Physicochemical Influences upon Floc Deformability, Density, and Permeability

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Abstract

Flocculation is a necessary component of many solid-liquid separations. However, the present state of understanding of floc structure, and particularly of how flocs respond to applied stress, is inadequate for process improvement. The production of large aggregates in turbulent flocculation processes occurs by primary particle addition, by floc-floc collisions, and even by multibody collisions at higher entity concentrations. Consequently, the spacing between adjacent components and the number of contact points (between component and aggregate) may vary significantly. This structural variability affects every aspect of solid-liquid separation performance, but especially those governed by floc deformability, density, and permeability.

The investigation reported here has shown that a centrifugally-stratified Couette flow can be used in the polymer flocculation of kaolin to yield large aggregates with a higher degree of structural order than those produced in inhomogeneous turbulence. The floc structures obtained in this work are regular, (nearly) spherical, and unusually compact. Determinations of aggregate density, permeability, and deformability have been used to characterize differences between these structures and those formed in conventional flocculation processes. The results obtained in this study suggest a means by which floc properties might be optimally tailored for specific solid-liquid separations.

Introduction

Conventional flocculation processes are carried out in inhomogeneous turbulence; this results in extremely variable collision energetics. As a result, large flocs may have components that are bound at multiple points, or loosely affiliated, or merely entangled in the aggregate structure. Early computer simulations of floc formation devised by Vold (1963) and Sutherland (1967) presumed that colliding particles and clusters would be rigidly fixed at the first point of contact. However, Adachi and Ooi (1986) pointed out that some colliding clusters might continue to move after initial contact until the aggregate attains a more stable configuration. Our hypothesis is that very particular types of shear flows might promote relative motion of interacting clusters, resulting in additional points of contact and more compact aggregate structures.
**Couette Flocculator**

The use of Couette devices for flocculation has been discussed by many authors, including Van Duuren (1968), Ives and Bhole (1975), and Glasgow and Luecke (1977). The advantages of such flocculators include a well-defined strain rate and minimized aggregate breakage. A Couette flocculator was constructed (with rotation of the outer cylinder) to explore the possibility that a *nearly* uniform shear field could produce desirable aggregate properties during floc growth. Application of the method of small disturbances to this flow has demonstrated that it is theoretically (though not practically) stable at any angular velocity.

![Couette Flocculator](image)

**Figure 1.** Couette apparatus utilizing outer cylinder rotation with $R_1=3.81$ cm and $R_2=4.445$ cm. To minimize end effects, the apparatus was built with a length-to-annular gap ratio of 115.

The governing equation for fluid motion in this device is:

$$\rho \frac{\partial V_\theta}{\partial t} = \mu \left[ \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial}{\partial r} (r V_\theta) \right) \right].$$

For the case in which the outer cylinder is rotating and the inner cylinder is at rest, the steady-state velocity distribution is:

$$V_\theta = \frac{\omega R_1^2 R_2^2}{R_2^2 - R_1^2} \left[ \frac{r}{R_1^2} - \frac{1}{r} \right].$$

The velocity gradient in the annulus varies with radial position as

$$\frac{dV_\theta}{dr} = \frac{\omega R_1^2 R_2^2}{R_2^2 - R_1^2} \left[ \frac{1}{r^2} + \frac{1}{R_1^2} \right].$$
Therefore, when the outer cylinder is rotating at 150 rpm, the velocity gradient varies from 118.4 s\(^{-1}\) at \(r=R_1\) to 102.7 s\(^{-1}\) at \(R_2\). At 350 rpm, the velocity gradient ranges from 276.3 to 239.6 s\(^{-1}\) from \(R_1\) to \(R_2\), respectively.

**Flocculation Conditions**

The dispersed-phase used in this work is colloidal kaolin, a two-layer clay. In water, the small kaolin particles are negatively charged; therefore, they repel each other resulting in a stable dispersion. The objective in flocculation is to destabilize the colloid so that the small particles can approach each other and—if conditions are right—coagulate. We can obtain a measure of the thickness of the ionic atmosphere surrounding a charged particle from the Debye length:

\[
\ell_D = \left( \frac{4\pi e^2}{\varepsilon kT} \sum N_i z_i^2 \right)^{-1/2},
\]

where \(\varepsilon\) is the dielectric constant, \(k\) is the Boltzmann constant, \(N_i\) is the number of ions per unit volume, and \(z_i\) is the charge on the type-i ion. The conditions we used yielded \(\ell_D \approx 17\ \text{Å, pH} \approx 10.5\), a conductivity of 1700 \(\mu\)S (micromhos), and primary particle number density of about \(3.8 \times 10^8\) per ml. The ionic strength is low; a high-molecular weight cationic polyelectrolyte is used as a coagulant and it is presumed to function through a combination of (patch) charge neutralization and by physically bridging the gap between proximate clay particles.

**Typical Aggregate Conformation with Couette Flocculator**

![Figure 2. Aggregates formed by flocculation of colloidal kaolin with a high molecular weight cationic polyelectrolyte in the Couette apparatus; the rotational](image-url)
speed was 292 rpm (30.57 rad/s) and the duration, 30 minutes. At this speed, the mean strain rate ($\gamma$) was about 213 s$^{-1}$ and the product, $\gamma t$, was about $3.84 \times 10^5$. The aggregate indicated by the arrow has a mean diameter of about 4 mm.

Note that the kaolin-polymer aggregates shown in Figure 2 are nearly spherical. Indeed, they are much more regular in shape than the “pellet” floc formed of polystyrene latex spheres with a cationic polyelectrolyte by Higashitani et al. (1986). Higashitani et al. observed in their work that “pellet” floc could not be formed unless the primary particle concentration was very high (typically about $10^{10}$ particles per ml); they noted that at lower number densities, “pellet” floc could not be formed even at the optimal polymer dose (for maximum turbidity reduction). In contrast, we have been able to form aggregates like those shown in Figure 2 with primary particle number densities as low as $\sim 3.8 \times 10^8$ per ml.

**Floc Density from Terminal Velocity**

The significance of floc density to solid-liquid separations has been reviewed by Gregory (1998) and the estimation of floc density from settling velocity has been studied by Adachi and Tanaka (1997) and Wu and Lee (1998), among others. For creeping flow conditions, the Brinkman model has been used to account for flow through a permeable sphere—which requires that the drag coefficient be corrected. Wu and Lee have extended that work to somewhat higher Reynolds numbers (40) using a CFD package; their computed results show that for low permeability spheres, the approaching fluid flows around, and not through, the settling entity. Matsumoto and Suganuma (1977) showed that if the ratio, $R/\sqrt{k}$, is greater than 20, then the effects of flow through the structure can be omitted with very little error. A small number of aggregates formed in this study have been examined for permeability using a micropipette tip. These limited data indicate $k \approx 3.3 \times 10^{-7}$ cm$^2$; taking a typical $R$ for our aggregates to be about 2 mm, we find:

$$\frac{R}{\sqrt{k}} \approx 346. \quad (5)$$

The density of the kaolin-polymer aggregates was determined from a digital video record of their terminal settling velocity in quiescent water. The aggregates were transferred individually to the settling chamber with a serological pipette. By force balance,

$$\frac{4}{3} \pi R^3 \rho_p g = \frac{4}{3} \pi R^3 \rho_f g = \frac{1}{2} \pi R^2 \rho_f V^2 f_{Re}, \quad (6)$$

where $R$ is the aggregate radius and $\rho_p$ and $\rho_f$ are the densities of the aggregate and the fluid medium, respectively. Therefore,
\[
\frac{\rho_p}{\rho_f} = \frac{3}{8} \frac{V^2 f_{Re}}{Rg} + 1.
\]  
(7)

The video record of the settling particle is used to measure \( R \) and \( V \); the Reynolds number (Re) is then calculated and used to get the drag coefficient, \( f_{Re} \). The drag-reducing effects of flow through the permeable structure are neglected.

Figure 3. Three sets of floc density data for kaolin-polymer aggregates formed in the Couette apparatus with the product of mean strain rate and residence time, \( \gamma t \), ranging from 3.84x10\(^5\) (filled diamonds) to 6.26x10\(^5\) (filled circles).

The data reported in Figure 3 demonstrate the effectiveness of the laminar shear field in promoting extremely compact and regular aggregate structures; for the case in which the product, \( \gamma t \), was 6.26x10\(^5\), the diameters of the spherical aggregates (filled circles) ranged from about 2 to 4.1 mm. These structures had an approximate average density of about 1.09 g/cm\(^3\). For the kaolin particles used in this study, this density corresponds to a volume fraction of water of about 94%. For conventional kaolin-polymer flocs formed in inhomogeneous turbulence, the typical volume fraction of water would be about 98 or 99%.
Floc Deformation in Compression Apparatus

A number of these highly regular clay-polymer aggregates have been tested in a novel piston-cylinder apparatus as described by Glasgow (2003) and Scott et al. (2004). Complete descriptions of the apparatus and procedure are given in the cited papers.

Both flocs and surrogate materials were tested; typical results from each are shown in Figure 4. The results obtained with the polyurethane foam core show three distinct phases as described by Weaire and Hutzler (1999): an elastic phase from about t=25 to 70 s, a buckling phase occurring from about t=75 to perhaps 275 s, and a compaction phase in which the force of compression increases very steeply. Contrast this behavior with that produced by the kaolin-polymer aggregate. In this case the initial increase in force is slow (and nearly linear) until about t=175 s. At this point, the measured force begins to increase very steeply, coinciding with the lateral dilation of the structure. Differences between the relaxation processes (following cessation of piston motion) are also worthy of note. For large kaolin-polymer aggregates, we see a precipitous decline of typically 30,000 to 35,000 dynes in just 9 or 10 s. In the case of the polyurethane foam cores, the decrease in measured force is smaller and slower, usually about 10,000 or 12,000 dynes occurring over a period of 30 to 40 s.

![Figure 4](image)

**Figure 4.** Force of compression measured for a polyurethane foam core (surrogate) and a large kaolin-polymer aggregate at a piston speed of 30 µm/s. The compression of the polyurethane foam was undertaken to provide a better characterized material for comparison.
It is convenient to define a deformation index:

\[ DI = \frac{\sqrt{A_{\text{proj}}}}{h}, \]  

(8)

where \( A_{\text{proj}} \) is the area determined from the bottom view and \( h \) is the aggregate height (distance from the cylinder floor to the bottom of the piston). Some typical results obtained with conventionally formed kaolin-polymer aggregates are provided in Figure 5; the data from 12 separate trials are included. For these flocs, a deformation index (DI) of 10 corresponds to a volume loss of about 65 to 75%. About 4000 to 5000 dyne-cm (cumulative work) are required to raise DI to 100.

Figure 5. Deformation index as a function of cumulative work performed upon twelve large kaolin-polymer aggregates. The piston speed for all trials was 30 \( \mu \text{m/s} \).

Discussion

There appear to be three main factors at work in the formation of these unusually regular aggregate structures in the Couette apparatus: the macromolecular coagulant, the tendency towards rotation of interacting entities entrained in the Couette flow, and the energetics of the interparticle collision process. Although macromolecular influences are certainly significant, they have
not been part of this investigation. However, the tendency towards rotation (relative motion of colliding clusters) and collisional energetics have been examined.

Consider an evolving aggregate (with d=3 mm) positioned at the center of the annular gap in the Couette device; the outer cylinder rotates at 300 rpm, corresponding to a centerline velocity of about 72.3 cm/s. If the structure’s center of mass is moving at that speed, then the relative fluid velocities past the aggregate (in the absence of rotation) would be +32.36 cm/s (top) and –33.47 cm/s (at the bottom). The result of this situation is aggregate rotation; for interacting clusters or components it is easy to visualize how this rotation could produce relative motion of the interacting pieces, resulting in additional points of contact.

It is also possible that the energetics of interparticle collisions in the Couette device favor formation of compact aggregates. In the initial stages of conventional turbulent coagulation, the collision of primary particles is virtually independent of the turbulence because $d_p << \eta$, where $\eta$ is the Kolmogorov microscale,

$$\eta = (\nu^3 / \varepsilon)^{1/4}. \quad (9)$$

$\nu$ is the kinematic viscosity and $\varepsilon$ is the dissipation rate per unit mass. In the case of water with $\varepsilon=500 \text{ cm}^2/\text{s}^3$, $\eta=66.9 \text{ \mu m}$, whereas the primary particle size is typically 1 to 2 \mu m. Accordingly, turbulence becomes more effective at promoting collisions as the aggregates grow. A rough assessment of the available energy in a turbulence-driven collision can be obtained in the following way. Assume that the colliding entities are being driven by eddies in the inertial subrange in which the spectrum of turbulent energy is given by

$$E(\kappa) = \alpha \varepsilon^{2/3} \kappa^{-5/3}. \quad (10)$$

A characteristic velocity for these eddies can be obtained from:

$$u(\kappa) = [\alpha \varepsilon^{2/3} \kappa^{-2/3}]^{1/2} \quad (11)$$

Since the eddy size is approximately $2\pi/\kappa$, a pertinent kinetic energy can be obtained using the entity diameter (d) and the dissipation rate per unit mass ($\varepsilon$). For example, taking $d=0.05 \text{ cm}$ and $\varepsilon=1000 \text{ cm}^2/\text{s}^3$, $u^2(\kappa)=5.98 \text{ cm}^2/\text{s}^2$; if the dissipation rate is increased to (the very large value) $10^4$, then $u^2(\kappa)=27.76 \text{ cm}^2/\text{s}^2$. Naturally, for an oblique collision, $u^2$ would be much lower. Contrast this with two 0.05 cm particles colliding in the Couette apparatus (at 300 rpm). Given the maximum allowable separation (still resulting in collision), the difference in velocities between the two entities corresponds to a $u^2$ of about 120 cm$^2$/s$^2$. 
Conclusions

Our experimental results show that the Couette flocculator can be used to generate kaolin-polymer aggregates with unusually regular morphologies. In addition, terminal velocity data were used to obtain apparent floc densities for these aggregates; the data indicate that densities exceeding 1.10 g/cm³ may be achievable, corresponding to a significant decrease in the amount of interstitial water held in the structure (relative to conventional flocs formed in inhomogeneous turbulence). At the present time, the effects of further increases in the product of the mean strain rate, $\gamma$, and the residence time, $t$, in the Couette reactor are unknown.

A limited number of permeability measurements have been made for these unusual aggregates; the average value of $k$ was found to be about $3.3 \times 10^{-7}$ cm². In addition, experiments have also been carried out in which kaolin-polymer aggregates were compressed in a novel piston-cylinder apparatus. The data obtained from these trials consisted of compressive force (as a function of time) as well as aggregate shape and volume. These results show that for large (d~4 mm) aggregates, the cumulative work required to produce a 70% loss in aggregate volume is about 1000 dyne·cm. The work required to expel water from these structures increases very sharply as the deformation index exceeds about 10.

We believe that it may be possible to exploit the phenomenon reported here for solid-liquid separations in which highly ordered floc structures coupled with reduced liquid volume fractions are advantageous. In the next phase of this work we plan to examine the effects of $\gamma t$'s approaching $10^6$, different primary particle morphologies, and elevated polymer (floculant) dosages.

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Literature Cited


