Breakup of Coagulated or Flocculated Clusters of Cellulosic Fines and CaCO$_3$ Particles Exposed to Hydrodynamic Stress

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Abstract

The capacity of fine particles to remain clustered together after being agglomerated by polyelectrolytes plays an important role in papermaking and in the treatment of wastewater. Tests were carried out with agglomerated suspensions of calcium carbonate and primary cellulosic fines in neutral buffer solution. Agglomeration was induced either by a high-charge cationic polyelectrolyte (a coagulant) or by sequential treatment with a coagulant and a very-high-mass anionic acrylamide copolymer (a flocculant). Particle size analysis, based on diffraction of laser light, showed that the coagulated suspensions were susceptible to being redispersed by hydrodynamic shear. By contrast, flocculated suspensions were only partly broken up. In a flocculated mixture of CaCO$_3$ and cellulosic fines, only the cellulosic fines could be separated from each other. The intensity of shear was more critical than its duration. Conventional shear stress was more effective for the breakup of the polyelectrolyte-induced agglomerates versus extensional flow or intense ultrasonic vibrations.
Key words: Polyelectrolyte-induced agglomerates; Redispersion; Hydrodynamic shear; Particle size distributions; Cellulosic fines; Precipitated calcium carbonate

I. Introduction

1.1. The manufacture of paper involves a delicate balance between efforts to achieve a highly uniform distribution of fibers in the sheet as it is being formed, while at the same time achieving efficient retention of fine particles.\textsuperscript{1-3} Excessively low retention efficiency of fine materials such as minerals, hydrophobic sizing agents, and cellulosic fines, can lead to decreased production rates, partial decomposition of certain chemical additives, and a two-sided character of certain paper products.\textsuperscript{5,6} In order to improve the efficiency of retention of fine particles, it is well known that one can add a sufficient dosage of a highly charged cationic polyelectrolyte to approximately neutralize the negative charges present on the surfaces of solids in a typical papermaking system.\textsuperscript{7-8} In addition, most paper machines in current operation employ very-high-mass copolymers of acrylamide, \textit{i.e.} “retention aid” polymers, to keep the retention efficiency at the desired levels.\textsuperscript{9} However, one of the potential adverse consequences of such polyelectrolyte addition, especially if it is excessive, can be a reduced uniformity of the paper due to an increased level of fiber flocculation.\textsuperscript{3,10}
One promising approach, in an attempt to achieve a suitably high level of retention of the fine particles while still avoiding excessive flocculation of the fibers with each other, involves the strategic use of hydrodynamic shear, which is inherent in the unit operations leading to the forming of a sheet of paper. By judicious selection of the points of addition for different chemical additives, the papermaker can influence the level of hydrodynamic shear that will subsequently act upon that additive, up to the point where the paper sheet has been fully formed. The choices are limited, however, since the levels of hydrodynamic shear associated with such devices as fan pumps, hydrocyclones (“cleaners”), pressure screens, and headboxes in a paper machine system are mainly a function of the design of the equipment and the rate of throughput. Papermakers can select to add retention aid polymers either before or after a set of pressure screens. Pre-screen addition is often favored by papermakers who are placing priority on the uniformity of the product and/or optimization of drainage/retention systems that employ either colloidal silica or bentonite (sodium montmorillonite) products. Post-screen addition of a retention aid is often favored by papermakers whose priority is to achieve the desired efficiency of retention at the lowest cost of retention aid polymer. In either case, it makes sense to fine-tune the types and dosages of the chemical additives used in the retention program so that they match well to the levels of hydrodynamic shear present in the paper machine system under consideration.

While past studies have dealt with the effects of hydrodynamic shear on different aspects of fine-particle retention, it has been less common to consider just the fine particles in isolation, apart from the fiber portion of a papermaking furnish. Notably, Liimatainen et
al. carried out work in which calcium carbonate particles were allowed to interact with stirred suspensions of cellulosic fines. In the absence of retention aid, the observations could be fit very well to a Langmuir adsorption isotherm. Though the authors noted that the Langmuir isotherm often implies a dynamic equilibrium between attachment and detachment, they did not confirm whether or not particles were being detached in their system.

The hydrodynamic forces required to detach colloidal particles from surfaces, after various treatments with polyelectrolyte coagulants and flocculants, have been considered in previous studies. A study based on turbulent flow in the annulus of coaxial cylinders showed that the shear stress required to detach TiO$_2$ particles from glass or cellulose surfaces could be greatly increased by treatment with polyelectrolytes. In particular, treatment with a very-high-mass cationic acrylamide copolymer was able to increase the required shear stress for detachment of the particles from glass from about 0.8 Pa in a neutral buffer solution to about 320 Pa following treatment of the glass with flocculating polymer. An important principle arising from the same series of work was the finding that, when other factors are kept constant, a larger particle size implies a lower shear stress required for detachment. In related work, Pelton and Allen showed that highly flexible polymeric bridges could account for attachment of polystyrene spheres to a surface, rendering them resistant to detachment when later exposed to flow.

The present work was undertaken in an effort to better understand the effects of hydrodynamic stress following two contrasting types of polyelectrolyte treatment –
coagulation and flocculation. These two types of treatment were examined in a previous article, which was concerned with the joining of particles together into agglomerates.\textsuperscript{24} The cited article showed that the coagulation treatment – based on addition of a high-charge cationic polyelectrolyte – was only marginally effective in bringing about increased agglomeration. On the other hand, flocculation, such as can be achieved by sequential addition of high-charge cationic polymer followed by anionic acrylamide copolymer (aPAM), resulted in large agglomerates that involved all of the particles present in the suspension. The present work was aimed at finding out how different kinds of hydrodynamic treatment affected polyelectrolyte-induced agglomerates of CaCO\textsubscript{3} particles, cellulosic fines, and their combination in terms of particle size distribution and microscopic appearance. In order to examine a broad range of flow types that might affect the state of agglomeration, ordinary shear flow with a stir-bar or impeller was compared with a more intensive action of a blender, exposure to an ultrasonic probe, and the extensional flow induced by rapid jetting of suspensions through a syringe.

2. Experimental

The experimental system employed in this work was in key aspects identical to what has been described in two previous articles by the authors.\textsuperscript{24-25} The descriptions that follow will therefore emphasize details that are unique to the present article.

2.1. Materials

2.1.1 Cellulosic primary fines

Cellulosic fine matter, largely consisting of delignified parenchyma cells, was isolated from unrefined bleached hardwood kraft pulp from a mill in the US southeast.\textsuperscript{25} After
dispersing the baled pulp in water, the suspension was passed through the last stage of a
Bauer-McNett classifier fitted with a 200-mesh screen. Rinsing was continued for at
least 10 minutes to allow most of the fines to pass through the screen openings and to be
collected in a barrel. After over-night sedimentation and collection, the primary fines
obtained in this manner were thickened by additional settling to reach a suitable solids
level in the range of 2-5%.

2.1.2 Mineral particles
Calcium carbonate particles were of the scalenohedral calcite type (PCC, Albacar® 5970
from Specialty Minerals Co.) with diameters of about 2-3 µm.

2.1.3 Water-soluble chemicals
Deionized water was used for initial dilution of the following polyelectrolytes to either
the 1% level (for coagulants) or the 0.1% level (for flocculants). A high-charge cationic
coadulant, poly-diallyldimethylammonium chloride (Aldrich cat. no. 40,901-4, having a
nominal molecular mass of 100,000 to 200,000 Daltons) was called “poly-DADMAC”.
A very-high-mass cationic co-polymer of acrylamide (Percol® 175 from Ciba Specialty
Chemicals, having a monomer molar content of 10% cationic groups) was identified as
“cPAM”, a cationic flocculant. The initial solutions of flocculants were allowed to stir
gently for an hour before being employed in experimentation. A very-high mass
copolymer of acrylamide (70%) and acrylic acid (30%), Floerger AN 934 (from SNF
Floerger), was called “aPAM”. Reagent-grade sodium sulfate and sodium bicarbonate
were used to prepare a pH 7 buffer solution having a NaHCO₃ concentration of 10⁻⁴ M
and an electrical conductivity of 1000 µS/cm at 20 °C, which was used as the suspending medium for the suspensions described in this work.

2.2 Equipment

A Horiba LA 300 particle size analyzer was used to evaluate particle size distributions. Zeta potentials of suspended particles were evaluated with a Lazer Zee microelectrophoresis analyzer from PenKem. An Olympus BH2 UMA microscope was used to obtain optical images of particles after suspensions had been allowed to sediment onto glass slides.

2.3 Preparation of agglomerated systems

Three combinations of suspended matter employed in a previous study were selected for the present work: a suspension of just CaCO₃, a suspension of just primary cellulosic fines, and a mixture of the two, usually 80% CaCO₃ and 20% fines, unless noted otherwise. For preparation of agglomerated systems, the percent solids was 0.5%. Destabilization of suspensions by "coagulation" entailed addition of the poly-DADMAC at a dosage (dry-mass basis) of 0.025%. Destabilization of suspensions by "flocculation" entailed sequential addition of poly-DADMAC (0.025%) followed by aPAM (0.015%) with selected tests done at other combinations of dosages.

2.4 Exposure of agglomerated systems to flow conditions
A set of contrasting flow conditions was selected in order to assess the ability of agglomerated particles to remain intact. The conditions were as follows:

1. Gentle Impellor Stirring: This level of shear was established by placing the beaker containing the sample to be tested on a stir plate (Thermolyne, Barnstead Intl., Nuova brand, model SP18425, 120 V, 7.3 amps), adding a 2 cm long magnetic stir bar, setting the stir plate to a level of 3, and then stirring for 30 s.

2. Intermediate stirring: This level of shear was accomplished by the same method as for Gentle Impellor Stirring, but with the stir plate set to 8 (where the maximum was 10). This level of shear was maintained for 60 s.

3. Blending: This condition was accomplished with a Waring Commercial Blender (model 51BL32, 120 V, 3 A). This blender allowed for high speed blending at one speed. Fifty milliliters of sample test solution were briefly transferred to the blender’s 100-mL container (Fisher cat. no. 14-509-18B) before the top was covered with its elastic seal and the container placed on the blender’s stand. The device was allowed to run for 60 s.

4. Low Ultrasonic Treatment: An ultrasonic homogenizer, the OMNI-Ruptor 250 by OMNI International, Inc., was set to a 4 magnitude POWER setting at a PULSER of ~30-32%. The timer was also set to just above three minutes. A probe with a diameter of 10 mm was then inserted into the 50 mL test sample, about a centimeter deep into the solution held within a 50 mL Erlenmeyer flask. At 60 seconds, the RESET button was hit to stop the treatment, and the probe was removed from the sample.
5. High Ultrasonic Treatment: This condition was the same as the previous, but with the POWER set to a magnitude of 6.

6. Syringe & Erlenmeyer Flask: This test regime involved jetting 50 mL of test solution in and out of an Erlenmeyer flask using a 60 mL syringe, continuously, for 10 minutes. The inner diameter of the tip of the syringe was approximately 1.8 mm, and each “in and out” cycle of squirting was completed in about 2 seconds.

In a further set of experiments, an impeller stirrer was used to provide a range of different shear environments, as specified later. Those tests were carried out in a Dynamic Drainage/Retention Jar device, Paper Research Materials, Inc., http://www.brittjar.com.

After each of the applications to flow, as listed above, the sample was immediately tested for particle size using the LA-300 Horiba Light Scattering Device. The Horiba LA-300 main compartment was filled with approximately 300 mL of the 1000 µS/cm buffer solution, or to the line in the main compartment. Drops of the newly tested sample were then added to the LA-300 Horiba main compartment via pipette until the dispersion T% reached an optimum level at approximately 85.3%, within the ideal range of 95-75% for the dispersion T%. The optional ultrasonication treatment, provided with the Horiba device, was not employed.

2. Calculation of shear stress
Estimates of the hydrodynamic stress applied to the suspensions under the described flow systems were obtained by reference to equations developed by others, as follows.

To estimate the typical shear stress experienced by suspended matter under the conditions of turbulent shear flow (for instance when using a blender), the following equation was used:

\[
\tau_{\text{max}} = 5.33 \rho (\varepsilon \nu)^{0.5}
\]

In this equation \(\rho\) is the density of the fluid (taken to be 1.00 g/cm\(^3\)), \(\varepsilon\) is the rate of energy dissipation (estimated as 360 W per 100 g of fluid, based on the rating of the blender and the amount of fluid employed), and \(\nu\) is the kinematic viscosity (taken to be 1 cSt, or \(10^{-6}\) m\(^2\)s\(^{-1}\)).

To estimate the extensional stress applied to suspended agglomerates passing through the center of a contracting nozzle (i.e. the syringe), the following equation was used to calculate the rate of extension:

\[
\dot{\varepsilon} = \frac{8Q}{\pi D^5} \frac{\sin^2 \theta}{1 - \cos \theta} = \frac{8Q}{\pi D^5} f(\theta)
\]

In this equation, \(Q\) is the flow rate, \(D\) is the smallest diameter of the nozzle, and \(\theta\) is the half-angle of the cone. The function \(f(\theta)\) can take on values in the range between zero and 1.3. Because the syringe employed in the present work had a half-angle of 60 degrees, an \(f(\theta)\) value of 1.3 was used (see Table 1 of the cited work). The extensional viscosity was estimated as three times the Newtonian viscosity of water. For the sake of...
of comparison, the shear rate and stress in the syringe system were calculated from the equations for flow through a capillary:

\[
\dot{\gamma} = \frac{4Q}{\pi R^3} \quad \text{and} \quad \tau_w = \frac{4Q\eta}{\pi R^3} \quad (3)
\]

Here the term \( R \) refers to the inner radius at the outlet of the syringe. In using these equations a dynamic viscosity of 1.002 mPas, corresponding to water at 20 °C, was assumed. The flow rate calculated based on the release of approximately 60 mL of aqueous solution in one second. The ultimate diameter of the syringe was 1.8 mm.

3. Results and Discussion

3.1. Zeta potential vs. poly-DADMAC treatment

As shown in Fig. 1, addition of poly-DADMAC to suspensions of either the precipitated calcium carbonate or the primary cellulosic fines resulted in a stable positive zeta potential, once the dosage exceeded about 0.3% on a dry-mass basis. The initial negative zeta potential of the cellulosic fines is consistent with the presence of carboxylic acid groups.\(^2,3\)0 The weakly cationic zeta potential of the untreated CaCO\(_3\) suspension is consistent with expectations for that material.\(^3\)1 Interestingly, the present results for the CaCO\(_3\) suspension were somewhat different from what was measured earlier,\(^2,4\) and the differences might be related to minor variations in handling and dilution.
Figure. 1. Effect of high-charge cationic polymer dosage (dry mass basis) on the zeta potential of suspensions of precipitated calcium carbonate and or primary cellulosic fines.

3.2. Breakup of agglomerates after coagulation with poly-DADMAC

Figure 2 shows optical micrographs of CaCO$_3$ suspensions collected on glass slides. Significant agglomeration is apparent in Part A of the figure, which corresponds to a suspension that had just been treated with poly-DADMAC at the 0.025% level. Part B of the figure shows a corresponding image after the suspension had been exposed to 30 s of intense shear in the blender. Though the latter image still shows some particles that have the appearance of being attached together, it can be concluded, in general, that the hydrodynamic shear had been effective in dispersing the particles from each other.
Figure 2. A: Before-shear appearance of precipitated calcium carbonate that had been treated with poly-DADMAC. B: Same system after 30 s of shear in a blender.

Figure 3 reports particle size distributions for a related system, based on diffraction of laser light. The suspended solids consisted of 80% CaCO₃ and 20% cellulosic fines, by mass, which had been freshly coagulated by addition of poly-DADMAC at the 0.025% level. The filled area (with the dashed line) represents the freshly coagulated system, before application of strong hydrodynamic shear. The pre-shear distribution of particle size had a modal value of about 40 µm, which was about the same as the value obtained earlier for an individual suspensions of the primary cellulosic fines. A shoulder in the pre-shear distribution, centered at about 8 µm, is consistent with the presence of clusters of CaCO₃ particles, possibly associated with very thin cellulosic fibrils. The rising dashed line in the figure shows the cumulative distribution, indicating a median size of 20 µm.
The distribution represented by the solid line in Fig. 3 makes it clear that the distribution became strongly bimodal after application of 30 s of intense shear in the blender. One of the maxima in the post-shear distribution, centered at 4 µm, is consistent with the presence of very small groups of CaCO₃ particles, including single particles, doublets, or triplets, etc. The other maximum in the distribution, centered at about 80 µm, is consistent with the cellulosic fines by themselves. The fact that the latter value was higher than what had been observed for a suspension of the cellulosic fines alone, provides evidence that the redispersion of the particles was not complete, or that the fines tended to come back together again, due to the neutralization of charges. In general, however, it is apparent that the hydrodynamic shear was sufficient to detach CaCO₃ particles from the cellulosic fines. Also, most large clusters of CaCO₃ particles appear to have been substantially separated into either single particles or small clusters.
Figure 3. Particle size distribution of mixed suspension with 80% CaCO$_3$ and 20% primary cellulosic fines after having been treated with poly-DADMAC. Filled area: Before application of shear. Solid line: Same, after subsequent exposure to 30 s of shear in blender. Rising curves show the corresponding cumulative distributions.

Related tests with poly-DADMAC (not shown) were carried out with suspensions of primary fines alone. In such cases was there insufficient agglomeration to justify subsequent experiments with application of hydrodynamic stress.

3.2. Breakup of agglomerates after flocculation with poly-DADMAC & aPAM

Figure 4 shows corresponding results following flocculation of an 80:20 mixture of CaCO$_3$ particles and primary cellulosic fines by sequential addition of poly-DADMAC (0.025% by mass) and then aPAM (0.015% by mass). Again, the pre-shear (gentle stirring) distribution is represented by the dashed line and the filled area. The fact that almost the entire distribution was larger than 10 µm is consistent with essentially all of the CaCO$_3$ particles having been incorporated into flocs that included cellulosic fines. The modal value of the distribution was essentially the same as that of a well-dispersed suspension of cellulosic fine particles, as reported earlier [25]. This result suggests that the CaCO$_3$ particles were mainly accumulating on the surfaces of the much larger cellulosic particles. Due to the great difference in size between the two, the apparent size of the agglomerates was close to that of the cellulosic fines by themselves.
The other two particle size distributions shown in Fig. 4 indicate the progressive effects of two levels of hydrodynamic shear. The dotted line is for a system sheared at a higher level of magnetic stirring (see Experimental). The solid line represents the effects of intense shearing in a blender. These curves show results that were strikingly different from the case where the same solids had been agglomerated by treatment with poly-DADMAC. In the flocculated system, the shape of the particle size distribution remained almost constant after the application of shear, though there was a moderate shift towards smaller agglomerate size in each case. Thus, the results are consistent with a splitting mechanism of dis-agglomeration, in which the product consisted of smaller agglomerates, but essentially no separation of individual CaCO$_3$ particles, since the latter would have been apparent in a size range of about 2 to 6 µm.$^{25}$ In other words, the results tend to rule out extensive erosion of individual CaCO$_3$ particles from the agglomerated matter.

Based on the laser diffraction analysis, the application of shear to the flocculated system of cellulosic fines together with CaCO$_3$ particles appeared to have produced agglomerates smaller than the cellulosic fines by themselves, whereas one would expect such agglomerates to be at least as large cellulosic fines by themselves. Apparently this aspect of the results is due to the way in which the system interacts with light, since the algorithm used in the fitting assumes that only perfectly spherical, uniform particles are present. This issue will be considered further when discussing the microscopic evidence for the system.
Figure 4. Particle size distribution of mixed suspension with 80% CaCO$_3$ and 20%
primary cellulosic fines after having been treated sequentially with poly-DADMAC, then
aPAM. Filled area: Before application of shear. Dotted line: Same, after brisk stirring.
Solid line: After subsequent exposure to 30 s of shear in blender. Rising curves show the
corresponding cumulative distributions.

A tendency for hydrodynamic shear to result in a splitting mechanism of breakdown of
agglomerated particles is supported by past work.$^{32-33}$ Lu and Spielman were among the
first to report a maximum stable floc size corresponding to a given level of hydrodynamic
shear.$^{34}$ The fact that small CaCO$_3$ particles were not dislodged during that process is
consistent with the known greater difficulty of detaching smaller particles from solids
exposed to a given level of shear stress.$^{22}$
The next two figures provide some context for the particle size distributions of systems treated with the two-component flocculent system. Figure 5 is from a suspension of just the primary cellulosic fines, after sequential treatment with poly-DADMAC, then aPAM. Part A shows a typical floc that was present before application of shear. Part B is from a related sample after the application of shear in a blender. Inspection of images of this type made it possible to conclude that though hydrodynamic shear was affective in breaking up the flocculant-induced agglomerates, the redispersion was only partial. It is worth emphasizing out that the polyelectrolytes are much smaller than what can possibly be seen in an optical micrograph; rather, the apparent tethered linkages among different cellulosic particles can be identified as cellulosic microfibrils attached to the surfaces.\textsuperscript{25} Presumably, the role of the poly-DADMAC and aPAM combination involved formation of bridges between cellulosic surfaces, including the very slender fibrils.\textsuperscript{35-36}

**Figure 5.** Suspension of primary fines after having been treated sequentially with poly-DADMAC, then aPAM. A: Before-shear appearance. B: Same, after subsequent exposure to 30 s of shear in blender
Figure 6 shows a related set of images, except that the solids consisted of 80:20 mixtures of CaCO$_3$ and primary fines. The image in Part A (pre-shear) shows a predominance of spheroidal agglomerates of various sizes. By contrast, Part B shows that after the application of shear in a blender the agglomerates tended to be elongated. Thus, it appears that the shear flow had stretched at least some of the larger agglomerates into narrower, longer clusters.

A tendency of hydrodynamic shear to distort and elongate agglomerates of flocculated particles was predicted by Higashitani et al. based on a finite-element model.$^{32}$ In the present work, the presence of cellulosic matter, which is inherently fibrous, may be expected to further facilitate the elongation of flocs. However, there is evidence that the distribution of CaCO$_3$ particles relative to the surfaces of cellulosic fines was not uniform, with larger concentrations of CaCO$_3$ present at different points along an individual cellulosic fine particle. In addition to the somewhat non-uniform distributions apparent in Fig. 6, such a distribution also can help explain why the modal particle size of the distributions shown in Fig. 4 after high shear in a blender (ca. 20 µm) was substantially lower than the corresponding distribution for a well-dispersed suspension of primary fines by themselves (ca. 40 µm).$^{25}$ Since the parenchyma cells that constitute most of the cellulosic fines are too strong to be broken by the blending action, there has to be a different explanation for the apparent reduction in size below that of the cellulosic fine particles by themselves. It appears that uneven clusters associated with different regions of a cellulosic fine particle can affect the diffracted light such that the instrument reports the presence of particles of a somewhat smaller size.
Figure 6. Mixed suspension of 80% CaCO₃ and 20% primary fines after having been treated sequentially with poly-DADMAC, then aPAM. A: Before-shear appearance. B: Same, after subsequent exposure to 30 s of shear in blender.

3.2. Comparing effects of intensity vs. duration of shear

The strength of polyelectrolyte-induced bridges and their ability to resist the effects of flow can be expected to depend on such variables as polymer dosage, the intensity of the flow event, and its duration. Figure 7 shows results of an experiment in which agglomerates of primary fines were first treated with poly-DADMAC at the 0.05% level, followed by different levels of aPAM treatment. Agitation was then applied by means of an impeller stirrer at three speeds of agitation. The error limits in the figure show the results of two replicate tests, which were averaged in each case. The most striking conclusion arising from this set of experiments was that the duration of hydrodynamic shear had no significant effect on the results. Rather, the key variables were the
flocculant dosage and the rotational speed of agitation. Higher dosages of aPAM yielded larger agglomerate size, whereas higher shear yielded smaller particle size.

**Figure. 7.** Comparing the effects of agitation speed and duration on the mean diameter of agglomerates of primary fines after sequential treatment with 0.05% low-mass poly-DADMAC and the indicated amounts of aPAM (30% anionic groups) at the impeller rotational speeds and durations shown.

Based on the results just presented it is possible to draw some general inferences regarding the polyelectrolyte-induced flocs. The fact that the agglomerate size, after exposure to each of the shear levels, tended to increase with increasing aPAM dosage is consistent with an increasing density of macromolecular bridge chains linking adjacent surfaces. A higher density of bridging thus renders the system more shear-resistant. The fact that the results did not depend on time, within the ranges of conditions tested,
suggests systems in which detachment was initiated mainly by rupture of polymer chains – an event that requires application of a force that exceeds a well-defined limit. For instance, it has been estimated that a force of 7 nN is needed to snap a single polyisoprene or polybutadiene chain, and that value would not be expected to depend on the duration of application of the force. The strong dependency of the agglomerate size on the agitation speed (Fig. 7) further supports this view. As predicted by Tomi and Bagster, based on a model in which a floc elements are joined together by flexible polymer bridges, the maximum particle size was strongly dependent on the intensity of the applied hydrodynamic shear. It appears that a 60 s exposure was a sufficient length of time to ensure that the polymer bridge attachments had been subjected to essentially the full range of local flow events that could be experienced during 30 minutes of agitation.

3.2. Comparing effects of different flow systems

Up to this point in the article, the only flow systems considered have been partially or fully developed turbulent shear flow, induced by either a magnetic stir bar, an impeller, or a blender device. Further tests were carried out to find out whether the polyelectrolyte-induced flocs were vulnerable to certain other types of hydrodynamic stresses, in addition to shear stress. The system under consideration consisted of an 80:20 mixture of CaCO₃ and cellulosic fines that had been treated sequentially with 0.05% poly-DADMAC followed by 0.05% aPAM. As shown in Fig. 8, the intense shear flow imparted by the blender was clearly the most effective in terms of reducing the agglomerate size. If one compares the first three groups of histogram bars, starting from...
the left of the figures, then it becomes clear that agglomerate size decreased with increasing intensity of shear.

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**Figure 8.** Comparing the effects of different flow systems imposed upon mixtures of 80% CaCO₃ and 20% primary fines after sequential treatment with 0.05% low-mass poly-DADMAC and 0.05% aPAM

The results in Fig. 8 corresponding to exposure of the flocculated suspensions to an ultrasonic probe showed a somewhat surprising result – the largest (or equal) measured diameters compared to any of the other flow systems, even including the gentlest stirring with a magnetic stir-bar. This is despite the fact that the ultrasonic probe system expends up to 250 Watts at its highest setting, which is in a similar range to the energy rating of the blender system (360 W). The difference is tentatively attributed to a highly flexible
nature of the polymer bridges and to the relatively short ranges of motion imparted by the

shock waves of ultrasonification. Vasilev et al. cited evidence that the amplitudes of
cavitation events inherent in the use of ultrasonic probes fall in the range of 15 to 90
µm. Because the ultrasonic waves being considered are acting within a condensed
aqueous fluid, and the solids present are similarly quite resistant to compression, it could
be expected that the changes in relative distances between adjacent particles in an
agglomerate, due to ultrasonic vibrations, would be a minor fraction of the cited
distances. It is well known that ultrasonic waves can be very effective not only in the
detachment of particles from surfaces, but also in the disruption of biological cells.
The fact that the present systems, agglomerated by poly-DADMAC and aPAM, were
not at all susceptible to ultrasonic disruption is further testimony to the flexibility and
toughness of the polymer bridging systems.

The last remaining set of histogram bars, to the far-right in Fig. 8, correspond to
experiments in which the suspension was repeatedly jetted through a 60 mL syringe, over
the course of 10 minutes. The extensional shear stress exerted on particles that happen to
be in the center of flow can be estimated from Equation 2, by inputting the critical
dimensions of the outlet from the syringe and estimating the rate of flow. The
extensional stress was calculated as 102 Pa, whereas the corresponding shear stress at the
wall of the syringe opening was calculated to be 78 Pa (by Equation 3). Bałdyga et al.
established that a tensile rupture mechanism is likely to predominate in extensional
flow. Kobayashi found that increasing flow through a syringe-type system was
increasingly effective in breaking up flocs of polystyrene latex particles, leading to
smaller floc diameters. The fact that significant detachment was not found for the
"Syringe squirt" condition shown in Fig. 8 suggests that the exerted force was below the level required to bring about tensile splitting of the agglomerates.

The magnitude of shear stress within the blender (not accounting for possible higher values near to the tips of the impellers) was 320 Pa (from Equation 1), which was considerably higher than what was calculated in the case of flow through the syringe system. This result appears consistent with the fact that the blender was considerably more effective in breaking up agglomerates in comparison to flow through the syringe. But such a comparison cannot account for the fact that the agitation with the magnetic stir bar, even at the gentle level of application, yielded substantially lower particle size in comparison to passage through the syringe. It should be kept in mind, however, that use of a magnetic stirring system creates an opportunity for colloidal materials to become pinched and rubbed in the zone of contact between the stir-bar and the vessel, and that effect could well explain the lower diameters recorded for those cases, in comparison to the ultrasonic and squirting treatments.

IV. Conclusions

Detachment of particulate suspensions including CaCO$_3$ particles, cellulosic primary fines, and their combination, following coagulation or flocculation with polymers, could be broken up to different degrees by application of hydrodynamic stresses. A high-charge density cationic polymer, poly-DADMAC (a coagulant), yielded increased agglomeration of CaCO$_3$ particles, but such agglomerates were readily dispersed by application of shear flow. By contrast, a sequential treatment with the coagulant
followed by an anionic acrylamide copolymer (a flocculant) effectively agglomerated CaCO$_3$ particles onto the shift the distribution of agglomerate size in the direction of smaller values, but individual CaCO$_3$ particles failed to be released. One of the main effects of hydrodynamic shear was to elongate the agglomerates, leading to a non-uniform distribution of CaCO$_3$ particles associated with the cellulosic fines. The flocculated systems were not at all susceptible to breakage by application of either extensional flow or the action of an ultrasonic probe, even though the amounts of energy imparted by ultrasonication were almost as large as that provided by the blender.

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