

# The Effects of Cationic Polymers on Flocculation of a Coal Thickener Feed in Washery Water as a Function of pH

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**ABSTRACT:** The flocculation of a thickener feed using three cationic polyacrylamide copolymers of high molar mass and different charge densities was studied at three pHs in washery water. The binding capacities were very dependent on pH but only slightly dependent on the polymeric charge density. The reverse was true for the settling rates. At pH 7, all three polymers were equally effective at clarifying the suspensions, but there were marked differences at pH 4 and 9. For the polymers of highest charge density, reducing the pH increased their effectiveness; for the polymer of lower charge density, changing the pH had little effect on the residual turbidity. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 783–789, 1997

**Key words:** cationic copolymers of polyacrylamide; flocculation; adsorption; turbidity

## INTRODUCTION

Processing and beneficiation operations involving the interaction of coal thickener feed (TF) with polymers are usually geared towards either selectively removing the clean coals from the rest, or towards the removal of the fines, and hence, the recovery of the water. The interactions of the polymers with the solids are dependent on many factors, which are for the most part interactive. The nature of the water that interacts with both solids and polymer, its temperature, pH, and ionic composition influence not only the solids' surfaces but the polymer conformation and, hence, adsorption properties as well.<sup>1</sup> Mixing, shearing by flow, and other mechanical influences in a processing operation are also important. Flocculation becomes a

resultant of all these parameters. In particular, we were interested in the effect of varying the charge density of the polymer, as previous flocculations involving kaolin and cationic polymers have given conflicting results.<sup>2,3</sup> These conflicting results also suggest that factors other than the charge density may be quite critical in determining the nature of the interaction.

This article describes the interactive influence of molecular weight, charge density, and pH on the flocculation of a TF in washery water by three cationic polymers. Polymers were chosen with a wider range of charge densities than had been used previously.<sup>2,3</sup> The flocculations are monitored in terms of settling rate, turbidity, and adsorption.

## EXPERIMENTAL

### Materials

Medium volatile bituminous coal and its associated clays in a TF was obtained from a Western

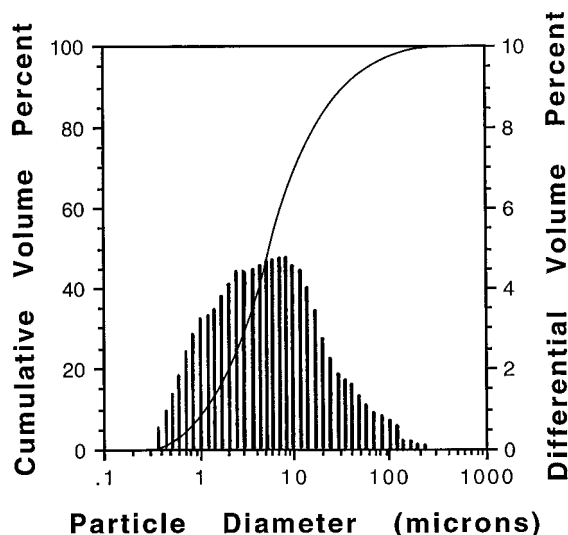
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**Figure 1** Size distribution of thickener feed solids suspended in 10% sodium hexametaphosphate as determined on a Microtrac FRA system. Differential volume percent (histogram) and cumulative volume percent (—) are shown as a function of particle diameter.

Canadian washery. The coal was considered to be slightly oxidized. Size distribution measurements were done on a Microtrac FRA (full range particle analyser) system (Leeds and Northrop, Florida), which was equipped with both low- and high-angle optics for light scattering and used a Helium neon laser source. The particles were sampled into 10% sodium hexametaphosphate solutions, sonicated for 3 min using a Branson bath sonicator for dispersing into discrete particles, and then the size distribution was determined using the small-volume recirculator cell and deionized water as the carrier fluid in continuous measurements of the populations. The instrument's detection range includes particles of diameters from 0.1 micron to 700 microns. Three runs were averaged and the average distribution is presented in a histogram (Fig. 1) showing the differential volume percent of particles plotted on the Y axis and diameter in microns on the X axis. Along side this data is the cumulative volume percent plotted on the second Y axis. The surface area was determined using the absorption of methylene blue.<sup>4</sup> Using a value of  $1.20 \text{ nm}^2$  for the flat molecular area of methylene blue, the surface area of the TFS was calculated to be  $40.2 \text{ m}^2 \cdot \text{g}^{-1}$ .

The solids content was determined by filtration through a membrane filter (millipore type RA,  $1.2 \mu\text{m}$ ) followed by drying ( $100^\circ\text{C}$ ) to constant weight. The ash content of the solids, determined

after ashing at  $750^\circ\text{C}$  for 1.5 h in platinum crucibles, was 46%, suggesting the presence of a considerable amount of clay.

On a larger scale, coal solids were separated by decanting the supernatant from 20 L buckets of thickener feed, first after normal settling and then after centrifugation at  $5000 \times g$ . Subsequent vacuum drying for approximately 24 h yielded a free-flowing powder with a moisture content of 7.8% (dried at  $105^\circ\text{C}$ ), which was stored at  $-20^\circ\text{C}$ . The supernatant liquid was filtered. Its pH was 8.1 and its ionic content was determined by ion chromatography on a Dionex System 12 Analyzer, and atomic absorption on a Varian 475 A.A. Spectrometer, to be as shown in Table I.

To prepare slurries for flocculation experiments, appropriate amounts of thickener feed solids (TFS) were suspended in TF supernatant with vigorous stirring and shaking for 1 h before settling rates were to be measured. The unadjusted pH of the slurries was 7.9.

Polymers were obtained from Stockhausen as follows: molecular weight 6 million and 90% charge density, referred to as C906M; MW 5 million and 50% charge density referred to as C505M; and MW 8 million and 25% charge density referred to as C258M. They are copolymers of acrylamide and 2-trimethylammonioethyl acrylate chloride.

Buffers used for pH standardization were ACS grade.

## Methods

All experiments were conducted at pH 4.0, 7.0, and 9.0 in washery water. Settling rate tests were conducted according to the conventional International Standard Organization in 100 mL measuring cylinders. After 5 end-to-end inversions, the movement of the sedimentation boundary was measured as a function of time. Polymer adsorption and supernatant turbidity were determined after 1 h.

Turbidities were measured with a Hach model 2100A Turbidimeter and are reported in NTU units.

Adsorption of the polymers was determined by the difference method, with polarographic maximum suppression of the  $\text{Hg}^{++}$  maximum<sup>5</sup> being used to determine the residual polymer concentration as follows: samples were centrifuged to remove suspended solids where necessary and then were chromatographed before analysis because of the presence of maximum suppressors

**Table I** Composition of Thickener Feed Filtrate

Ion	ppm	mM	Method of Determination
Na <sup>+</sup>	65.3	2.84	Ion Chromatography
K <sup>+</sup>	1.2	0.03	Ion Chromatography
Ca <sup>++</sup>	35.6	0.89	Atomic Absorption
Mg <sup>++</sup>	9.8	0.40	Atomic Absorption
SO <sub>4</sub> <sup>-</sup>	126.0	1.31	Ion Chromatography
NO <sub>3</sub> <sup>-</sup>	12.7	0.20	Ion Chromatography
Cl <sup>-</sup>	3.4	0.10	Ion Chromatography
F <sup>-</sup>	0.4	0.02	Ion Chromatography
Alkalinity	3.4 mequiv/L		Titration

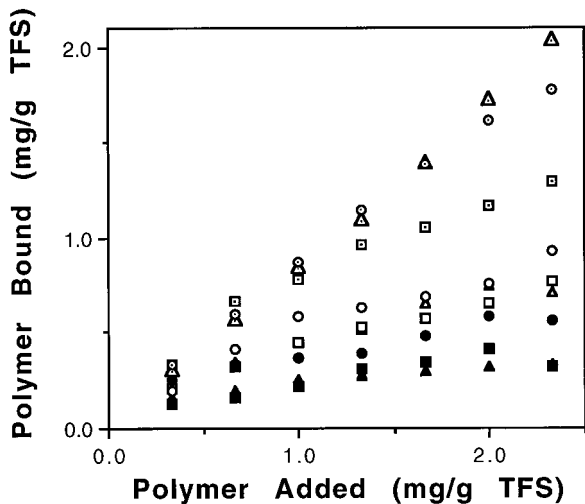
other than those added in the TF supernatant. Anion exchange chromatography was performed using a  $0.5 \times 7$  cm column of Rexyn strong-base anion exchange resin in the chloride form (Fisher Scientific). The resin was first Soxhlet extracted with methanol to remove maximum suppressors, washed with 1M NaCl, and rinsed with water before use. Samples (4.0 mL) were chromatographed and the column then rinsed with 1.0 mL water. To the resulting 5.0 mL sample was added 0.5 mL of a solution containing 2.75M KCl + 0.011M HgCl<sub>2</sub> (Fisher Scientific). The actual polarographic measurement was refined from that reported previously<sup>5</sup> as follows: the potential was held at -200 mV, where the suppression was measured, for the duration of the analysis rather than scanning from 0 V. This ensured that the signal could be seen to have become steady before a reading was taken, and also allowed the signal to be averaged over time if necessary. Standard curves were constructed by spiking the supernatant liquids from blank suspensions (i.e., those not containing added polymer) with polymer solution.

## RESULTS

Initial experiments with TF as obtained from the processing plant indicated that the solids content (1%) was too low to allow a sedimentation boundary to form. In addition, coal is subject to surface oxidation. Thus, the solids were separated from the supernatant, dried, and stored in a freezer. They could then be resuspended in filtered washery water prior to use to give suspensions of any chosen concentration with the same surface properties. Preliminary experiments were performed using C505M to decide on a suitable solids content for the flocculation experiments. Suspensions of

2, 3, and 4% solids had similar polymer binding capacities. A 5% suspension was found to have a slightly higher capacity. Settling rates and specific sedimented solids volume decreased with increasing solids content. High molecular weight polymers have been predicted to form smaller flocs in concentrated suspensions<sup>6</sup> than in dilute suspensions, and because sedimentation rate increases with floc size,<sup>7</sup> lower settling rates are to be expected. Because smaller flocs can pack more closely than larger ones can, they produce a smaller sediment volume.<sup>7</sup> Lower settling rates allow more time for adsorption of polymers onto the surfaces of suspended particles. It was decided that a resuspended solids content of 3% (dry weight) would be used for subsequent experiments.

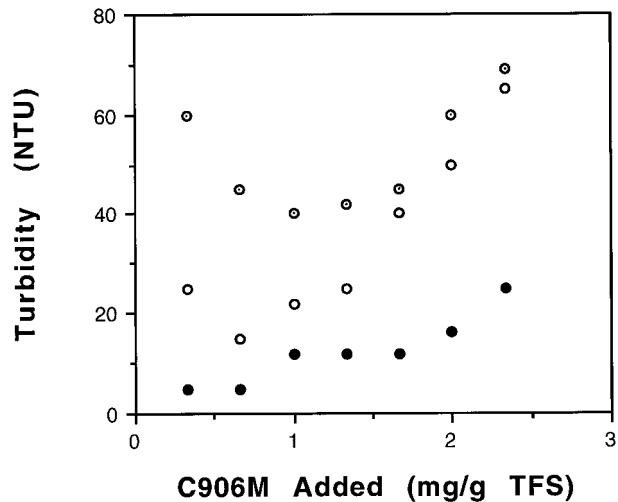
Flocculations were carried out at pHs 4, 7, and 9. The surface charge of the particles would be expected to increase with pH. Particles can approach each other most closely when they are not highly charged so that increasing the surface charge of particles should cause stabilization of a suspension. This is indeed what happens. In the absence of a polymer a suspension let to sit at pH 4 was much less turbid (100 NTU) than one let to sit at a higher pH (2100 NTU at pH 9). Increasing the pH and thus the surface charge also might be expected to allow greater interaction of the particles with positively charged polymers, as was indeed found. Because the functional group on the copolymer is a quaternary ammonium ion, we would not expect changes in the charge density of the polymers between pH 4 and 9. However, the conformation of cationic polymers can vary with ionic strength and pH, even though the charge density stays constant. Mabire et al. have reported that in solutions of ionic strength greater than  $10^{-2}$ M NaCl, these copolymers appear as coiled (as determined by viscometry studies) and



**Figure 2** Bound polymer in 3% suspensions of thickener feed solids in washery water as a function of polymer added for C258M, pH 4 ■; C258M, pH 7 □; C258M, pH 9 □; C505M, pH 4 ▲; C505M, pH 7 △; C505M, pH 9 △; C906M, pH 4 ●; C906M, pH 7 ○; and C906M, pH 9 ○.

positively charged, but that dissociation of chloride ions is complete only when the charge density is less than 30%.<sup>8</sup>

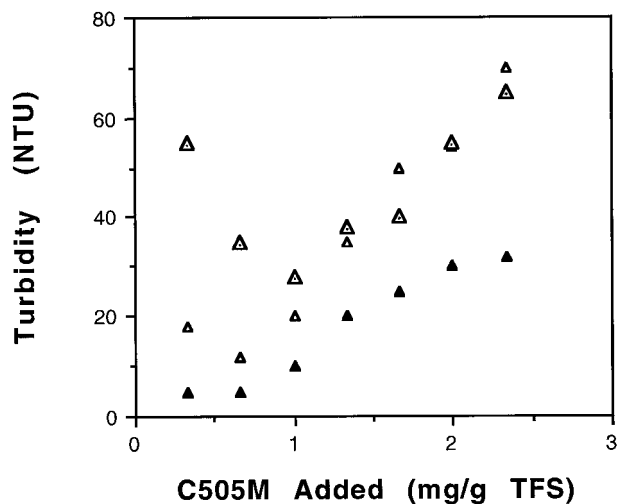
For each polymer, it was observed that the binding capacity increased with pH, with this change in binding capacity being somewhat smaller with C258M, which has the lowest charge density (Fig. 2). At pHs 4 and 7 the binding capacities increased with charge density, but the differences involved were very small. However, at pH 9 the binding capacity of C258M was significantly less than that of the other two polymers. This was an indication that the action of C258M was different than that of the more highly charged polymers. Overall, the pH, and thus the surface charge of the particles involved, was much more important in determining the binding of polymer than was the charge density of the polymer itself. The increased binding of polymer at the higher pHs can be attributed to the increased surface charge and more open chains. If the polymers are binding mostly in trains, very flat to the surface, then approximately the same amount of each should bind. Those of higher charge would cause more neutralization of surface charge and thus produce smaller flocs and lower settling rates. As surface charge increases, more polymers are attracted onto the surface, with the attractive forces between the oppositely charged surface and polymer helping to compensate for the repulsive forces



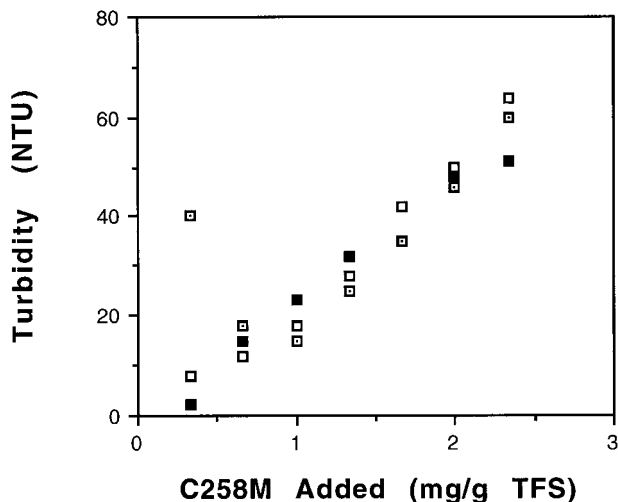
**Figure 3** Turbidity in 3% suspensions of thickener feed solids in washery water as a function of C906M added for pH 4 ●; pH 7 ○; and pH 9 ○.

between charged functional groups. This attractive effect is least with C258M, which is only slightly charged, and this polymer may form more loops and tails than trains.

By comparing Figures 3, 4, and 5, we see that C258M is generally the most effective polymer in terms of reducing the residual turbidity. Note that we have not included zero points (with their very high turbidities) on the figures for turbidity so that we can use a scale where the differences as a function of pH and polymer are readily apparent. At pH 9, a turbidity minimum occurred after



**Figure 4** Turbidity in 3% suspensions of thickener feed solids in washery water as a function of C505M added for pH 4 ▲; pH 7 △; and pH 9 △.



**Figure 5** Turbidity in 3% suspensions of thickener feed solids in washery water as a function of C258M added for pH 4 ■; pH 7 □; and pH 9 □.

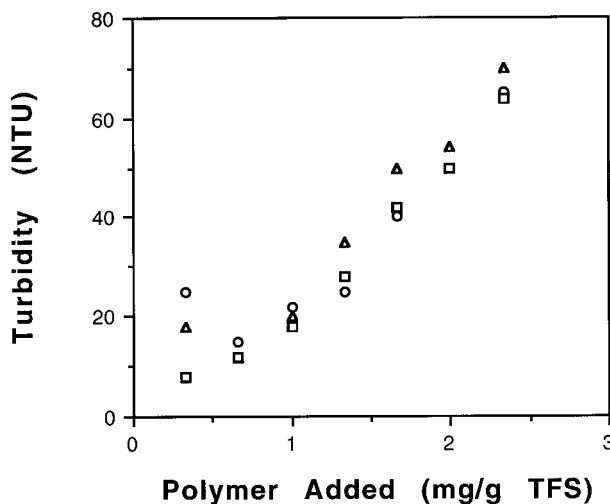
the addition of  $1 \text{ mg} \cdot \text{g}^{-1}$  TFS of any of the polymers. At pH 7, minimum turbidity was achieved with the first addition of C258M, but required  $0.66 \text{ mg} \cdot \text{g}^{-1}$  TFS of either of the other two polymers, while at pH 4, minimum turbidities were achieved after the first addition of any polymer. In general, the actual turbidity values at the minima differed with pH and polymer, decreasing as pH and polymer charge density decreased. However, at pH 7, the residual turbidity was independent of the charge density of the polymer for concentrations of  $0.66 \text{ mg} \cdot \text{g}^{-1}$  TFS or greater (Fig. 6), and with C258M, the effect of pH was very small. For all polymers at all pHs, adding excess polymer increased the turbidity (stabilized the solution). At pH 4, increasing the dose of C505M and C906M did not increase the residual turbidity as much as did increasing the dose of C258M. In fact, at pH 4, at polymer concentrations above  $0.33 \text{ mg} \cdot \text{g}^{-1}$ , C906M was by far the most effective polymer for clarifying the suspension. Even at polymer concentrations of  $0.33 \text{ mg} \cdot \text{g}^{-1}$  or less, C258M was only slightly more effective. Thus, the choice of polymer for a particular flocculation where residual turbidity is important would depend on the conditions that would be present, especially the pH, and whether the concentrations of polymer present could be precisely controlled.

The increase in the polymer concentration required to achieve minimal turbidity as the pH is increased reflects the increased amount of polymer required to neutralise the surface charge. Residual turbidities have also been correlated with

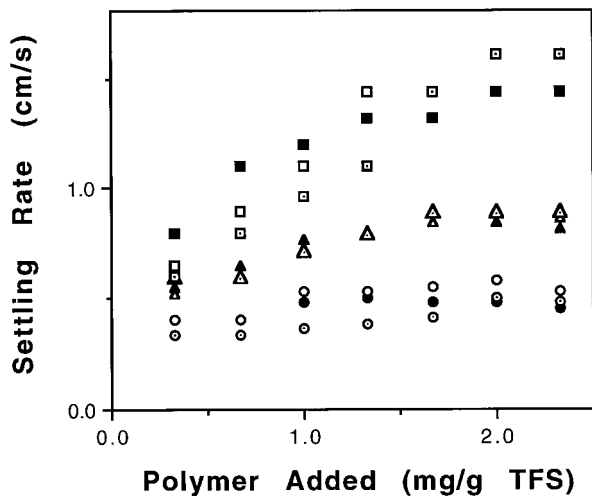
surface charge<sup>9</sup> in other studies. The results agree with our suggestion that C258M initiates flocculation in a different manner than do the more highly charged polymers, as changing the surface charge (pH) had very little effect on the ability of C258M to reduce the turbidity. The fact that a combination of high surface charge and high polymer charge density lead to reduced stabilization of the suspension suggests that the presence of loops and tails around a particle may be more important in suspension stabilization than the presence of charged trains on the particle's surface.

In contrast to turbidity, settling rates were relatively independent of pH, but very dependent on the actual polymer used (Fig. 7). C258M produced much higher settling rates than did the other two polymers. This result can be attributed both to its low charge density and to its high molar mass, and again suggests that a bridging mechanism contributes significantly to the flocculations in which it participates. In looking at the settling rates produced by the other two polymers, the rate decreased as the charge density increased, even though the molar mass also increased. This result suggests that for these two polymers, a charge neutralization mechanism predominates.

Comparing settling rate with the amount of binding (Fig. 8) confirms that C258M is the most efficient polymer of the three, and we must attribute this to its low charge density. Although the highest settling rates were obtained with C258M as flocculant regardless of pH, its binding capacity



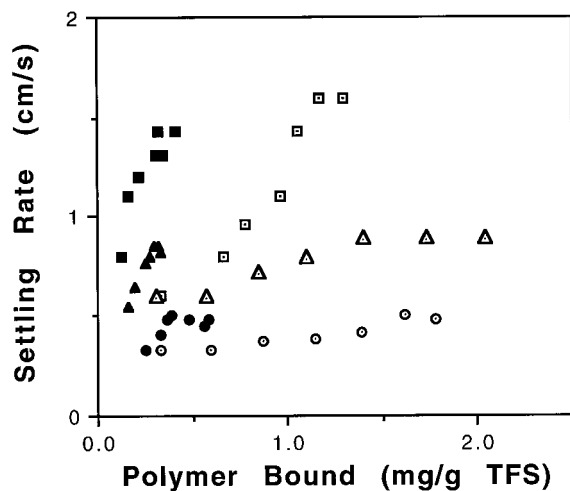
**Figure 6** Turbidity in 3% suspensions of thickener feed solids in washery water at pH 7 as a function of polymer added for C258M □; C505M △; and C906M ○.



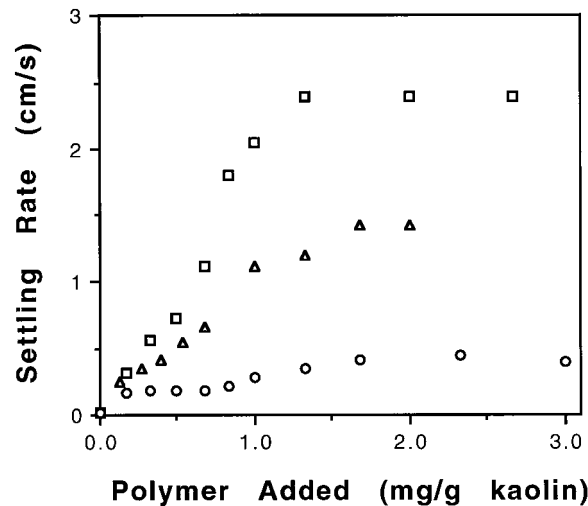
**Figure 7** Settling rates of 3% suspensions of thickener feed solids in washery water as a function of polymer added for C258M, pH 4 ■; C258M, pH 7 □; C258M, pH 9 □; C505M, pH 4 ▲; and C505M, pH 7 △; C505M, pH 9 △; C906M, pH 4 ●; C906M, pH 7, ○; and C906M, pH 9 ○.

was only significantly different from that of the other two polymers when the comparison was made at pH 9. Thus, we conclude that settling rate is not directly related to binding capacity.

Gill and Herrington, in experiments with suspensions of kaolin,<sup>2</sup> concluded from experiments with polymers similar to those used here that charge density was not a deciding factor in how



**Figure 8** Settling rates of 3% suspensions of thickener feed solids in washery water as a function of bound polymer for C258M, pH 4 ■; C258M, pH 9 □; C505M, pH 4 ▲; C505M, pH 9 △; C906M, pH 4 ●; and C906M, pH 9 ○.



**Figure 9** Settling rates of 3% suspensions of kaolin in washery water at pH 7 as a function of polymer added for C258M □; C505M △; and C906M ○.

well cationic polymers of high molar mass produced flocculation. However, Smith-Palmer et al.<sup>3</sup> found some dependence on charge density in comparable flocculations. Thus, we performed flocculation studies on 3% kaolin suspensions in washery water using the three cationic polymers of interest to us. We found a very definite dependence of settling rate on the nature of the polymer used (Fig. 9).

One postulate we have considered previously when bridging is responsible for flocculation is that if the settling rate is fast, the amount of polymer bound should be small. As particles are bound together into flocs by one or several polymers wrapping around them and forming bridges between them, their surfaces are no longer available for further adsorption. The charge density of a polymer should not be of great consequence if a bridging mechanism holds, except to the extent that it can cause extension of a polymer chain allowing better bridge formation. However, it seems that the differences in the charge densities of the polymers in this study are causing large differences in the settling rate, which supports the postulate, that for at least two of the polymers, charge neutralization must play an important role in the flocculation process.

## CONCLUSIONS

1. Settling rates decrease with the charge density of the flocculant, but are little af-

ected by pH. Settling rates depend on the nature of the flocs formed. Larger flocs are generally formed when bridging has occurred. Thus, we suggest that the amount of bridging decreases as the charge density of the polymer (which is independent of pH) increases.

2. More polymer is bound as the pH, and thus, the surface charge of the particles, is increased. This increased amount of polymer is used to neutralize the extra surface charge and does not improve the flocculation (as measured by turbidities or settling rates).
3. The pH was much more important than the nature of the polymer in determining the extent of polymer binding.
4. The residual turbidity was dependent on both the pH and the charge density of the polymer, and thus, the choice of polymer for a flocculation where minimum residual turbidity is critical would differ, depending on the pH, the ability to control polymer concentrations precisely, and whether the rate of settling or the residual turbidities was the most important end result of the flocculation.
5. It would seem that C258M acts predominantly by a bridging mechanism, while charge neutralization plays a much larger

part in flocculations initiated by C505M, and even more so in those involving C906M.

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