Monitoring the Dynamics of Concentrated Suspensions by Enhanced Backward Light Scattering

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Abstract

The shear-induced flocculation of kaolin-polymer flocs in a stirred tank is investigated at medium to high solids concentrations ($\phi = 1 - 10\%$ w/w). The evolution of the average floc size is monitored by the change in intensity of laser light scattered in the 180° direction. The measurements reflect the change in particle number concentration as flocculation proceeds. As flocculation begins, coagulation dominates and the floc size increases (total particle number decreases) and then levels off at a steady state value as fragmentation becomes significant and balances coagulation. At steady state, the measurements indicate the extent of flocculation. Increasing the shear rate increases the coagulation and fragmentation rates, resulting in smaller floc sizes at steady state. Increasing the flocculant concentration increases the steady state floc size by strengthening the bonds between primary particles to resist fragmentation. At constant shear rate and flocculant concentration, increasing the solids fraction decreases the steady state floc size indicating formation of weakly bonded flocs. Flocculant mixing was the most important factor for flocculation efficiency at high solids concentrations.

1 Introduction

Particle removal from suspension in a liquid is relevant to numerous areas of research and industry. The efficient recovery of commodity particulate products during crystallization, precipitation, polymerization, and fermentation processes requires the efficient sedimentation and/or filtration of particles from a suspending liquid. Municipalities rely on the flocculation of small particles to form larger flocs that can be easily removed in the treatment of wastewater and drinking water.

Flocculation proceeds as velocity gradients, produced by stirring (shearing) the suspension, promote collisions between particles (coagulation). If the electrostatic double layer interactions between particles are suppressed by the addition of a flocculant, the particle collisions result in adhesion and the formation of a floc. The average particle size is therefore increased by coagulation. Shear stresses within the fluid can also induce breakage of the flocs once they become sufficiently large. After a characteristic time, a steady state is reached between coagulation and fragmentation and the floc size distribution no longer changes [1].

Historically, the theoretical and experimental work carried out on flocculation has been extensive, but directed predominantly toward dilute suspensions of particles (i.e. volume fraction $\phi = 10^{-6} - 10^{-3}$). However, improvements in process technology as well as the growing significance of biotechnology and materials processing emphasize the need for a shift in the focus of flocculation research toward more concentrated suspensions of particles. An example is industrial cell cultures, these suspensions can reach volume fractions up to $\phi = 0.4$ in an attempt to maximize the productivity of a process [2]. Flocculation is an integral part of many separation process loops, but the control and maintenance of such processes remains largely empirical. This is often the result of the lack of fundamental understanding of the physical phenomena of flocculation, especially with suspensions of high solids fractions. Concentrated suspensions are more difficult to characterize relative to more dilute ones, although characterization techniques are available.

The opacity of most concentrated suspensions makes it impossible to apply standard light scattering techniques that rely on forward scattered light without dilution of the sample. Dilution, however, can bias a measurement and is best avoided. One method that allows *in situ* characterization of concentrated suspensions measures backward scattering, or the intensity of light scattered directly back toward its incident source. Lasentec uses one version of this technology in their commercial Focused Beam Reflectance Measurement (FBRM) instrument. The FBRM focuses a rapidly rotating laser into a stirred suspension to scan the suspended particles as they move through the laser focal point. When a particle crosses the circle traced by the laser focal point, it reflects light back toward the probe optics and the resultant "pulse" is recorded. The duration of the backward scattered light is then used to calculate the chord length of the particle scanned during each backward scattering pulse [3].

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A less quantitative method is to consider the entire assembly of particles and take advantage of the multiply scattered light that is ultimately directed back toward the incident light. It can be shown that the light scattered in this direction exceeds that at all other angles because of the constructive interference between the multiple scattering peaks of each particle [4–5]. This phenomenon (referred to as enhanced backward scattering) has been used to characterize concentrated suspensions by simultaneously directing incident light into the suspension and monitoring the light scattered backwards [6]. *Heffels* et al. [7] interpreted enhanced backward scattering intensity patterns using a simple laser-camera-image analysis system and monitored relative changes in the solids volume fraction and the average particle size in latex and glass bead suspensions up to $\phi = 0.6$. Although this method does not provide a direct measure of particle size distributions and must be calibrated, its simplicity and potential makes it attractive as a sensor for evaluating deviation from a set point in an industrial process.

Gregory and *Gubai* [8] and *Gubai* and *Gregory* [9] examined the polymer flocculation of suspensions of clay at solids fractions of 1–3% w/v using a commercial optical instrument (PDA 2000, Rank Bros. Ltd.) that measures the amount of light transmitted through the suspension. This technique is limited to solids concentrations that permit light transmittance (< 3% w/v) and requires the suspension be pumped through narrow tubing for analysis, increasing the risk of altering the floc size distribution. *Gregory* and *Gubai* [8] observed the attainment of a steady state between coagulation and fragmentation by the suspension after only a few minutes, compared to the several hours required for more dilute suspensions [10, 11]. The flocculation kinetics at large solids fractions were significantly affected by the amount of mixing applied during flocculant addition but not at more dilute fractions. Increasing the solids fraction produced a substantial increase in the amount of flocculant required to bring about the same degree of separation. The optimum flocculation behavior was observed when the flocculant was added gradually over a period of time, rather than immediately.

Williams et al. [12] used an FBRM instrument to follow the flocculation of silica particles at 1–5% v/v with a polymer flocculant. They observed that the average floc size at steady state decreased with increasing shear rate. At constant shear rate and flocculant concentration, the average steady state floc size decreased with increasing solids concentration, probably because of the reduced influence of the flocculant. Incremental addition of the flocculant was found to produce a larger steady state floc size than for the simultaneous addition of the entire amount, in agreement with *Gregory* and *Gubai* [8].

The objective of this work is to evaluate the ability of an inexpensive, easy to construct apparatus allowing *in situ* monitoring of shear-induced kaolin flocculation at large weight fractions ($\phi = 0.01 - 0.1$) in a stirred tank. The effect of shear rate, flocculant concentration, and solids concentration on kaolin-polymer flocculation dynamics are determined. The results of the flocculation experiments are compared with literature data obtained using more sophisticated commercial instruments on concentrated and dilute suspensions.

2 Particle Characterization by Backward Light Scattering

Multiple light scattering begins as light enters a concentrated assembly of particles and is first scattered by a single particle. At dilute solids fractions ($< 10^{-4}$), the light would most likely pass out of the assembly without encountering another particle, but as the solids fraction is increased the probability of a second particle encounter increases. If this occurs, the phenomenon is termed multiple scattering. An interesting aspect of this phenomenon is the so called "enhanced" backward scattering that occurs at the 180° angle from the scattering event through constructive interference effects [4]. The result is a large scattering peak at 180° from the targeted particles that varies with particle and suspension properties.

No exact theory of multiple light scattering by particles has been developed, although numerous researchers have observed the anomalous enhanced scattering of light backward toward its source when relatively high solids fractions are studied [4, 6, 13, 14]. *Heffels* et al. [7] observed enhanced backward scattering in suspensions above solids volume fractions of 0.01 and found the peak scattered intensity correlated with the solids volume fraction. The magnitude of scattered light will increase with increasing solids fractions (number of particles) as there is a higher probability that light will encounter and be scattered by a larger number of particles at higher solids fractions. Thus, measurement of the peak scattered intensity provides a qualitative measure of the number of particles present and their dynamics will correlate. The scattered light also contains information about the full floc size and structure distribution, implying future applications in sophisticated particle characterization at high solids fractions. For now, enhanced backward scattering provides a simple basis for qualitative monitoring of particle dynamics in concentrated suspensions.

3 Experimental

Kaolin (Aldrich) was suspended in deionized water at three solid mass fractions (1, 5, and 10% w/w) and flocculated using Percol 728 (Allied Colloids), a very high molecular weight cationic polyelectrolyte with medium charge density (equivalent to Zetag 92 in UK). The suspension was flocculated in a baffled plexiglass stirred tank with height and diameter of 15 cm, baffles 1.5 cm in diameter, and a Rushton radial flow impeller (d = 5 cm) positioned just above the bottom of the tank to prevent sedimentation of the dense kaolin ($\rho \approx 3$ g/cm^3). Pumping of the flocculated suspension through the flow cell of *Heffels* et al. [7] caused fragmentation of the fragile flocs and biased the measurements. In order to avoid floc shearing by pumping, the apparatus used in this work is a form of that of *Heffels* et al. [7] modified to allow *in situ* characterization of the suspension (Figure 1). In Figure 1, incident light (solid arrows) from a 5 mW laser (Melles Griot) passes through a beam splitting cubic prism (Edmund Scientific), and into the suspension. Backward scattered light (dotted arrows) then passes back through the cube to a CCD camera (Model 260 SW, Spindler and Hoyer).

At the beginning of a series of experiments, the backward scattering peak was located using 100 μm glass beads [7] and the apparatus locked into position. Initially, the backward scattering peak is found by locating the high intensity reflection from the prism-water interface (dashed line in Figure 2) which tends to obscure the relatively low intensity backward scattering peak (dotted line in Figure 2). The tank and attached prism and CCD are then rotated about the tank's central axis to shift the reflection peak away from the camera but allow the backward scattering peak to be discerned. Images of the backward scattered light are digitized during the experiment and the radial intensity of the enhanced backward

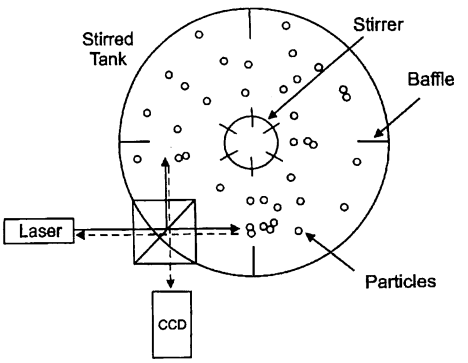

Fig. 1: Overview of the enhanced backward scattering apparatus used to monitor changes in particle size during flocculation in a stirred tank.

scatter peak analyzed using an image analysis software package (Optimas) about once per second. The entire acquisition and analysis process is automatically performed using a simple macro program.

Flocculation is carried out by first adding a measured mass of kaolin to the suspension and mixing for 5 minutes at 500 RPM to disperse the powder. A given volume of 0.1% (w/w) flocculant solution is then added to the suspension at the impeller tip and allowed to rapidly mix at 500 RPM for 10 seconds. The impeller rotational speed is then reduced to a constant value (220, 350, or 500 RPM) to allow flocculation to occur. The impeller speeds used here are necessary to prevent sedimentation of the dense kaolin.

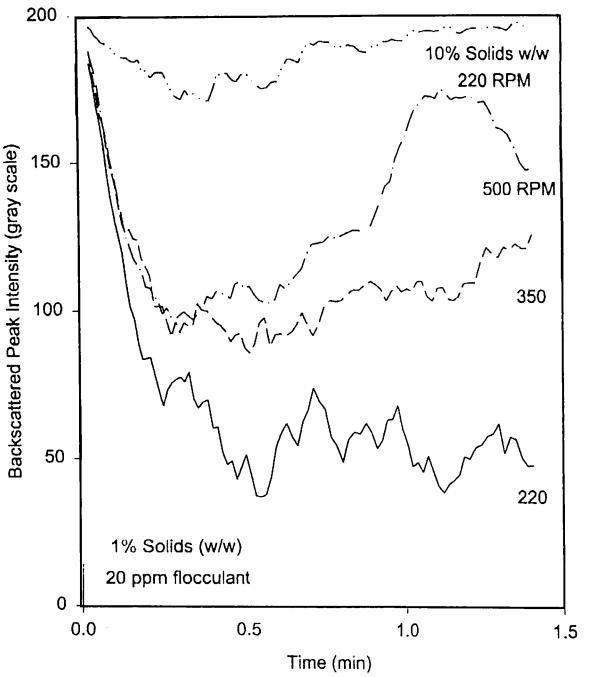

Fig. 3: Evolution of backward scattered light intensity during flocculation of a suspension with 1% and 10% w/w solids at 20 ppm flocculant at three impeller speeds. Flocculation decreases the number of particles, increases the average particle size, and decreases the multiply scattered light. Increasing the impeller speed increases the steady state scattered light intensity.

4 Results and Discussion

The results of the backward scattering measurements are plotted in units of gray scale varying from 0 (black) to 255 (white) and the raw data following image analysis are time averaged to remove systematic variation. Figure 3 shows the results for the flocculation of 1% (w/w) kaolin with 20 ppm of flocculant at various impeller speeds (220, 350, and 500 RPM) and solids concentrations (1%, 10% w/w). Initially, the unflocculated suspension is composed of a large number of particles. The resultant large degree of multiple scattering produces a large gray scale value between 200 and 250 depending on the ambient light. Thus, these measurements reflect a relative change in light as a result of flocculation.

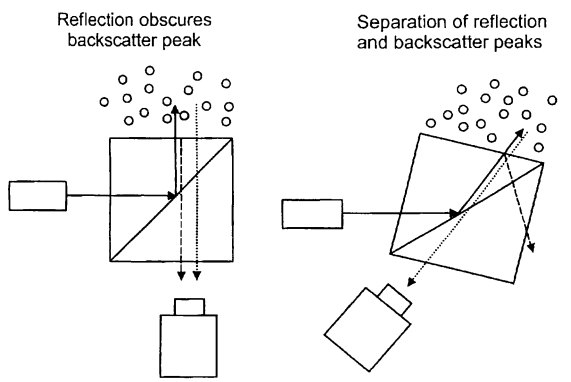

Fig. 2: Schematic of the method for separating the lens-water interface reflection peak and the backward scattering peak by rotation of the stirred tank.

In Figure 3, when the particles are flocculated at 220 RPM and 1% w/w solids, there is an initial rapid drop in the scattered light intensity, indicating a rapid decrease in the number of particles available to multiply scatter the incoming light. This decrease is the result of rapid particle-particle collisions to form larger flocs (coagulation). The slope of this line then decreases as fragmentation becomes significant, reducing floc growth rates. Finally, the light intensity levels off within variation to a steady state value, indicating the attainment of a steady state between coagulation and fragmentation of particles. This result is in excellent agreement with literature results at much lower solids fractions [10, 11, 15] and at comparable solids fractions using commercial instruments [8, 12]. It should be noted, however, that here steady state is attained within minutes while dilute suspensions require over one hour [10, 11].

When the impeller rotation rate is increased to 350 RPM at 1% w/w solids, the data in Figure 3 exhibit a trend similar to that at 220 RPM. However, at this higher speed, larger shear stresses exist within the suspension that limit floc growth to a smaller size by increasing the fragmentation rate. As a result, the steady state light intensity is higher than for 220 RPM, indicating that a larger number of smaller particles exist at this steady state as a result of the higher shear stresses. After some time at steady state (1 minute), the data for 350 RPM begin to increase slightly, indicating degradation of the steady state flocs into smaller, more compact structures. This is the result of polymer-particle bond degradation following repeated growth-breakage-regrowth cycles [16], and, if flocculation is continued, further degradation will occur. A more intense degree of shearing intensifies this effect; at 500 RPM the backward scattered light reaches a larger steady state value than at 350 RPM because of the increased fragmentation rates but then

begins to increase as the flocs are rapidly degraded. Qualitative observations of the floc size were made during each experiment as the flocs were large enough to be discerned visually (1–5 mm). The trends in backward scattered intensity were in excellent agreement with the evolution of floc size observed visually. Figure 3 demonstrates the ability of the backward scattering technique to indicate the point at which a flocculation process should be terminated or, conversely, when inadvertent particle aggregation occurs and product quality may be detrimentally affected (e.g. $t = 0.7$ minutes at 350 RPM and 1% w/w solids).

The effect of increased solids percentage (10% w/w) on flocculation at a constant flocculant concentration is also shown in Figure 3 for 220 RPM. The same trend during flocculation is observed as for 1% solids. An initial decrease in scattered intensity is followed by a rapid leveling off at a steady state value that is significantly larger than the corresponding case at 1% solids. After 30 seconds or so, the scattered light intensity increases and approaches the initial unflocculated conditions. This is a result of the particle polymer bond degradation cited above, an effect intensified by the increased solids concentration. Increasing the solids fraction without increasing the flocculant concentration reduces the strength of bonds between particles and produces weaker floc structures that are unable to resist sustained shearing. As a result, flocculation is short lived and ineffective in particle size enlargement and subsequent solid-liquid separation unless closely monitored. These results are in excellent agreement with the results obtained by [8, 12] using commercial particle sizing instruments.

Figure 4 shows the effect of varying the flocculant concentration on the evolution of the backward scattered light intensity for flocculation of 1% kaolin at 220 RPM. Increasing the flocculant concentration increases both the rate of particle flocculation and the steady state average floc size, as indicated by the behavior of the backward scattered light intensity.

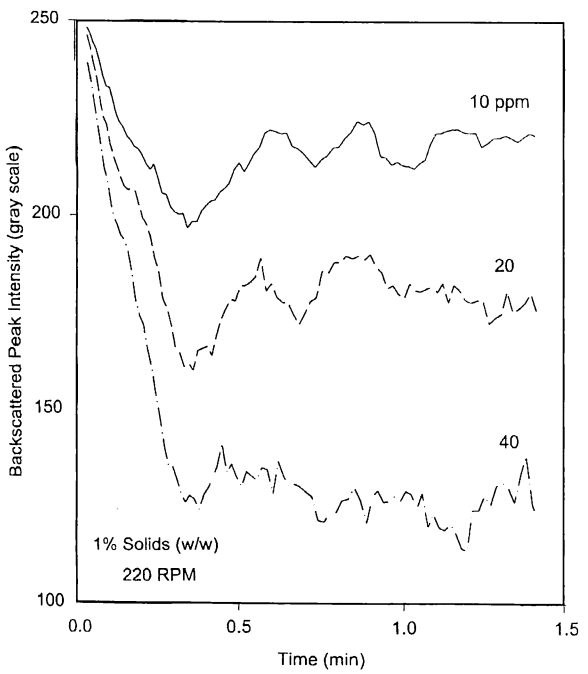

Fig. 4: Effect of flocculant concentration on flocculation performance at 1% solids (w/w). Increasing the flocculant concentration increases the coagulation rate and resulting floc strength, producing larger particles at higher flocculant concentrations.

Increasing the number of polymer molecules in the suspension increases the polymer surface coverage of a kaolin particle, thus increasing the probability of a successful particle-particle collision to form a floc. In addition, the greater surface coverage of particles by polymer molecules produces stronger particle-particle bonds within a floc, creating stronger flocs more capable of resisting shear-induced fragmentation. This effect is seen in Figure 4 as a smaller steady state scattered intensity, indicating a significantly larger average floc size at steady state with increasing flocculant concentration, in agreement with [8]. The measurement of light intensity was not isolated from ambient light sources, thus measurements carried out on different days exhibit different baseline intensities. This effect can be easily remedied by shielding the apparatus, but in the current configuration produces a result that is unique to the day of the experiment. As a result, the data at 20 ppm in Figure 4 differ from those in Figure 3, but only in magnitude. A relative data comparison is still possible as shown in Figure 4.

Figure 5 shows the ability of the backward scattering method to monitor flocculation at a solids fraction (5%) that does not permit any transmission of light. In Figure 5, at a constant flocculant concentration (40 ppm), flocculation occurs more rapidly than for 1% solids as seen by the immediate attainment of a steady state value by the scattered intensity (floc size). At the lowest impeller speed (220 RPM), steady state is maintained for 1 minute before some sign of floc degradation is observed, indicated by the slight increase in scattered intensity. Increasing the impeller speed to 350 RPM, however, produces a markedly different behavior, as the intensity passes through a minimum then increases almost immediately and approaches the steady state value attained at 220 RPM. This result highlights the importance of adequate mixing at high

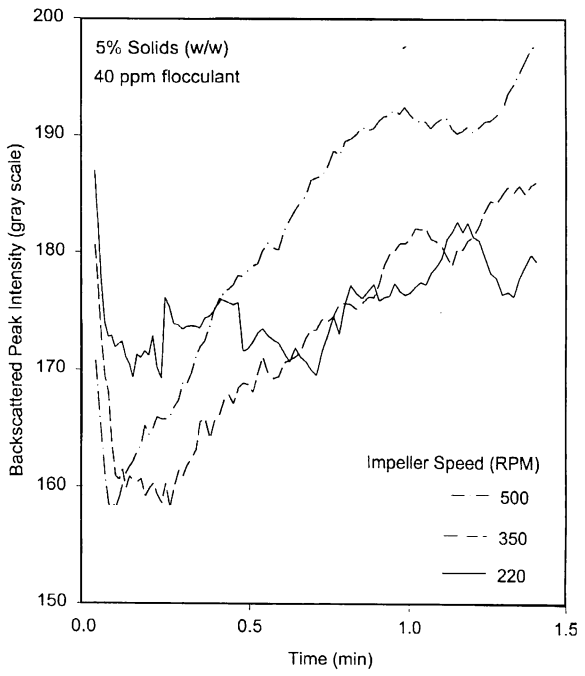

Fig. 5: Effect of increased solids fraction (5% w/w) and impeller speed on flocculation. Increasing the impeller speed has a more profound negative effect at higher solids fractions since the decreased number of polymer-particle bonds resist shear fragmentation less effectively. Initially higher impeller speeds promote better mixing and enhanced flocculation over lower speeds. Increased fragmentation rates quickly cancel the effects of flocculation.

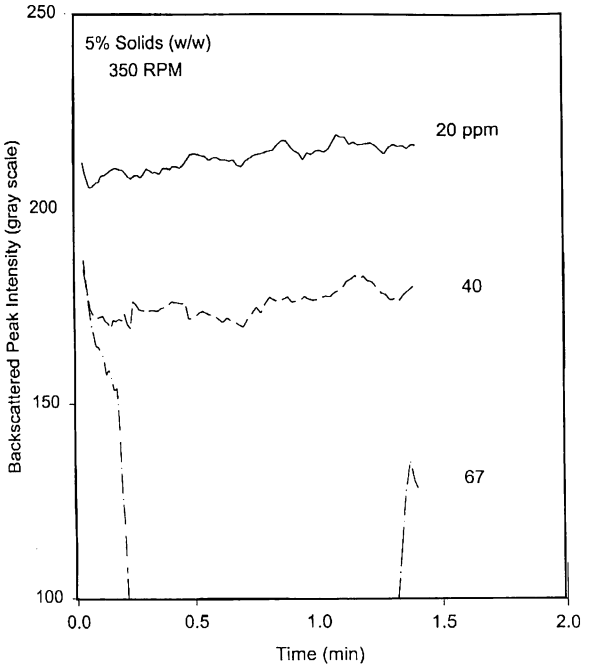

Fig. 6: The effect of flocculant concentration at 5% w/w solids by following the backward scattered peak intensity. Increasing the flocculant concentration increases coagulation rates and floc strength, increasing the steady state floc size. At 67 ppm flocculant, sedimentation occurs in spite of stirring and the scattered light intensity drops accordingly.

solids fractions. Initially, the degree of flocculation achieved at 350 RPM is significantly greater than at 220 RPM, probably because the flocculant is better distributed at the higher shear rate and more particles are destabilized and able to flocculate. However, the increased shear rate soon works against the process by fragmenting the newly formed flocs and degrading the suspension to smaller particles by effectively reducing the extent of flocculation (as indicated by the rapid increase in scattered intensity after about 15 seconds). This effect is repeated at 500 RPM, only over a shorter time scale and ultimately producing a smaller steady state floc size (larger scattered intensity). *Williams* et al. [12] also observed this type of behavior and overcame it with incremental addition of the flocculant instead of one single addition as used here.

At larger solids fractions, the amount of flocculant used and its method of application becomes even more important. Figure 6 shows the effect of flocculant concentration on flocculation performance at 5% solids and 350 RPM. Increasing the flocculant concentration from 20 ppm to 40 ppm significantly increases the flocculation performance, a larger steady state floc size is produced as a result of the increased floc strength and thus resistance to fragmentation. Further increasing the flocculant concentration to 67 ppm produced a startling result, rapid floc formation followed by almost instantaneous floc sedimentation. This flocculant concentration is clearly the optimal amount of flocculation as the flocs settled immediately despite the rapid stirring. This effect was also captured by the light scattering measurements, in Figure 6 the rapid settling is indicated by the rapid drop in scattered intensity to a value of 0, followed by an increase as the flocs fragmented in the shear field around the bottom-positioned impeller and were re-suspended. The backward scattering technique thus offers a means of monitoring not only the flocculation but also the sedimentation characteristics of a flocculated suspension.

5 Conclusions

A new, simple backward light scattering technique is shown to be effective for monitoring changes in the particle size distribution during flocculation of kaolin with a cationic polymer at high solids fractions (1–10% w/w) in a stirred tank. Measurements of the enhanced backward scattered light intensity indicate that flocculation reduces the total number of particles and increases the average particle size until a steady state is reached between coagulation and fragmentation, exactly as observed at dilute solids fractions. Increasing the impeller speed increases the steady state scattered intensity (decreases steady state average floc size) by increasing the fragmentation rate. Increasing the flocculant concentration decreases the steady state scattered intensity by increasing the floc strength and thus the extent of flocculation. The experimental results were in excellent agreement with literature results using more established commercial instruments, indicating the potential of the technique to monitor bulk changes in suspension properties during dynamic particulate processes like flocculation and sedimentation.

6 Acknowledgments

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7 Symbols and Abbreviations

ϕ solids volume fraction (-)

8 References

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