 1967). Realistic descriptions of flocculation account for the high shear region around the impeller (impeller zone) and various bulk regions above and below the impeller with significantly lower relative shear rates. Koh et al. (1984, 1987), for example, coupled multicompartamental models of a stirred tank with the population balance equations to fit data on scheelite flocculation but considered only coagulation with no fragmentation. A two-compartment model gave results as good as those of models using a larger number of compartments. Kim and Glasgow (1987) developed a Monte Carlo model of coagulation and fragmentation assuming random movement/shearing of particles, a size-dependent fragmentation rate, and a time step based on the frequency of exposure to the impeller zone. Few comparisons with experimental data were performed, and good agreement with the evolution of the average size of kaolin–polymer flocs was reported (Kim and Glasgow, 1987). Kusters (1991) combined a six-compartment stirred-tank model with analytical velocity profiles to track particle residence times in each compartment. He derived expressions for the frequency of successful coagulation and fragmentation and predicted the evolution of the average floc size well. Recently, Seckler et al. (1995) studied stirred-tank hydrodynamics using computational fluid dynamic (CFD) models coupled with a moment model of the particle size distribution during precipitation. The model identified specific regions of particle formation in a precipitation reactor.

The shape of the asymptotic PSD affects the efficiency of a solids removal process. Theoretical investigations have indicated that pure shear-induced coagulation does not result in a self-preserving PSD (Swift and Friedlander, 1964; Pulvermacker and Ruckenstein, 1974), that is, a PSD whose shape scales with the average particle size. Theoretical (Tambo and Watanabe, 1979; Family et al., 1986; Meakin, 1988; Cohen, 1992; Spicer and Pratsinis, 1996a) and experimental (Spicer and Pratsinis, 1996b) studies have shown, however, that the steady-state PSD from coagulation–fragmentation processes is self-preserving with respect to process conditions. When self-similarity is observed, the individual coagulation and fragmentation rates in the suspension may be determined by deconvolution of the steady-state PSD (Narsimhan et al., 1980; Wright and Ramkrishna, 1994).

The time lag for attainment of steady state by a coagulation–fragmentation process has been investigated previously (Blatz and Tobolsky, 1945; Peled et al., 1995), but models incorporating realistic, size-dependent rate expressions have not been used. In addition, few studies have been carried out on the effect of heterogeneous flow conditions on a flocculating particle size distribution. The objective of this study is to determine the time lag for attainment of steady state by coagulation and fragmentation using rates commonly encountered during flocculation (Lu and Spielman, 1985). To meet this goal, a population balance model is used.
(Spicer and Pratsinis, 1996a) that has successfully simulated experimental data of polystyrene particle flocculation (Oles, 1992). Furthermore, the effect of constant and varying shear rates on the time lag and the polydispersity of the steady-state PSD is investigated and related to controllable process variables through dimensionless groups.

**Theory**

The dynamic behavior of the particle size distribution undergoing simultaneous coagulation and fragmentation is given by (Friedlander, 1977; Kusters et al., 1993):

$$\frac{d n_i}{d t} = \frac{1}{2} \sum_{j+k=i} \alpha_j \beta_{j-k} n_j n_k - n_i \sum_{k=1}^{\max} \alpha_k \beta_{i-k} n_k - S_i n_i + \sum_{j=1}^{\max} \gamma_i \sum_j S_j n_j$$

where $n_i$ is the number concentration of flocs of size $i$ (meaning that a single floc contains $i$ primary particles). The first term on the right-hand side (RHS) of eq 1 represents the formation of particles comprised of $i$ primary particles by collisions of smaller $j$- and $k$-sized particles. The second RHS term denotes the loss of particles of size $i$ by collision with particles of any other size. The third RHS term describes the loss of particles of size $i$ by fragmentation, and the fourth RHS term describes the formation of particles of size $i$ by the fragmentation of larger particles. The index max represents the largest particle size. Equation 1 is the discrete form of the population balance equation, that is, it describes the change in number concentration of each individual particle size. Thus, in order to model the evolution of the detailed particle size distribution during flocculation, the solution of an enormous number of differential equations would be required using a discrete model. To ease computations, the particle size distribution is divided into size classes or sections.

Equations are written describing the change in particle number concentration in each section based on Hounslo et al. (1988) and Spicer and Pratsinis (1996a):

$$\frac{d N_i}{d t} = \sum_{j=1}^{i-2} 2^{i-j+1} \alpha_j \beta_{j-i} N_{i-1} N_j + \frac{1}{2} \alpha_j \beta_{i-j} N_{i-1} - \sum_{j=1}^{i} \alpha_j \beta_{i-j} N_{i-j} - S_i N_i + \sum_{j=1}^{\max} \Gamma_{ij} S_j N_j$$

where $N_i$ is the number concentration of flocs of size class $i$ (meaning that a single floc contains $1.5 \times 2^{i-1}$ primary particles), $\alpha$ is the collision efficiency for coagulation, $\beta_{ij}$ is the collision frequency for particles of size class $i$ and $j$ with characteristic volumes $v_i$ and $v_j$, $S_i$ is the fragmentation rate of flocs of volume $v_i$, and $\Gamma_{ij}$ is the breakage distribution function defining the volume fraction of the fragments of size $i$ coming from $j$-sized particles. The index $i$ max is the number of sections used in the model (here $i$ max = 30).

The collision frequency for turbulent shear-induced coagulation, in the absence of viscous retardation and floc structural effects, is (Saffman and Turner, 1956)

$$\beta_{ij} = \beta(v_i, v_j) = 0.31G(v_i^{1/3} + v_j^{1/3})^3$$

where $G$ is the spatially averaged shear rate (Clark, 1985) given for fluctuating shear rates by:

$$G = G' + \omega \sin(t)$$

$G'$ is a constant (e.g., 50 s$^{-1}$) and $\omega$ is the maximum magnitude of the fluctuation in $G$. A range of $\omega$ values were examined here ($\omega$ = 0, 30, 40, 50 s$^{-1}$).

The fragmentation rate is a function of particle volume (Pandya and Spielman, 1982):

$$A = A' G$$

where $y$ is a constant inversely proportional to the floc strength and $A'$ is a proportionality constant that is determined experimentally. The value of $y = 1.6$ was used in all calculations corresponding to kaolin—polymer and polystyrene flocs (Pandya and Spielman, 1982; Spicer and Pratsinis, 1996a). The constant $A'$ affects the relative strength of fragmentation relative to coagulation and a value of 0.0047 is used here (Oles, 1992; Spicer and Pratsinis, 1996a).

For all calculations, binary breakage was assumed (Spicer and Pratsinis, 1996a):

$$\Gamma_{ij} = v_i / S_j \quad \text{for } j = i + 1$$

$$= 0, \quad \text{otherwise}$$

Equations 3–7 were substituted into eq 2, and the sectional model was solved numerically using DGEAR, an ordinary differential equation solver (IMSL, 1989).

The behavior of a coagulation—fragmentation system is a function of the relative significance of the rates of coagulation and fragmentation (Blatz and Tobolsky, 1945). As a result, it is convenient to define a dimensionless group that characterizes the relative significance of coagulation versus fragmentation, $CF$:

$$CF = S_0 V_0 / \phi \beta_{0,0}$$

where $\phi$ is the volume fraction of suspended particles, $V_0$ is the volume of a primary particle, and $\beta_{0,0}$ and $S_0$ are obtained by substituting $V_0$ into eqs 3 and 5, respectively.

**Results and Discussion**

Unless stated otherwise, all calculations were carried out for $G = 50$ s$^{-1}$, $\alpha = 1$, $\omega = 0$, $A' = 0.0047$, $\gamma = 1.6$, initial diameter $d_0 = 2.17 \mu m$, and initial number concentration $N_1 = 9.3 \times 10^6$ cm$^{-3}$ (Oles, 1992; Spicer and Pratsinis, 1996a). The model was validated by comparison with analytical solutions for the case of pure coagulation with a size-dependent kernel (Golovin, 1963), pure fragmentation (Williams, 1990), and the combined case (Blatz and Tobolsky, 1945). At all conditions excellent agreement between the numerical and analytical solutions was obtained (Spicer and Pratsinis, 1996a).

**Development of the Steady-State Floc Size Distribution**. Figure 1 shows the evolution of the initially
The geometric standard deviation of the floc size distribution, $\sigma_g$, quantitatively characterizes the width of the distribution (Hinds, 1982). Figure 2 shows the evolution of $\sigma_g$ for various shear rates, G ($\omega = 0$). After an initial lag period, the number-based geometric standard deviation, $\sigma_{gn}$, increases as the distribution broadens into the larger size classes (Figure 1a). A maximum value is reached (e.g., $\sigma_g = 3.27$ at $r = 15$ for $G = 10$ s$^{-1}$) corresponding to the maximum displacement of the larger mode from the primary particle mode of the distribution. As the primary particles are depleted (Figure 1a), $\sigma_{gn}$ decreases until leveling off at an asymptotic value, $\sigma_{gnss}$, corresponding to the attainment of the steady-state size distribution ($\sigma_{gnss} = 2.22$ at $r = 28$ for $G = 10$ s$^{-1}$).

Increasing the shear rate, G, results in an increased fragmentation rate (eq 5), preventing further growth of the steady-state particle size distribution. As a result, the steady-state PSD is displaced to smaller sizes and narrowed as the number of primary particles present at steady state is increased compared to the steady-state PSD at lower shear rates (e.g., at $G = 50$ s$^{-1}$ the concentration of primary particles at steady state is $N_{1ss} = 5\%$). This is shown in Figure 2 where $\sigma_{gnss}$ decreases with increasing G. Furthermore, the maximum in $\sigma_{gn}$ decreases with increasing G since the two size modes (primary particles and flocs) become increasingly indistinguishable. For example, the primary particle concentration at steady state is 5% for $G = 50$ s$^{-1}$ and becomes 18% for $G = 100$ s$^{-1}$ (Spicer and Pratsinis, 1996a).

Figure 2 also shows the evolution of the geometric standard deviation, $\sigma_{gv}$, of the corresponding volume-based PSD. A rapid increase in $\sigma_{gv}$ is initially observed as the distribution broadens and larger particles are formed (Figure 1b). As with the number-based PSD, a maximum is reached, corresponding to the maximum separation of the primary particle and floc modes. At a constant G, the maximum $\sigma_{gv}$ is smaller than the maximum $\sigma_g$ because of the larger relative contribution of the primary particles to the number- versus the volume-based PSD. At the employed shear rates the primary particles contribute little to the latter distribution, so the same $\sigma_g$, is attained at all shear rates. The steady-state $\sigma_{gv}$ is unchanged by the shear rate, consistent with Spicer and Pratsinis (1996b), who found that shear does not change the width of the polystyrene floc size distribution at steady state, so it is self-preserving with respect to shear.

Figure 3 shows the steady-state geometric standard deviation for the number- and volume-based PSD ($\sigma_{gnss}$...
and $\sigma_{g_{nss}}$ respectively) as a function of the coagulation–fragmentation group, CF, for various shear rates $G$. $\sigma_{g_{nss}}$ increases as CF decreases, allowing flocculation to broaden the size distribution. An asymptotic value is reached below a critical value of CF, indicating a self-preserving steady-state PSD that includes very few primary particles (broken line: $N_{1ss} < 0.01N_T$).

At low CF, a large difference between $r_{nss}$ and $r_{vss}$ is observed. Lower values of CF correspond to increased collision rates for small particles (eq 8). As a result, the size distribution is able to develop into larger sizes before fragmentation halts its progress. Increasing the CF decreases $r_{nss}$ for both number and volume distributions as a result of the increased fragmentation rates and the resulting decreased extent of PSD development. It is interesting to note that the scaling of $r_{nss}$ is unchanged by a deviation from the self-preserving $G$ of the steady-state size distribution (i.e., the values of $r_{nss}$ collapse onto a single curve even to the right of the broken line, indicating the point of deviation from the self-preserving size distribution). $r_{vss}$ is significantly larger than $r_{vss}$ as a result of the larger effect of the primary particle dynamics on steady-state attainment by the number-based PSD.

**Effect of Shear Rate Fluctuations on the Attainment of Steady State.** Equation 4 is a simplified description of the variation of the instantaneous shear rate within the turbulent flow field of the stirred tank. This description is based on the concept of an average circulation time for a suspended particle or fluid element (Oldshue, 1984; Kim and Glasgow, 1987). Particles are exposed to a spectrum of shear rates during the flocculation process. For example, fluid elements start from a region of say, average G, reach the region of maximum G at the impeller zone, then reach the relatively stagnant region above the impeller, and finally return back to the high shear impeller zone. This is consistent with the flow pattern for a radial flow impeller such as a Rushton configuration (Holland and Chapman, 1966). Increasing the amplitude of the shear rate fluctuation, $\omega$, increases the range of G experienced by the sus-
Figure 5. Evolution of the dimensionless mass mean diameter as a function of the maximum amplitude of the fluctuation in $G$, $\omega$. The mean floc size increases during the growth-dominated regime and then levels off once steady state is attained. Increased $\omega$ decreases the steady-state value as a result of increased fragmentation.

Figure 6. Evolution of the number- and volume-based geometric standard deviation of the size distribution as a function of the amplitude of the spatially averaged shear rate, $G$. Larger amplitudes increase fragmentation, suppressing the development of the size distribution and thus decreasing its width.

Figure 7. Effect of $\omega$ on the shape of the self-preserving steady-state floc number and volume distributions. The steady-state number-based PSD narrows as a result of the increased fragmentation at higher $\omega$, but the volume-based PSD does not since primary particles contribute less to the latter PSD. The effect of increasing $\omega$ is smaller for $\sigma_{vn}$ than for $\sigma_{gn}$ but similar: the maximum $\sigma_{gn}$ reached decreases as the shear fluctuations increase in magnitude. This reflects the restriction of floc growth into the larger sizes, producing a distribution of smaller relative particle sizes (Figure 5). As for the case of $\omega = 0$, however, the distribution is able to fully develop before fragmentation balances growth completely. As a result, $\sigma_{vOSS}$ changes very little with respect to $\omega$. The fluctuation of $G$ shifts the steady-state PSD into the lower sizes (Figure 5) but does not significantly influence its shape since the contribution of the primary particles to the steady-state volume-based PSD is very small.

The results in Figure 6 indicate the importance of shear fluctuations on the development of the PSD. The asymptotic behavior of the system is also affected by the fluctuations. Figure 7 shows the steady-state floc number and volume distributions, plotted in normalized form (i.e., $v_i$ normalized by the number-average volume, $v_n$) to evaluate their self-preserving properties, as a function of $\omega$. In all four number distributions in Figure 7, the large shoulder of the normalized distribution collapses onto a single line. The only deviation from
self-similarity is at the lower size range of the number-based PSD, where restriction of the distribution by fragmentation prevents total depletion of the primary particles (Spicer and Pratsinis, 1996a). Increasing $\omega$ accelerates fragmentation, resulting in a larger fraction of primary particles. In Figure 7, full self-similarity of the steady-state floc volume distribution is observed for all $\omega$. Shear fluctuations do not affect the shape of the asymptotic volume distribution when the primary particles contribute less than 1% of the mass of the suspension (Figure 6).

Figure 8 shows the effect of $\omega$ on the steady-state time lag for the number and volume distributions. Increasing the amplitude of the shear fluctuations decreases the time required for both distributions to attain steady state, while increased shear decreases the time lag for steady state as the distribution is halted at smaller sizes. As $\omega$ is increased, the intensity of fragmentation increases, and the distribution attains steady state more rapidly because less particle growth is possible.

Conclusions

A theoretical model of coagulation and fragmentation has been used to describe shear-induced flocculation. The initially monodisperse size distribution broadens as particles grow by shear-induced coagulation. The width of the size distribution increases initially, passes through a maximum as two particle size modes are formed, and then decreases as the fine size mode is depleted to reach an asymptotic value at steady state. Increased shear rates decrease the number-based $\sigma_g$ at steady state and to a lesser extent the volume-based $\sigma_g$, $\sigma_v$ is used as a criterion to quantify the attainment of steady state and determine the time lag for attainment of steady state, $t_{SS}$. $t_{SS}$ decreases with increased significance of fragmentation by halting development of the distribution at smaller particle sizes. A dimensionless group, CF, is found that describes the relative significance of coagulation and fragmentation. For CF $< 0.013$ the steady-state size distribution has fully grown and has a number- or volume-based geometric standard deviation of 2.22 or 1.79, respectively.

The heterogeneous flow field of a stirred tank is simulated using a sinusoidally varying average shear rate. Increasing the shear rate amplitude, $\omega_t$, decreases the steady-state mass mean floc size and the steady-state time lag, but it does not affect the width of the distribution provided that most primary particles (> 99%) have grown into larger particles.

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