DISPERSION OF COAGULATED PARTICLES BY CONTRACTILE FLOW TO ORIFICE

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The breakup of flocs composed of a small number of constituent particles by orifice contractile flow is investigated extensively by measuring the size of broken flocs of PSL particles on a Coulter counter. It is found that (1) flocs of maximum strength are obtained when they are formed in an electrolyte concentration greater than the critical coagulation concentration, and the strength is independent of the valency of electrolyte; (2) the average size of broken flocs and the maximum number of constituent particles in a broken floc are successfully expressed as a function of the energy dissipation at the orifice; and (3) the mechanism of floc breakup in the contractile flow is different from that by ultrasonication (flocs are split into smaller agglomerates in the former case, but particles are ripped off one by one from the surface of flocs in the latter case).

Introduction

Many materials for advanced technology, such as electronic, magnetic, optic and fine ceramic materials, are manufactured from suspensions of microscopic colloidal particles. Highly dispersed suspensions are required to produce materials of high performance. Sometimes, it is necessary to avoid agglomerates completely. Hence the breakup of flocs composed of a small number of constituent particles is an investigation topic of immediate importance.

The flow of fluids can be used to deflocculate flocs hydrodynamically. It is known that orifice contractile flow is one of the effective flows for floc breakup. Regarding the breakup of flocs in liquid contractile flows, Sonntag and Russel found that flocs of polystyrene latexes (PSL) change their shape from spherical to elongated around the orifice, and the average number of particles per broken floc is inversely proportional to an overall average strain rate. Kerekes observed that pulp flocs tend to deform and rupture in a tensile mode rather than in a shear mode. Higashitani et al. reported that flocs are broken by the abrupt change of flow field before entering into the orifice but not within or after the orifice and that the breakup is mainly attributable to the difference in the drag force exerted on constituent particles located at different axial positions. On the breakup of flocs in converging air flows, Yamamoto and Suganuma reported that the average size of dispersed powders is proportional to \( \varepsilon^{-0.2} \), where \( \varepsilon \) is the energy dissipation at the orifice. Yuu and Oda found that the change in particle size distribution of powders can be evaluated by the population balance, assuming that the breakup is due to the difference in the inertia and drag force on the constituent particles. Investigations, except those of Higashitani et al. and of Yuu and Oda, have been concerned with flocs composed of a large number of constituent particles. Hereafter, flocs composed of a large or small number of constituent particles are called large-numbered and small-numbered flocs respectively. It seems that the strength of flocs varies with size; that is, the structure of large-numbered flocs is relatively uniform and soft, and their strength increases with decreasing floc size. Hence it is questionable whether the results obtained for large-numbered flocs are applicable to small-numbered flocs.

In this study, characteristics of the breakup of small-numbered flocs in aqueous solutions by orifice contractile flow are investigated quantitatively by measuring the size of broken flocs of PSL particles on a Coulter counter. Effects of the kind of electrolyte, the electrolyte concentration, the applied pressure, the orifice size and the size of constituent particles on the size of broken flocs are examined.
1. Experiment

Polystyrene latex (PSL) particles listed in Table 1 were employed in this study. All the particles were synthesized in our laboratory and purified by the method reported elsewhere. The diameter $D_0$ was measured on a Coulter counter (Coulter Model ZM) and confirmed on a photon correlation spectrocope (Ohtsuka DSL 700) and an electron microscope (Topcon ABT-32), as described in Table 1. A floc solution whose particle concentration was $2.23 \times 10^8$ cm$^{-3}$ on the basis of constituent particles was prepared by stirring PSL particles in an electrolyte solution of given concentration before being stored in the floc tank. Electrolytes used as coagulants were KCl, CaCl$_2$, and LaCl$_3$ of reagent grade.

Figures 1(a) and (b) show respectively a schematic drawing of the experimental apparatus and details of the cylindrical test section. The coordinates $r$ and $z$ were taken as shown in Fig. 1(b), where $z$ was directed in the direction of flow and the origin was located at the orifice surface on the upstream side. A solution without flocs but having the same electrolyte concentration as that of the floc solution, called medium solution here, was fed constantly into test section F from a large reservoir C (inner diameter = 30 cm, height = 35 cm) and flowed out to a drain through flow meter I. The floc solution in floc tank J (inner diameter = 4.3 cm, height = 6 cm) was injected from nozzle G (diameter = 0.1 cm) at $z = -15$ cm into the flow of the medium solution. This method of floc injection was used so as to dilute the floc solution enough to prevent re-coagulation of dispersed particles and to clarify the effect on floc breakup of the initial radial position of the flocs. Flow rates of the medium and floc solutions were controlled by regulating the pressure of the nitrogen cylinders in such a way that flocs were injected at nearly the same velocity as the medium solution. The diameter of the orifice was either 0.01, 0.05 or 0.1 cm.

Flows of the medium and floc solutions were stopped instantaneously by shutting three electromagnetic valves E simultaneously, before sampling flocs. Sampling was carried out at the locations $K_2$ to $K_4$ shown in Fig. 1(b), using a syringe with a needle of 0.1 cm diameter. The size of individual flocs was measured on the Coulter counter and so the diameter of a floc composed of $i$ constituent particles, $D_i$, was expressed by the equivalent volume diameter, $D_{eq}^{1/3}$. The average size of flocs was represented by the number-averaged diameter, $D_{av}$, calculated from the size distribution of flocs. Hence $D_{av}$ indicates the equivalent volume diameter of flocs with the number-averaged size. All the experiments were carried out at room temperature.

<table>
<thead>
<tr>
<th>Particles</th>
<th>Density ($g/cm^3$)</th>
<th>Diameter $D_{av}$ (SD$^3$) ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSL</td>
<td>1.05</td>
<td>0.59(0.04), 0.71(0.07), 0.77(0.07)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.91(0.08), 1.03(0.09), 1.27(0.05)</td>
</tr>
</tbody>
</table>

* Values of $D_{av}$ were measured on Coulter counter. They were confirmed on photon correlation spectrocope and electron microscope.

* Values of SD were measured on photon correlation spectrocope.

2. Results and Discussion

Figure 2 shows typical size distributions of initial PSL particles, coagulated particles and particles dispersed by an orifice contractile flow, where $i$ is the number of constituent particles in a floc. It is seen that flocs of a wide size distribution are formed by coagulation in the stirred tank and that flocs are dispersed well by a contractile flow. Hereafter the value of $D_{av}$ calculated from this kind of size distribution is employed in comparing the data.

To determine the sampling point, values of $D_{av}$ measured at the points $(r, z) = (0, 8), (0, 25), (0, 42)$ and $(2, 25)$ cm were compared, where flocs were injected at $(r, z) = (0, -15)$ cm. Since it was found that the value of $D_{av}$ was not affected by sampling position under the present experimental conditions, the sampling point of $(r, z) = (0, 25)$ cm was employed without losing generality.

Figure 3 shows the dependence of $D_{av}$ on the
Fig. 2. Typical size distributions of (a) initial particles, (b) coagulated particles and (c) particles broken by contractile flow. \((C_c = 0.05 \text{ kmol/m}^3 \text{ of CaCl}_2; \ D_0 = 0.91 \mu \text{m}; \ d = 0.1 \text{ cm})\)

Fig. 3. Dependence of \(D_{av}\) on the radial position of floc injection. \((C_c = 0.2 \text{ kmol/m}^3 \text{ of KCl}; \ D_0 = 0.91 \mu \text{m}; \ d = 0.1 \text{ cm})\)

radial position of floc injection at \(z = -15 \text{ cm}\). It is found that the value of \(D_{av}\) is not influenced by the radial position of injection at \(0 \leq r \leq 1.3 \text{ cm}\), but the magnitude becomes slightly larger at \(r \geq 1.7 \text{ cm}\). Since floc breakup is mainly caused by an abrupt change of flow field, \(^3,^{16}\) it is likely that the increase of \(D_{av}\) at \(r \geq 1.7 \text{ cm}\) is attributable to the slow change of flow field. We consider that the above deviation will not contribute greatly to the value of \(D_{av}\) averaged across the cross section of the flow pipe, because the flux of flocs passing across the region of \(r \geq 1.7 \text{ cm}\) is about 13% of the total flux. Hereafter the injection point \((r, z) = (0, -15 \text{ cm})\) is employed.

It was suspected that the magnitude of \(D_{av}\) of flocs injected from the nozzle was different from that in the floc tank. Hence values of \(D_{av}\) at \(K_3\) were compared between flocs injected from the nozzle and flocs poured very carefully at \(z = -42 \text{ cm}\) which were supposed to have the same size distribution as the flocs in the floc tank. Fortunately the difference was found to be negligible. This indicates that a contractile flow reduces floc size to one that is balanced with the given flow condition, whatever the size of injected flocs may be.

The effect of sampling by the syringe with a needle on the value of \(D_{av}\) was considered to be negligible, because the flow rate in the needle was much smaller than that in the orifice.

2.1 Dependence of \(D_{av}\) on applied pressure and electrolytes

Figure 4 shows the dependence of \(D_{av}\) on the applied pressure \(\Delta P\) for various electrolyte concentrations \(C_e\). It is found that relations of \(D_{av}\) vs. \(\Delta P\) are expressed by straight lines of the same negative slope in a log-log graph irrespective of \(C_e\). That is, \(D_{av}\) decreases exponentially with increasing \(\Delta P\). \(D_{av}\) increases with \(C_e\) and all the data at \(C_e \geq 0.5 \text{ kmol/m}^3\) are expressed by a single relation. This result indicates that the adhesive force \(F_{ad}\) between constituent particles in the floc increases with \(C_e\) and becomes maximum at \(C_e \geq 0.5 \text{ kmol/m}^3\), which is approximately equal to the critical coagulation concentration (CCC).\(^2\) Hereafter our attention is paid only to the breakup of flocs at \(C_e \geq \text{CCC}\).

Figure 5 shows the dependence of \(D_{av}\) on \(\Delta P\) for electrolytes of three different valencies at \(C_e \geq \text{CCC}\). It is clear that all the data fall on a single line irrespective of valency. Hence the maximum value of \(F_{ad}\) given by electrolyte coagulants is independent of valency.

2.2 Dependence of \(D_{av}\) on sizes of orifice and constituent particles.

Figure 6 shows the dependence of \(D_{av}\) on \(\Delta P\) for various orifice diameters \(d\). It is clear that relations of \(D_{av}\) vs. \(\Delta P\) are expressed by straight lines with the
same negative slope irrespective of $d$, and that $D_{av}$ decreases with decreasing value of $d$, as expected.

According to Yamamoto and Suganuma,\textsuperscript{16} the energy dissipation of the orifice contractile flow $\varepsilon$ can be estimated by the following equation.

$$\varepsilon = \Delta P_o u/(2.5d) \quad (1)$$

where $\Delta P_o$ and $u$ are the pressure drop and average velocity of the solution at the orifice respectively. Since the fluid velocity at the orifice is extremely higher than that in the other flow sections, it is plausible to assume that the energy is dissipated mostly at the orifice so that $\Delta P_o = \Delta P$.

The data in Fig. 6 are replotted against the value of $\varepsilon$ calculated by Eq. (1) and is shown in Fig. 7 with the data for particles of $D_0=0.71$ and 1.27$\mu$m. It is interesting to know that the data are expressed by a relation with the slope of $-0.035$, irrespective of $d$, and that similar correlations of $D_{av}$ vs. $\varepsilon$ are found also for the other particles. Hence, as long as the size of constituent particles is the same, the size of dispersed flocs is determined solely by the energy dissipated by the contractile flow.

The reduced average diameter of flocs, $D_{av}/D_0$, and $D_{av}$ at given values of $\varepsilon$ are plotted against $D_0$ in Fig. 8. Here the relations of $D_{av}$ vs. $\varepsilon$ for particles of $D_0=0.59$, 0.77 and 1.03$\mu$m are also employed to obtain these relations. It is found that $D_{av}$ increases with $D_0$ monotonically, but $D_{av}/D_0 = (1/\varepsilon_{av})$ decreases exponentially with $D_0$ at $D_0 \leq 0.91 \mu$m and becomes nearly constant at $0.91 \leq D_0 \leq 1.27 \mu$m, where $\varepsilon_{av}$ is the number of constituent particles in a floc of average size. These results indicate that flocs composed of smaller constituent particles are more brittle, but are more difficult to be broken into a floc with the same value of $\varepsilon_{av}$.

It is not known why $\varepsilon_{av}$ is constant at $0.91 \leq D_0 \leq 1.27 \mu$m while $D_{av}$ increases with $D_0$. According to the DLVO theory,\textsuperscript{7} an infinitely strong attractive force acts between coagulated particles, but the force of finite strength acts in the real system because there exists an adsorbed layer of ions and water molecules on the particle surface.\textsuperscript{8} In this case, the depth of the primary minimum of the interparticle potential increases with $D_0$, and so do the magnitude of $F_{ad}$ and the floc strength.\textsuperscript{9} On the other hand, the hydro-
dynamic drag force on flocs increases with $D_0$, as expected from the results in Fig. 7. Hence the constant value of $i_{uw}$ at $0.91 \leq D_0 \leq 1.27 \mu m$ is possibly explained as the result of a near-balance of the increase in floc strength with the increase in drag force in this region.

The results in Figs. 7 and 8 enable us to derive the following equation to estimate the magnitude of $D_{uw}$ under the conditions of $C_e \geq C_{CCl}$, $0.59 \times 10^{-6} \leq D_0 \leq 1.27 \times 10^{-6}$ m, $i_{uw} \geq 6$ and $4 \times 10^{7} \leq \varepsilon \leq 1 \times 10^{10}$ J/m$^3$s.

$$D_{uw}/D_0 = 2.78 f_1 \varepsilon^{-0.035}$$  (2)

where $f_1 = 1.17 \times 10^{-2} D_0^{-0.32}$ at $D_0 \leq 0.91 \times 10^{-6}$ m and $f_1 = 1$ at $0.91 \times 10^{-6} \leq D_0 \leq 1.27 \times 10^{-6}$ m.

According to Yamamoto and Suganuma$^{10}$, $D_{uw} \sim \varepsilon^{-0.2}$ in the case of powder in air converging flow. Sonntag and Russel$^{15}$ reported that $i_{uw} \sim (Q/\pi d^3)^{-1}$ for colloidal agglomerates in contractile flow, where $Q$ is the flow rate. If $\dot{\varepsilon} \sim u^3 \sim Q^3$, then $D_{uw} \sim \varepsilon^{-0.11}$. These relations and Eq. (2) differ in power. It is plausible to assume that the power decreases with increasing floc strength and so with decreasing particle size. $i_{uw} \leq 6$ for our flocs, but $i_{uw} \leq 400$ for the flocs of Sonntag and Russel. Hence the small power in Eq. (2) will be attributable to the high strength of our small-numbered flocs. Further detailed investigations are necessary to clarify the difference precisely.

### 2.3 Maximum floc size

It is important to know the maximum floc size in a suspension because the existence of large flocs influences the performance of materials, even if the amount is small. Figure 9 shows the dependence of the maximum number of constituent particles in a floc, $i_{max}$, on $\varepsilon$. Relations of $i_{max}$ vs. $\varepsilon$ are given by straight lines in a log-log graph, irrespective of $d$. These correlations are very similar to those of $D_{uw}/D_0$ vs. $\varepsilon$ in Fig. 7. Values of $i_{max}$ at given values of $\varepsilon$ are plotted against $D_0$ in Fig. 10. It is interesting to know that the correlations in this figure are also very similar to the relations in Fig. 8. The following equation for $i_{max}$ is derived under the same conditions as for Eq. (2).

$$i_{max} = 139 f_2 \varepsilon^{-0.11}$$  (3)

where $f_2 = 7.42 \times 10^{-16} D_0^{2.50}$ at $D_0 \leq 0.91 \times 10^{-6}$ m, and $f_2 = 1$ at $0.91 \times 10^{-6} \leq D_0 \leq 1.27 \times 10^{-6}$ m.

Higashitani et al.$^{13}$ observed the behavior of flocs composed of spherical particles of 90 $\mu m$ diameter along the centerline of an orifice contractile flow, and found that $i_{max}$ is proportional to $\dot{\gamma}_{cc}$, where $\dot{\gamma}_{cc}$ is the elongation rate on the centerline. Since $\varepsilon \sim \dot{\gamma}_{cc}$, $i_{max} \sim \varepsilon^{-0.1}$. We consider that this dependence of $i_{max}$ on $\varepsilon$ agrees well with Eq. (3).

### 2.4 Comparison between flocs dispersed by contractile flow and ultrasonication

Ultrasound disrupters have been widely used to disperse coagulated particles.$^{6}$ It is important to know whether there is any difference in the flocs dispersed by the present method and those by ultrasonication. Figures 11(a) and (b) show size distributions of flocs dispersed by the present method and by an ultrasonic cleaner (Branson B-3200J-4) respectively. Although the magnitude of $D_{uw}$ is nearly the same, the size distributions differ. The fraction of single constituent particles and large coagulated particles is much higher in the case of ultrasonication than in the case of orifice flow. This result implies that single particles are ripped off one by one from the floc surface in the former case, while flocs are split into smaller agglomerates in the latter case, as illustrated schematically in Fig. 12. The former mechanism is called erosion and the latter splitting.

**Conclusion**

The following conclusions are drawn for the dispersion of coagulated PSL particles by orifice
Fig. 11. Comparison of size distribution between flocs dispersed by (a) orifice contractile flow and (b) ultrasonic disperser

Contractile flow.

1. The strength of flocs increases with increasing electrolyte concentration, and maximum strength is obtained when particles are coagulated in the rapid coagulation region. The maximum strength is independent of the valency of electrolyte.

2. Flocs are effectively dispersed by orifice contractile flow, and the average size of broken flocs and the maximum number of constituent particles are successfully expressed as functions of energy dissipation and constituent particle size.

3. The mechanism of floc breakup in orifice contractile flow differs from that by ultrasonication. Flocs are split into smaller agglomerates in the former case, but particles are ripped off one by one from the floc surface in the latter case.

Acknowledgement

The authors would like to thank Ms. A. Kage and Messrs. K. Okamoto, K. Yoshida and T. Hosokawa for their experimental assistance.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>CCC</td>
<td>critical coagulation concentration of electrolyte</td>
<td>[kmol/m³]</td>
</tr>
<tr>
<td>C_e</td>
<td>electrolyte concentration</td>
<td>[kmol/m³]</td>
</tr>
<tr>
<td>D_m</td>
<td>average floc diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>D_i</td>
<td>diameter of flocs composed of i constituent particles</td>
<td>[m]</td>
</tr>
<tr>
<td>D_p</td>
<td>diameter of constituent particles</td>
<td>[m]</td>
</tr>
<tr>
<td>d</td>
<td>orifice diameter</td>
<td>[m]</td>
</tr>
<tr>
<td>F_a</td>
<td>interparticle adhesive force</td>
<td>[N]</td>
</tr>
<tr>
<td>f_1</td>
<td>correction factor defined by Eq. (2)</td>
<td>[—]</td>
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<tr>
<td>f_2</td>
<td>correction factor defined by Eq. (1)</td>
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</tr>
<tr>
<td>i</td>
<td>number of constituent particles in a floc</td>
<td>[—]</td>
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<td>i_n</td>
<td>number of constituent particles in the floc of number-averaged size</td>
<td>[—]</td>
</tr>
<tr>
<td>i_max</td>
<td>maximum number of constituent particles in a floc</td>
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</tr>
<tr>
<td>Q</td>
<td>flow rate of fluid at orifice</td>
<td>[m³/s]</td>
</tr>
<tr>
<td>r, z</td>
<td>coordinates of test section</td>
<td>[m]</td>
</tr>
<tr>
<td>u</td>
<td>average velocity of fluid at orifice</td>
<td>[m/s]</td>
</tr>
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<td>\dot{r}</td>
<td>elongation rate on the centerline of an orifice contractile flow</td>
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<td>ΔP_e</td>
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<td>ε</td>
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<td>[J/m³ s]</td>
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Literature Cited

6) Higashitani, K., N. Tanise, K. Yoshida and H. Murata: To be published