

# The Shear Degradation of High-Molecular-Weight Flocculant Solutions

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## SYNOPSIS

Solutions of polyacrylamide and poly(acrylamide-co-sodium acrylate) flocculants with varying molecular weights were shear degraded under a range of mixing conditions. The viscosity and flocculant activity of the solutions generally decreased with time to limiting values dependent on the mixing intensity. The activity of 10 and 20% anionic flocculants displayed quite different trends from those for nonionic flocculants of equivalent molecular weight, with less apparent degradation due to mixing, particularly at low dosages. However, viscosity measurements on sheared solutions diluted with a salt buffer suggest that nonionic and anionic flocculants with similar initial molecular weights were degraded to the same degree. Multiangle laser light-scattering measurements were used to confirm that the shearing process resulted in a reduction in molecular weight which was independent of anionic character. The apparent shear resistance of anionic flocculants observed from activity measurements was attributed to different flocculation mechanisms for the nonionic and anionic flocculants. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Long chain polymers used in industrial flocculation processes may be subjected to considerable shear forces, either from pumping to unit operations or from the high degree of turbulence experienced during the mixing of the flocculant with the substrate suspension. The degradation of polymers under conditions of high stress is well known.<sup>1</sup> The efficiency of flocculation is dependent on the molecular weight and size of the flocculant molecules in solution, and it is therefore important to ensure that any shear degradation is minimized.

The most common commercial flocculants are based on variable proportions of acrylamide and acrylic acid (sodium or ammonium salts) monomer units, as shown in Figure 1. Homopolymers consisting of only acrylamide units ( $y = 0$ ) are termed nonionic flocculants, while those with both monomer

units are anionic in character. Cationic monomer units may also be incorporated.

The degradation of polyacrylamide solutions under controlled agitation has been examined by a number of groups.<sup>2-9</sup> Nagashiro and Tsunoda<sup>4</sup> found that high-speed stirring of polyacrylamide solutions caused the viscosity to decrease initially, then reach a lower constant value which depended on the stirring speed. The lower viscosity was attributed to a reduction in molecular weight. Similar results were obtained by Nakano and Minoura<sup>5</sup> for solutions of polyacrylic acid and sodium polyacrylate in pure water. They also noted that sodium polyacrylate solutions appear to be degraded further than those of polyacrylic acid, suggesting that the expanded (more rigid) polymer chains were more readily ruptured.

Raising the degree of polymer anionic character leads to an increase in the solution shear stress developed during agitation. Surprisingly, Henderson and Wheatley<sup>8</sup> observed that resistance to shear degradation increased as the anionic charge was increased from 7 to 32%, suggesting that the extended conformation of the anionic polymer gives greater protection from breakage than the coiled confor-

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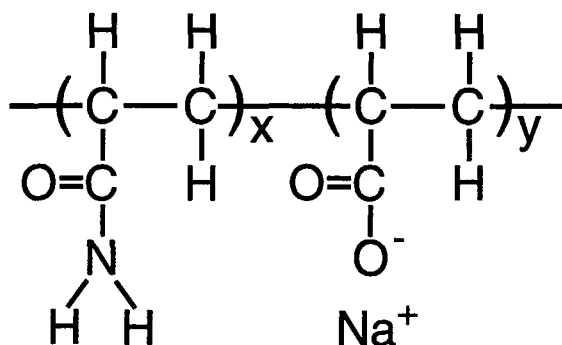


Figure 1 Poly(acrylamide-co-sodium acrylate).

mation of the uncharged polymer. This was in conflict with results obtained in solutions of high ionic strength, where the more coiled conformation reduced degradation.

Several authors have also examined the flocculant activity of polymer solutions after shear degradation. Sylvester and Toure<sup>6</sup> sheared dilute solutions of several nonionic, anionic, and cationic flocculants over fixed periods of time at one agitation intensity. The viscosity and flocculation activity of the solutions were then determined with kaolin suspensions. In each case, shearing led to a continuous decrease in reduced viscosity ( $\eta_{red}$ ), indicating polymer degradation. The reductions in viscosity over 24 h ranged from 19 to 81% but did not appear to be related to ionic character. Flocculation effectiveness decreased with increasing shear time, although the optimal dosage for each polymer only shifted slightly. Rupture of the longer chain polymers to shorter chains was thought to reduce the probability of particle bridging. Henderson and Wheatley<sup>8</sup> found that the reduction in viscosity for sheared solutions coincided with a drop of 70–80% in flocculation activity with coal tailings. A good relationship was achieved between  $\log(\text{settling rate})$  and polymer intrinsic viscosity, independent of the polymer anionic charge. No such relationship was obtained with kaolin, for which the polymer charge had a greater effect.

While these studies report similar general trends for the shear degradation of polyacrylamides, there is some confusion as to whether anionic polymers are subject to a higher or lower degree of degradation than nonionic polymers. The effect of shear degradation on flocculant activity is also not fully understood. The purpose of this study is, therefore, to establish relationships between viscosity and flocculant activity for solutions of flocculants of known molecular weight and anionic character which have been subjected to controlled agitation.

## EXPERIMENTAL

A range of powder flocculants, with three different molecular weights (13, 17.5, and  $24 \times 10^6$  Da) and three different degrees of anionic character (0, 10, and 20%), were obtained from one manufacturer. For reasons of commercial sensitivity, in this study, these flocculants are described only by the codes given in Table I.

Aqueous stock solutions (0.5 wt %) of the flocculants were prepared with ethanol as a wetting agent (1.0 wt % of the final solution mass). Gentle agitation was applied to these solutions for 3 h, after which they were stored in the dark for 3 days to ensure complete dissolution. Stock solutions were diluted to 0.01 wt % immediately prior to all experiments.

An Ubbelohde capillary viscometer (No. 75) was used to measure dilute polymer solution viscosities at 30°C. The procedures for the use of such viscometers and the calculation of viscosities have been described in detail elsewhere.<sup>10,11</sup>

The activity of flocculant solutions was determined by batch settling tests (cylinder tests) conducted with tailings from the Argyle Diamonds Mine (Western Australia). These tailings were an aqueous suspension of mainly quartz, feldspar, hematite, goethite, and montmorillonite. The solids were nominally  $<100 \mu\text{m}$  in size, with a  $d_{50}$  of  $\sim 11 \mu\text{m}$  and a density of  $\sim 2.5 \text{ g cm}^{-3}$ . Concentrated tailings ( $\sim 30 \text{ wt } \%$ ) were diluted to 6 wt % with a synthetic process liquor ( $0.096 \text{ g L}^{-1} \text{ MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $0.076 \text{ g L}^{-1} \text{ MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $0.061 \text{ g L}^{-1} \text{ CaCl}_2 \cdot 2\text{H}_2\text{O}$ , and  $0.168 \text{ g L}^{-1} \text{ NaHCO}_3$ ; pH 8.1). The diluted tailings were stirred for 30 min prior to use. Argyle tailings were found to give highly reproducible results over extended periods.

Table I Properties of the Commercial Flocculants Studied

Flocculant Code	% Anionic Character	Nominal Molecular Weight ( $\times 10^6$ Da)
13M-N	0	13
13M-10A	10	13
13M-20A	20	13
17M-N	0	17.5
17M-10A	10	17.5
17M-20A	20	17.5
24M-N	0	24
24M-10A	10	24
24M-20A	20	24

Cylinder tests were conducted with stoppered 100 mL graduated cylinders with plastic removable bases (Fortuna NS 24/29). A peristaltic pump was used to transfer 50 mL of the tailings slurry to a graduated cylinder from an 8 L bulk sample. Deionized water was then added to a predetermined volume so that with the addition of flocculant, the final volume would be 100 mL. The cylinder was stoppered, and its base was removed and then placed in the cylinder rotator (Fig. 2). The rotator was driven by a reducing gearbox connected by a flexible drive to a variable speed mixer and was set to rotate at 30 rpm. After five inversions, the cylinder was adjusted to the vertical position and the required mass of dilute flocculant solution was added through an appropriate syringe. Immediately after flocculant addition, the cylinder was stoppered and rotation recommenced. After the required number of inversion cycles, the cylinder was again returned to the vertical position and the rate of fall of the mudline was followed. The hindered settling rate was taken as the initial linear slope of a plot of the mudline height against time. Turbidity measurements were made on the supernatant from each cylinder test 10 min after mixing commenced with a Hach Ratio/XR turbidimeter. The concentration of flocculant in the cylinder test suspension is reported as a flocculant dosage (grams of flocculant per ton of dry solids).

Flocculant solutions (0.01 wt %, ~ 200 mL) were sheared in a 250 mL pyrex beaker fitted with glass baffles. The baffles were 7 mm wide and 55 mm high, spaced at 60° intervals around a circular frame. Agitation in the range 250–1,500 rpm was provided by an Aldrich Z17143-3 stainless steel impeller controlled by an overhead stirrer. Mixing times ranged from 1 min to 15 h. A plastic lid was fitted to the apparatus to reduce evaporation. With this method of agitation, the extent of degradation, as measured by viscosity, was found to be very reproducible. After shearing,  $\eta_{red}$  was measured and the flocculant activity was determined with 3 wt % Argyle tailings.

Multiangle laser light-scattering (MALLS) measurements were performed on selected flocculant solutions with a Dawn-F photometer (Wyatt Technology Corporation, Santa Barbara, CA) fitted with a helium-neon laser (wavelength, 632.8 nm) and a K5 flow cell. Aqueous solutions for MALLS were made up in high-purity water freshly filtered through a 0.2- $\mu\text{m}$ -pore-size prefilter (Millipore Opticap™) followed by a 0.1- $\mu\text{m}$ -pore-size Durapore membrane (Millipore Millipak®-40). The instrument was calibrated with 0.02- $\mu\text{m}$ -pore-size filtered toluene, and the detectors were normalized with a 0.2- $\mu\text{m}$ -pore-size filtered solution of low-molecular-weight dex-

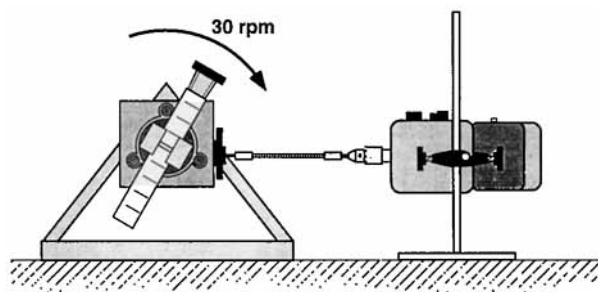


Figure 2 Cylinder rotator used in cylinder settling tests.

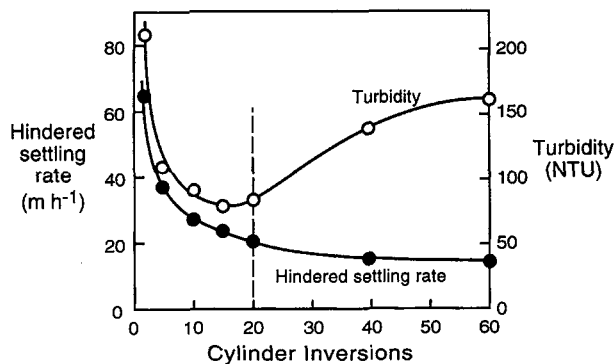
tran (T10, Pharmacia). Flocculant solutions were diluted with an equal volume of 1.0 M NaCl (58.44 g L<sup>-1</sup>), with all subsequent dilutions made with 0.5 M NaCl. Samples of each dilution were then injected into the Dawn-F flow cell after passing through a 3.0- $\mu\text{m}$ -pore-size membrane filter (Versapor®, Gelman Sciences, Ann Arbor, MI). A syringe pump was used to provide a constant flow rate (~ 0.2 mL min<sup>-1</sup>). MALLS was used to determine the relative change in the weight-average molecular weights ( $M_w$ ) of flocculants before and after shearing. Appropriate literature values for the specific refractive index increment of the polymers were used.<sup>12,13</sup> Four dilutions in the range  $5 \times 10^{-6}$ – $2.2 \times 10^{-5}$  g mL<sup>-1</sup> were used, with the MALLS data being analyzed by the Debye method<sup>14</sup> with the DAWN® software from Wyatt Technology.

## RESULTS AND DISCUSSION

### Optimizing Flocculation Conditions

Cylinder tests are used routinely as a laboratory method for evaluating flocculant activity.<sup>8,15,16</sup> The mixing of flocculant and slurry is generally achieved through repeated manual inversion of the cylinder or with the use of a plunger. However, such mixing can be difficult to reproduce, being very dependent on the operator. The use of a mechanically driven mixing apparatus, such as that shown in Figure 2, substantially improves the reproducibility of flocculation achieved by cylinder inversion.

The optimal conditions for flocculation were established by choosing a fixed flocculant dosage and varying the number of inversions, as shown in Figure 3 for the nonionic flocculant 24M-N. At a low number of inversions, the hindered settling rate was high because of the formation of large aggregates, but inadequate flocculant dispersion resulted in poor fines capture and a high supernatant turbidity. The hindered settling rate decreased to an almost con-



**Figure 3** Effect of number of cylinder inversions on the activity of flocculant 24M-N (dosage, 114 g t<sup>-1</sup>).

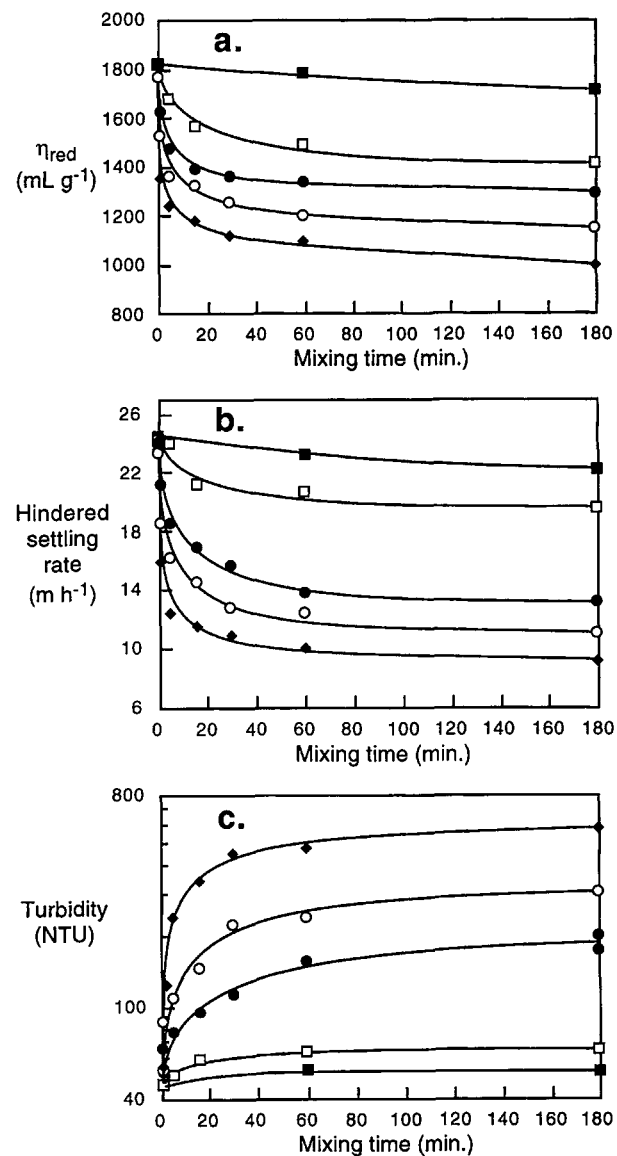
stant value after 40 inversions, reflecting a reduction in aggregate size to one stable under the applied shear conditions. In contrast, the turbidity curve displayed a minimum between 10 and 20 inversions, suggesting there is an optimal level of mixing to achieve maximum fines capture, with any additional inversions leading only to an increase in fines due to aggregate rupture. For all subsequent cylinder tests, 20 inversions were used as the standard mixing conditions. Replicate experiments produced results generally varying by less than  $\pm 5\%$  for both hindered settling rates and supernatant turbidity.

### Flocculant Shearing

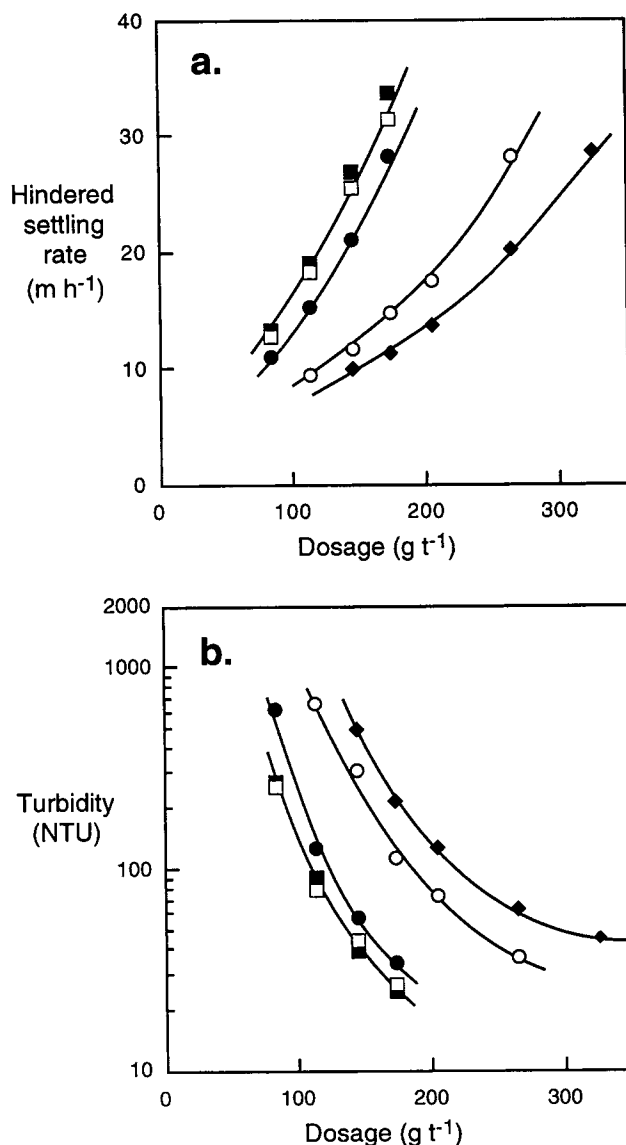
Figure 4 shows the effect of mixing rate and time on the viscosity and flocculant activity of the non-ionic polyacrylamide 17M-N. Flocculant solution viscosity was found to decrease rapidly during the first few minutes of agitation. In most cases, an essentially constant viscosity was achieved after about 60 min, the magnitude being dependent on the stirring speed. Extended agitation up to 15 h produced little additional change in solution viscosity (<5%). Limiting viscosities have been observed in previous studies<sup>4,8</sup> and have been related to reaching a critical molecular weight below which the surviving polymer chains will not degrade further under the magnitude of the applied shear conditions.<sup>17</sup> The viscosity of a solution of 24M-N agitated for 1 h at 1,500 rpm remained relatively low when aged without further shear over a 30 day period. The absence of any observed "relaxational" effect confirms chain rupture rather than conformation changes as the cause of the decreased solution viscosity.

The loss in viscosity as the polymer molecules were sheared was reflected by a corresponding loss in flocculant activity, as shown by the hindered settling rate and turbidity results from cylinder tests

[Fig. 4(b) and (c)]. Hindered settling rates measured with the sheared solutions show similar trends to  $\eta_{red}$ , reflecting a diminished capacity for polymer bridging at lower molecular weights and presumably a lower aggregate size. The effect of shear on activity was most visible in supernatant turbidity measurements, which rose sharply during the initial stages of flocculant solution agitation (within 5 min). Limiting turbidity values ranged from  $\sim 50$  NTU at 250 rpm to 600 NTU at 1,500 rpm. The higher sensitivity of turbidity to shear degradation suggests that a reduction in molecular weight may have a



**Figure 4** The effect of mixing rate and time on flocculant degradation by agitation in baffled beakers. Mixing rates: (■) 250, (□) 500, (●) 750, (○) 1,000, and (◆) 1,500 rpm. Flocculant 17M-N: dosage, 135 g t<sup>-1</sup> in (b) and (c).



**Figure 5** Dosage curves obtained for solutions of the flocculant 17M-N degraded by agitation in baffled beakers. Mixing rates: (□) 250, (●) 500, (○) 1,000, and (◆) 1,500 rpm, 3 h of agitation; (■) unsheared solution. (a) Hindered settling rate and (b) turbidity measured with Argyle tailings.

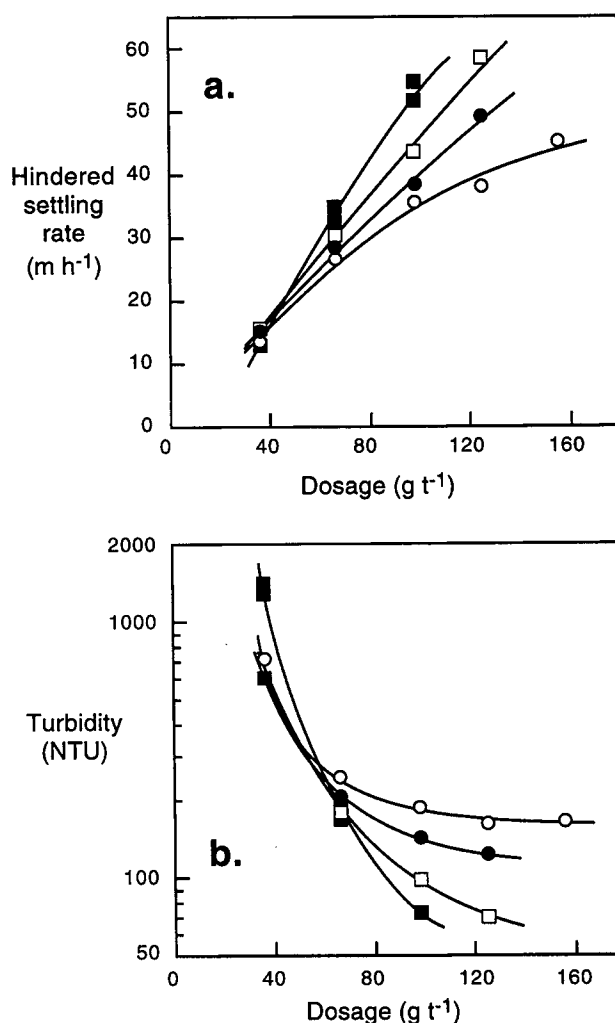
greater effect on fines capture than on aggregate size and density.

### Dosage Curves

The results in Figure 4 show the effect of shear on flocculant activity at a fixed dosage. In their assessment of the flocculant activity of sheared solutions, Henderson and Wheatley<sup>8</sup> used a fixed flocculant

dosage for polymers covering a range of anionic charge. However, studying only one dosage may not give a true indication of the flocculant activity and resistance to shear degradation.

To give a clearer indication of flocculant performance, hindered settling rates and supernatant turbidities were measured as a function of flocculant dosage for sheared and unsheared solutions (Figs. 5 and 6). Limiting values of viscosity and flocculant activity were generally achieved after 3 h of agitation, so this was taken as the standard mixing time for solutions used to prepare dosage curves. Figure 5 shows dosage curves obtained for flocculant 17M-N, which were typical of the nonionic poly-



**Figure 6** Dosage curves obtained for solutions of the anionic flocculant 24M-10A degraded by agitation in baffled beakers. Mixing rates: (□) 750, (●) 1,000, and (○) 1,500 rpm, 3 h of agitation; (■) unsheared solution. (a) Hindered settling rate and (b) turbidity measured with Argyle tailings.

acrylamides studied. For the unsheared solution, the hindered settling rate rose rapidly as the dosage was increased in the range 80–180 g t<sup>-1</sup>. A similar curve was obtained for the solution sheared at 250 rpm, but slightly higher dosages were required to reach the same settling rate. This effect became more obvious as the mixing rate to which the flocculant solution was exposed increased, reflecting the greater difficulty in forming quickly settling aggregates with sheared polymer. The dosage required to achieve a settling rate of 20 m h<sup>-1</sup> with a solution degraded at 1,500 rpm was more than twice that for the un-sheared solution.

Because of the high sensitivity of turbidity measurements to flocculant shear, a logarithmic scale was required when plotting such measurements as a function of dosage [Fig. 5(b)]. The trends exhibited in turbidity closely mirror those for hindered settling rate, with similar effects on the dosages required to maintain a constant turbidity.

The hindered settling rates and turbidities achieved with different dosages of sheared solutions of flocculant 24M-10A are shown in Figure 6. These curves, typical of those obtained with all anionic flocculants, show quite different trends from those exhibited by nonionic flocculants. The degradation due to mixing appears to be much less, particularly at low dosages. In fact, the turbidity curves indicate an improved flocculant performance for sheared solutions at the lowest dosage studied. At higher dosages, the activity of the sheared solutions drops below that of the un-sheared to an extent dependent on the intensity of mixing, although never to the same magnitude as the nonionic flocculants.

This behavior is summarized in Table II, which shows the effect of shear on the dosages required to achieve selected hindered settling rates and turbidities for a range of flocculants. For the nonionic flocculants, the applied shear generally caused these dosages to more than double. However, for flocculants with anionic character, the effect was much smaller. In the case of flocculant 17M-20A, the dosage required to give a hindered settling rate of 20 m h<sup>-1</sup> remained unchanged after shearing, while that to give a turbidity of 200 NTU dropped by 21%.

### Solution Viscosity

The results shown in Table II appear to support the claim by Henderson and Wheatley<sup>8</sup> that resistance to shear degradation increases with increasing anionic character. A similar trend may be seen in the viscosities measured before and after shearing. The values of  $\eta_{red}$  measured in water displayed a large

drop after shear for the nonionic flocculants, but much smaller drops for the anionic polymers of the same molecular weight (Table III).

The high viscosities observed with anionic flocculants are thought to be a result of charge repulsions along the polyelectrolyte chain, favoring an expanded or extended chain conformation.<sup>18</sup> It was thought that the higher shear stresses developed on these more viscous solutions may in fact lead to greater degradation. A clearer indication of the extent of degradation was obtained by diluting the sheared solutions into 0.1M NaCl, eliminating the polyelectrolyte effect, and allowing the flocculants to take a more coiled conformation. As expected, the addition of salt had little or no effect on the relative change in viscosity for the nonionic flocculants. However, for the anionic flocculants, the viscosity changes were substantial. From Table III, it can be seen that flocculants of the same initial molecular weight exhibited very similar viscosity changes after shear when measured in 0.1M NaCl, indicating that the extent of degradation was independent of anionic character. The exception to this was the  $24 \times 10^6$  molecular weight series, for which the changes in  $\eta_{red}$  measured in salt suggested a higher degree of degradation for the anionic flocculants compared with the nonionic. Solutions of these anionic flocculants were very viscous, and these results may reflect the higher shear stresses developed during agitation.

### MALLS

To confirm that significant molecular weight degradation was resulting from shearing, MALLS was performed on the  $17.5 \times 10^6$  molecular weight series flocculants. Light-scattering measurements are highly sensitive to particulate contamination, and so, the solutions for these shearing experiments were prepared with extensively filtered high-purity water. Dust particles which may be present in the commercial flocculants can be removed from solution with appropriate membrane filters, where the pore size is sufficiently fine to trap the dust particles but not retain the polymer molecules. The smallest pore size membrane which could be used to filter out the majority of the contaminant solid impurities without retaining dissolved flocculant was found to be 3.0  $\mu\text{m}$ . The effect of any remaining dust contamination was largely eliminated by slowly injecting the flocculant solutions through the flow cell and using only the scans showing the lowest scattering intensity from those taken over a 10 to 20 min period.

**Table II Effect of Anionic Character and Shear Degradation on the Activity of Flocculant Solutions (0.01 wt %, 3 h Agitation)**

Flocculant	Mixing Speed (rpm)	Hindered Settling Rate		Turbidity	
		Dosage <sub>SR20</sub> <sup>a</sup>	% Change from Unsheared	Dosage <sub>T200</sub> <sup>b</sup>	% Change from Unsheared
13M-N	0	122	—	99	—
	500	154	27	124	25
	1000	213	75	161	63
	1500	270	122	197	99
13M-10A	0	43	—	60	—
	1000	51	18	65	8
	1500	55	27	75	26
13M-20A	0	41	—	53	—
	1000	41	0	40	-24
	1500	44	7	45	-16
17M-N	0	123	—	91	—
	500	143	17	103	13
	1000	221	79	152	67
	1500	267	117	178	95
17M-10A	0	38	—	53	—
	1000	42	11	58	10
	1500	48	26	66	26
17M-20A	0	35	—	52	—
	1000	35	0	38	-27
	1500	35	0	41	-21
24M-N	0	102	—	86	—
	500	117	15	105	22
	1000	189	86	150	75
	1500	253	148	180	111
24M-10A	0	46	—	64	—
	1000	48	6	73	14
	1500	48	6	89	38
24M-20A	0	47	—	72	—
	1000	36	-24	43	-40
	1500	39	-17	51	-29

<sup>a</sup> Dosage required to give a hindered settling rate of 20 m h<sup>-1</sup>.

<sup>b</sup> Dosage required to give a turbidity of 200 NTU.

Figure 7 shows the angular dependence for the scattering obtained from one dilution of a solution of flocculant 17M-10A before and after agitation for 3 h at 1,500 rpm. The drop in scattering intensity after shearing is significant, indicating a reduction in  $\bar{M}_w$  and confirming the results from viscosity measurements in salt solution. MALLS measurements for the three 17M samples show that the percent decrease in molecular weight was independent of the flocculant's anionic character (Table III), again consistent with the viscosity results.

A more complete understanding of the effect of shear may be achieved by studying the molecular weight distributions of the flocculant solutions. The

measurement of  $\bar{M}_w$  alone may, to some extent, mask changes at the high end of the distribution, where shear is most likely to have an effect. A technique for determining the molecular weight distributions of high-molecular-weight flocculants is currently being developed.

### Effect of Molecular Weight

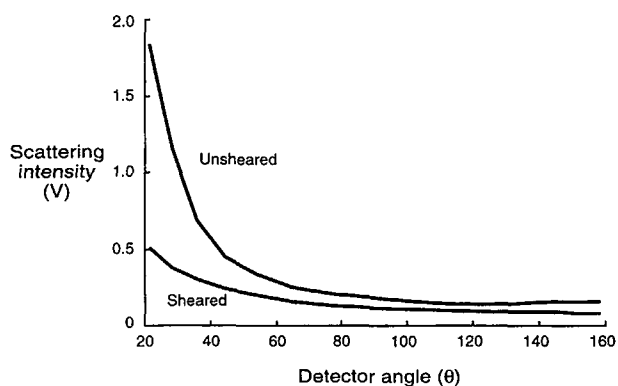
The apparent resistance of anionic flocculants to shear suggested by the performance data, as shown in Table II, can be explained in terms of a different adsorption mechanism for anionic flocculants compared with their nonionic equivalents. For substrates

**Table III** Effect of Shear Degradation on the Viscosity and  $\bar{M}_w$  of Flocculant Solutions (0.01 wt %, 3 h Agitation)

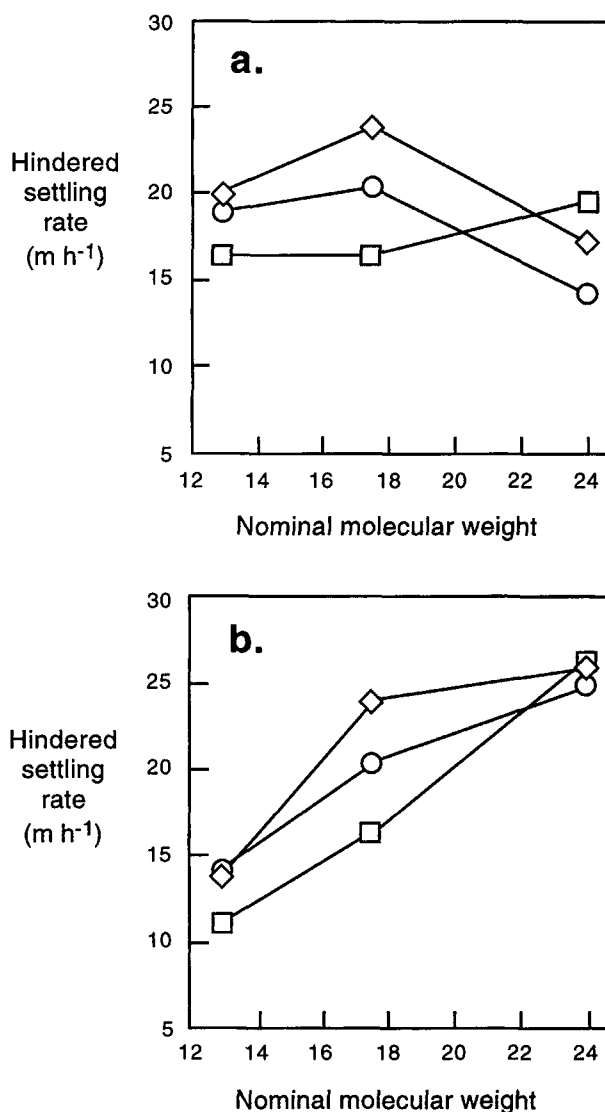
Flocculant	% Decrease from Unsheared Solution for:		
	$\eta_{red}$ (Water)	$\eta_{red}$ (0.1 M NaCl) <sup>a</sup>	$\bar{M}_w$ from MALLS
13M-N	34.2	33.7	—
13M-10A	8.0	29.4	—
13M-20A	14.8	26.8	—
17M-N	39.4	40.6	39
17M-10A	11.6	42.3	45
17M-20A	16.2	41.3	44
24M-N	48.2	53.0	—
24M-10A	21.3	62.8	—
24M-20A	40.1	63.0	—

<sup>a</sup> Sheared and unsheared flocculant solutions diluted with equal volumes of 0.2M NaCl.

where flocculation occurs by a polymer-bridging mechanism, the increased molecular weight of linear polymer flocculants generally leads to improved performance.<sup>18</sup> This is not readily apparent from Figure 8(a), which shows the performance (in terms of hindered settling rate) for 0, 10, and 20% anionic flocculants with different molecular weights at a constant polymer dosage. A slight increase in the hindered settling rate was seen for the nonionic flocculants, while for the 10 and 20% anionic flocculants, increasing the molecular weight from  $17.5 \times 10^6$  to  $24 \times 10^6$  gave a significant drop in settling rate. However, it should be noted that, by keeping the polymer dosage constant, increasing the



**Figure 7** The effect of agitation in a baffled beaker (1,500 rpm, 3 h) on light scattering from a solution of anionic flocculant 17M-10A. Dilution to  $1 \times 10^{-5}$  g mL<sup>-1</sup> in 0.5M NaCl.



**Figure 8** The effect of molecular weight on hindered settling rates measured with Argyle tailings for (□) nonionic, (○) 10% anionic, and (◇) 20% anionic flocculants. (a) Constant dosages: nonionic flocculants,  $100 \text{ g t}^{-1}$ ; anionic flocculants,  $40 \text{ g t}^{-1}$ . (b) Constant number of flocculant molecules [dosages for the  $17.5 \times 10^6$  flocculants, as shown for (a)].

molecular weight leads to a reduced number of flocculant molecules in solution.

By assuming that the molecular weights of all of the flocculant molecules are close to their nominal values, given in Table I, an approximation to the actual number of molecules in solution can be calculated and used to determine the flocculant dosages required to provide a constant number of molecules in solution. Flocculant molecules do not have such narrow molecular weight distributions, but this approximation serves to demonstrate the effect of mo-



lecular weight on activity. Figure 8(b) shows the hindered settling rates achieved with the same number of flocculant molecules for 0, 10 and 20% anionic flocculants. These results suggest that increased molecular weight does improve flocculant performance on a per-molecule basis. For the non-ionic flocculants, this dependence is almost linear, while for the 20% anionic flocculants, there is only a slight increase in hindered settling rate on going from the  $17.5 \times 10^6$  to the  $24 \times 10^6$  molecular weight flocculant.

This effect can be viewed in terms of differences in the way the uncharged and charged polymers are adsorbed on the substrate surface.<sup>19-21</sup> For nonionic polymers, the thickness of the adsorbed flocculant layer shows a strong correlation with molecular weight, because of the significant fraction of the polymer chain present as loops and tails at all but the lowest polymer concentrations. However, for anionic polymers, electrostatic repulsions between chain units prevent the formation of thick adsorbed layers, and as a consequence, they tend to adsorb in a flat conformation.<sup>19</sup> At low ionic strengths, the layer thickness for anionic flocculants therefore exhibits little dependence on molecular weight. At higher ionic strengths, the behavior of the anionic flocculants may be expected to approach that of the uncharged polymer. The synthetic process liquor used in these experiments contained low levels of salts, which may explain the degree of molecular weight dependence shown by anionic flocculants with Argyle tailings [Fig. 8(b)].

These arguments may be used to explain the behavior shown in Figures 5 and 6. The performance of the nonionic flocculant decreased as mixing rates were increased (Fig. 5), indicative of the dependence of flocculant activity on the molecular weight of the sheared polymer fragments. For an anionic flocculant at low dosages (Fig. 6), the variation of hindered settling rate and turbidity with molecular weight was much smaller—in some cases, performance improved with shearing, possibly because of an increase in the actual number of flocculant molecules in solution.

Lyklema and Fleer<sup>20</sup> have suggested that charged polymers may act electrostatically rather than sterically during flocculation. Bridging flocculation may still occur, but because of the relatively low number of short tails, close approach of the surfaces is required for adsorption to occur. While the results obtained in this study clearly suggest that there are differences in the flocculation mechanisms for charged and uncharged polymers, they do not allow any further conclusions to be made.

## CONCLUSIONS

Under reproducible shear conditions, flocculant solution viscosity and activity decreased with increasing shear time to limiting values dependent on the mixing intensity. The absence of relaxational effects indicated that the decreased viscosity was due to chain rupture rather than conformational changes. On the basis of viscosity measurements in salt solutions and molecular weight determinations by MALLS, nonionic and 10 and 20% anionic flocculants of the same molecular weight were degraded to similar extents. However, the assessment of flocculant activity by the use of cylinder tests showed that the performance of anionic flocculants was less affected by shear than was the performance of non-ionic flocculants. This apparent shear resistance of anionic flocculants may be explained in terms of differences in the flocculation mechanisms with charged and uncharged polymers, rather than a reduced degree of chain rupture.

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