

Water-Soluble Acrylamide Copolymers. X. Flocculation Efficiencies of Poly[acrylamide-co-*N,N*-dimethylacrylamide], Poly[acrylamide-co-methacrylamide], Poly[acrylamide-co-*N-t*-butylacrylamide], and Their Cationic Derivatives

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Received 26 March 2001; accepted 17 September 2001

ABSTRACT: A hydrated, 1% by weight Na-kaolinite suspension in deionized water was prepared, completely characterized, and reproducible measures of flocculation efficiency were validated. Flocculation tests of copolymers of acrylamide (AM) with dimethylacrylamide (DMA), methacrylamide (MeAM), or *N-t*-butylacrylamide (NTBAM) with 1% Na-kaolinite suspensions gave average settling rate rates which decreased as the proportion of DMA, MeAM, or NTBAM in the copolymer increased. However, for a similar weight-average molecular weight and slightly lower $\langle r_g \rangle$, the copolymer from DMA-co-AM-3 gave settling rates and supernatant turbidities comparable to similar types of commercial polymers. This new copolymer was also more resistant to changes in pH or the presence of an electrolyte than were the tested commercial polymers. Cationic derivatives of the new copolymers gave lower average settling rates and higher supernatant turbidities than those of Percol 721 (cationic PAM), probably because of their lower charge densities. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2090–2108, 2002; DOI 10.1002/app.10562

Key words: polyamides; copolymerization; solution properties; colloids

INTRODUCTION

Earlier articles in this series described the preparation of a series of polyacrylamides and their

copolymers and cationic derivatives, together with their characterization and solution properties.^{1–4} The objective of these polymer preparations was to produce samples to examine how polymer structures correlated with solution properties and, ultimately, their flocculation efficiencies. Here, we report on the concluding phase of this work, the measurement of flocculation efficiencies and supernatant clarification capabilities of each of these polymers under carefully controlled conditions. The results of these experiments have been correlated as far as possible to the previously reported solution properties of the candidate polymers.

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Contract grant sponsors: Energy Mines and Resources, Devon, Alberta; Government of British Columbia; University of Victoria.

Journal of Applied Polymer Science, Vol. 84, 2090–2108 (2002)
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Flocculation Background

Solid/liquid separations are often required for suspensions of solids in water for applications such as raw and wastewater clarification, sludge dewatering, mineral processing, papermaking, and other industrial processes. Addition of a coagulant or flocculant to these systems can often greatly facilitate this process.⁵⁻⁷

Coagulation refers to the agglomeration of suspended particles by the addition of inorganic flocculants such as the soluble salts of aluminum and iron, and flocculation refers to particle aggregation by the addition of polymeric flocculants, such as polyacrylamides.⁸⁻¹⁰ Synthetic polymeric flocculants are more expensive to use than are coagulants. However, they compensate for this by producing flocs which are larger, stronger, and formed more rapidly to give smaller settled sludge volumes than can be obtained with inorganic coagulants.⁸ They also have an added feature, if it is a waste sludge, and final disposal is by incineration, since polyacrylamides are completely combustible, unlike inorganic coagulants. The end result is a smaller final volume of non-corrosive ash, unlike the highly corrosive ash residue obtained from the incineration of coagulant sludges.

Electrostatic Interactions

Due to the preferential adsorption of certain ionic species, dissociation of surface groups, and isomorphic substitution, aqueous suspensions of colloid particles typically bear a negative charge.^{9,11} The particle is surrounded by an electric double layer which yields a net electroneutrality to the surface charge. In this double layer is the Stern layer of counterions which contains slightly less charge than would achieve complete neutralization of the surface charge. The balance of the surface charge occurs in a diffuse outer layer termed the Gouy–Chapman layer. Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory predicts the observed repulsion between the double layers of colloid particles.^{9,12}

The addition of a polymer to a colloidal dispersion can either stabilize or destabilize it. Stabilization contributes to a positive free energy and, therefore, a repulsion of colloid particles which generally occurs with high concentrations of a polymer and/or the use of a dispersion medium which has a high affinity for the polymer.¹³⁻¹⁵ Destabilization contributes to a negative free en-

ergy of the colloidal dispersion and, therefore, an attraction of the particles of the dispersion causing aggregation. This can be achieved through polymer addition, which increases the susceptibility of the colloid particles to added electrolyte (sensitization) and flocculates the system.^{9,10}

Mechanisms of Polymeric Flocculation

Polymeric flocculants are classified by charge type, charge density, and molecular weight. Anionic and cationic polymers are classed as polyelectrolytes, and nonionic polymers, as nonelectrolytes. High or ultrahigh molecular weight nonionic polymers (10^6 to 5×10^6 or $>5 \times 10^6$ g/mol) and polyelectrolytes having low charge densities function as flocculants by a bridging mechanism.^{8,15} Small segments of the polymer are adsorbed onto colloid particles so as to leave loops or trains of polymer dangling in solution. If these loops are sufficiently extended, and they do not have a high affinity for the dispersion medium, then polymer bridging results.^{8,9}

Polyelectrolytes having low or medium molecular weights, moderate charge densities, and charge types opposite to those of the colloid particles function as flocculants by charge neutralization or the “electrostatic patch mechanism.”^{8,15,16} This occurs when the electrostatic interaction of positively and negatively charged patches on the surface of each particle causes agglomeration.

It is generally accepted that flocculation develops via the interaction of four distinct processes: adsorption, reformation, aggregation, and degradation (Fig. 1).¹⁰ Adsorption of nonionic polymers may occur by hydrophobic association, hydrogen bonding, or dipole–crystal interactions and is generally rapid and irreversible.^{8,17} Orthokinetic flocculation, which involves agitation, increases the rate of collisions relative to polymer adsorption and/or colloid particle aggregation processes which favors bridging flocculation.^{8,17} For this reason, the rate of aggregation or bridging of colloidal particles is affected by agitation. Both the colloid concentration and the agitation rate can affect floc strength and size. An opposing process called degradation can occur, which breaks flocs. Flocs formed via the bridging mechanism are more susceptible to the shearing forces of agitation than are other aggregates and, thus, are most affected by degradation. A more detailed survey of the modern understanding of flocculation theory was recently summarized.¹⁸

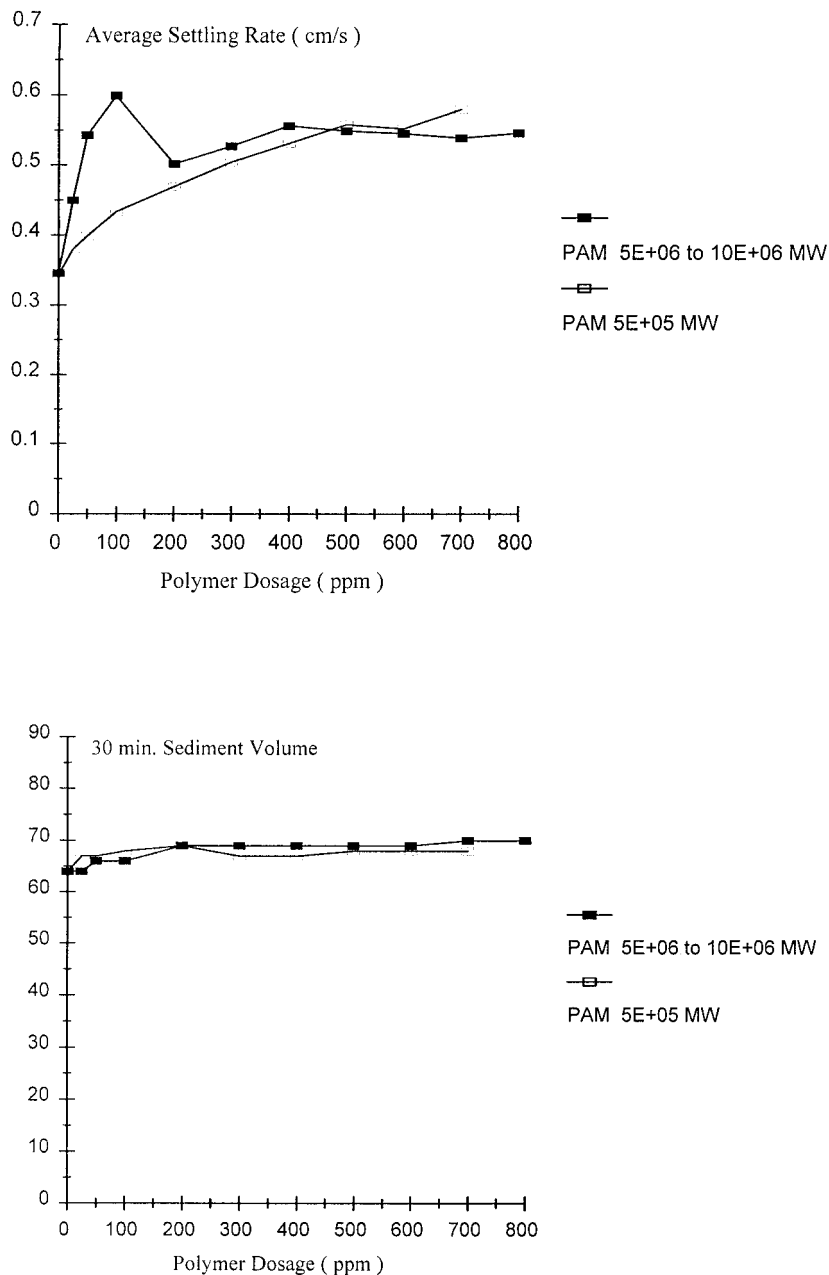


Figure 1 (a) Average settling rate versus polymer dosage for flocculation of 3% Na-kaolinite using PAM (5E+05 MW, Polysciences) or control PAM (5E+06 to 10E+06 MW). Conditions: 1000 rpm agitation, addition of 10 mL of polymer solution (10^{-4} to 10^{-3} MW) over 60 s. (b) Sediment volume versus polymer dosage for flocculation of 3% Na-kaolinite using control PAM (5E+06 to 10E+06 MW) or PAM (5E+05 MW, Polysciences). Conditions: as for (a).

EXPERIMENTAL

Percol 351 (nonionic polyacrylamide, 20 million molecular weight, batch BOP2293B, July '93), Percol E-24 (10% hydrolyzed polyacrylamide, 15 million molecular weight, batch BEX2322A, July

'93), and Percol 721 (ca. 10% cationic polyacrylamide, 20 million molecular weight, batch 74630 Jan. '91) were obtained from Allied Colloids (Canada) Ltd. (Brampton, Ontario, Canada). The other acrylamide polymers tested were previously prepared and characterized in these laboratories

and are identified by the same codes.¹⁻⁴ The kaolinite used was Reed Creek Sample Number RC-32, Lot Number T187, obtained from the Thiele Kaolin Co. (Sandersville, GA). It was converted to its sodium form (Na-kaolinite) before use by the procedure described by Van Olphen.¹⁹ Deionized water was used throughout.

The adsorption isotherm for nitrogen gas on the specially prepared Na-kaolinite was measured at the Alberta Research Council Laboratory, Devon, Alberta, using a Digisorb 2600 instrument. This was converted to the surface area of homoionic Na-kaolinite by the method developed by Brunauer, Emmett, and Teller.²⁰ Laurier Schramm of the Petroleum Recovery Institute (Calgary, Alberta) measured the isoelectric point of the homoionic Na-kaolinite using a microelectrophoresis apparatus fitted with a rotating prism and video viewing system.

Flocculation experiments were conducted in 400-mL beakers (7.6-cm diameter) fitted with four evenly spaced 0.76-cm-wide Plexiglas baffles cemented vertically to the beaker wall.^{21,22} A Plexiglas turbine impeller with six blades, 2.53-cm diameter (1/3 that of the beaker), was mounted on a stainless-steel shaft driven by a Gallenkamp stirrer with a digital rpm readout. A Sage syringe pump (Single-Channel Model 341B) was used for reproducible addition of polymer solutions.

Supernatant turbidities were measured with a Hack Model 2100A turbidimeter with an operating range of 0–2000 nephelometric turbidity units (NTU). Capillary suction times were obtained using a Triton-W.R.C. multipurpose filtration unit, Model TW166, by the method of Baskerville and Gale.²³

Flocculation Test Suspensions

Heteroionic kaolinite in deionized water in a weight ratio of 1:2 was vigorously mixed for 15 min and then diluted to 1:30 (w/w) with deionized water. The diluted slurry was mixed for 15 min and then settled for 24 h. The supernatant was then siphoned away to leave a sediment volume equivalent to that of the original 1:2 slurry. This treatment was repeated 10–12 times.

The final pretreatment used first 2*M* and then 1*M* aqueous NaCl solutions in a procedure identical to that used with water, except that the salt solution replaced water for the first cycle to produce the 1:2 kaolinite slurry. This was followed by repeated washing cycles with deionized water un-

til the electrolyte concentration in the supernatant of the settled slurry approached 1.5×10^{-4} M NaCl and the pH stabilized at 6–7. Dry Na-kaolinite was recovered from the settled slurry by freeze-drying in several portions, which were combined and thoroughly mixed in a pestle and mortar and then rolled before use. The flocculation test media were prepared by adding 3 or 1% (w/w) treated Na-kaolinite to deionized water on 10- or 20-L scales and then thoroughly mixing for 30 min each day for 10 days before use.

Supernatant NaCl Concentration Measurement

One liter of a 1.00×10^{-2} M stock solution was prepared from 0.5843 g of NaCl in deionized water, and from this, 1.0×10^{-4} , 2.0×10^{-4} , and 5.0×10^{-4} M standard solutions were prepared by serial dilution. The specific conductance ($S\text{ cm}^{-1}$) was measured for each solution using an Accumet Model 50 pH/ion/conductivity meter, previously standardized by entering 1408.07 $\mu\text{S/cm}$ for a 0.7453 g/L KCl standard.²⁴ The specific conductance of a 250-mL aliquot of the supernatant of the settled kaolinite slurry was measured and the concentration determined from a calibration plot of equivalent conductance ($S\text{ cm}^2$) versus the square root of concentration (eq/cm^3)^{0.5} prepared from the NaCl standards.

Three Percent Na-Kaolinite Test Procedure

A 10-mL aliquot of a 10^{-4} to 10^{-3} g/mL polymer solution was added, at a controlled rate via a 30-mL plastic syringe and syringe pump, to 290 mL of 3% Na-kaolinite. Solution delivery was just below the surface of the test medium between two baffles. Calculated concentrations of the stock and standard solutions were based on the ratio of the dry mass of polymer to the dry mass of Na-kaolinite. The 0–1000-ppm polymer solution standards were prepared from a 1000 ppm stock solution by adding approximately 90 mg of the freeze-dried polymer to 1000 g of deionized water followed by gentle stirring overnight.

To measure settling rates, flocculant-treated slurry was poured into a 250-mL graduated cylinder with graduations extended to 300 mL, and timing was started at this instant. The first time was recorded when the mud-line first formed and subsequent times for 10-mL volume increments from 290 to 210 mL and for 20-mL increments from 210 to 90 mL.

Individual settling rates were calculated from the height in centimeters between successive volume increments (9-cm height per 10-mL volume increment) divided by the elapsed time in seconds. The method of successive averages was used to calculate the initial average, the average to compaction, and the average settling rate from the individual settling rates.²⁵ In most cases, the initial average settling rate was calculated for the times elapsed between the 290- and 250-mL volume increments. The average settling rate to compaction and the average settling rate were calculated as the averages of the individual settling rates between the 290- and 170-mL levels and the 290- and 90-mL levels, respectively.

The sediment volume and the supernatant turbidity were measured 30 min after the flocculated slurry was poured into the graduated cylinder. A rubber stopper gauge used on the 20-mL sampling pipette enabled consistent sampling of the supernatant from the 190-mL level. Turbidity was measured using the 0–2000 NTU range of the turbidimeter to be able to measure the initial 3% Na-kaolinite suspension in the same range. This was calibrated using a 0–2000 NTU standard before each measurement.

The capillary suction time was measured by first redispersing the 280 mL of the settled test solution remaining in the graduated cylinder by several inversions and then quickly pouring this into the a Triton-W.R.C. multipurpose filtration unit. The liquid phase was drawn into absorbent paper (Whatman No. 17) by capillary suction and the timing was started when the liquid phase reached the electrical contact at 3.2 cm. When the liquid phase reached the electrical contact at 4.5 cm, the timing device stopped to give the capillary suction time. These were measured in triplicate and averaged.

Flocculation Test Variables

Prior to each flocculation test, a 290-mL aliquot of the Na-kaolinite test medium was dispersed at 1500 rpm for 5 min and then adjusted to the desired rpm for an additional 5 min. PAM from control-6 (complementary to MeAM-co-AM-6) was used to prepare 0–1000-ppm polymer solution standards. After addition of the 10-mL aliquot of the polymer solution to the Na-kaolinite test medium, agitation was stopped.

The effect of the polymer dosage on the flocculation performance was measured by stirring at 1000 rpm while exactly 10 mL of the polymer solution was added for 60 s. The effect of agitation

on the flocculation performance was studied for agitation rates of 500, 750, 1000, and 1250 rpm, using a constant polymer dosage (700 ppm) and rate of polymer addition (10 mL over 60 s). The influence of the rate of polymer addition on the flocculation performance was measured by the addition of 10 mL of the polymer solution during 30, 60, and 90 s, while keeping the agitation rate (1000 rpm) and polymer dose (700 ppm) constant.

Flocculation of 3% Na-Kaolinite

The sensitivity of the flocculation test procedure to polymer chain extension was determined from average settling rates, supernatant turbidity, sediment volume, and capillary suction times for 3% Na-kaolinite using the copolymers from MeAM-co-AM-2b to -4 and PAM from control-6 (complementary to MeAM-co-AM-6).² These tests all used a polymer dosage of 700 ppm, stirring at 1000 rpm, and polymer solution addition at 10 mL (of 10^{-4} to 10^{-3} g/mL) during 60 s.

Flocculation of 1% Na-Kaolinite

The sensitivity of the flocculation test to polymer chain extension, using the 1% Na-kaolinite, was measured for PAM from control-6 (5×10^6 to 10×10^6 g/mol) and PAM (5×10^5 g/mol, Poly-science Inc., Warrington, PA). Polymer dosages from 0 to 1000 ppm, 1000 rpm agitation, and a polymer solution addition rate of 10 mL (of 10^{-4} to 10^{-3} g/mL) over 60 s were used. As before, settling rates, supernatant turbidity, sediment volume, and capillary suction time were used for evaluation.

The effect of agitation rates and addition rates on flocculation was measured using the same polymers as used for the 1% Na-kaolinite sensitivity test above. Average settling rates and supernatant turbidities were recorded for polymer dosages of 25, 50, and 100 ppm and various agitation and polymer solution addition rates.

Copolymers from DMA-co-AM-3 to -6, MeAM-co-AM-2b to -5 (including PAM from control-6), and NTBAM-co-AM-1b (cloudy layer), -1b (clear layer), and -2 (dialysis fraction) as well as the purified cationic derivatives of DMA-co-AM-7, MeAM-co-AM-2b, NTBAM-co-AM-1b (cloudy layer), PAM from control-6 (complementary to MeAM-co-AM-6), and the commercial polymers Percol 351 (nonionic PAM), Percol 721 (cationic PAM), and Percol E-24 (anionic PAM)^{1–4} were separately tested at 25, 50, and 100 ppm polymer concentrations using the 1% Na-kaolinite suspension. The

agitation rate (1000 rpm) and the polymer addition rate (10 mL of 10^{-4} to 10^{-3} g/mL polymer solution over 60 s) were kept constant for this series.

RESULTS

NaCl Concentration in the Supernatant of Settled Slurry

Equivalent conductance, Λ (S cm²), was calculated from the specific conductance, k (S cm⁻¹) using eq. (1), where C is the concentration in equivalents/cm³:

$$\Lambda = \frac{1000k}{C} \quad (1)$$

The 10.3 μ S/cm specific conductance measured for the supernatant of the settled Na-kaolinite was converted to equivalent conductance by elaborating eq. (1) to the form of eq. (2):

$$\Lambda = \frac{1000 \times 10.3 \mu\text{S/cm}}{c} = \frac{0.0103\text{S/cm}}{c} \quad (2)$$

Substituting the above relation for equivalent conductance into the equation for the best straight line calculated from the calibration plot of the equivalent conductance versus the square root of concentration for the NaCl standards gave a cubic equation in concentration, c :

$$c^3 - (1.505 \times 10^{-6})c^2 + (2.106 \times 10^{-11})c - 7.813 \times 10^{-21} = 0 \quad (3)$$

This was solved by using a published substitution method.²⁶ The result, in equivalents per liter, was converted to 1.138×10^{-4} mol per liter for the concentration of NaCl in the supernatant of the settled Na-kaolinite.

Surface Area of the Na-Kaolinite

The adsorption isotherm for nitrogen gas on dry Na-kaolinite was used to measure the surface area of the Na-kaolinite particles using the "BET equation," developed by Brunauer, Emmett, and Teller²⁰:

$$\frac{x}{n(1-x)} = \frac{1}{\text{cm}} + \frac{(c-1)x}{\text{cm}} \quad (4)$$

where x is the relative vapor pressure p/p_0 ; n , the weight of vapor adsorbed at a given vapor pressure; m , the weight of the vapor adsorbed at monolayer coverage; and c , a constant related to the energy of adsorption of the first monolayer.

Linear regression gave a slope, $m = 0.184548 \pm 0.000965$, an intercept, $c = 0.001543 \pm 0.000141$, and a correlation coefficient, $r = 0.9999$ for the plot of $x/n(1-x)$ versus x . The surface area was calculated as 23.3928 ± 0.1225 m²/g. The BET surface area of Na-kaolinite prepared here was slightly less than the 26.8 m²/g found for a Na-kaolinite from Kaolin des Charentes.²⁷ The same procedure was used for conversion of both kaolinites from heterionic to Na-kaolinite.

Isoelectric Point

The isoelectric point of the Na-kaolinite was determined by plotting the electrophoretic mobility (cm² s⁻¹ V⁻¹) versus the solution pH for 50 mg/L pH-adjusted Na-kaolinite standards, measured at $25.0 \pm 0.5^\circ\text{C}$. The applied potential was kept below 60 V to minimize interference from thermal current-induced Brownian motion, and the electric field was kept on for 20 s or less for each measurement. For zero electrophoretic mobility, the data curve gave a solution pH of 2.7. Typically, the isoelectric point of pure Na-kaolinite in deionized water is 3.0.^{28,29}

Flocculation Performance with 3% Na-Kaolinite Suspensions

Effect of Dosage, Agitation Rate, and Polymer Addition Rate

Somewhat variable average settling rates were observed for PAM from control-6 (MeAM-co-AM-6) from polymer dosages ranging from 50 to 1000 ppm, with apparent maxima at 400, 700, and 1000 ppm, based on the dry mass of the polymer to the dry mass of 3% Na-kaolinite. A plot of the average settling rate versus the impeller speed gave a maximum 0.82 cm/s average settling rate at 500 rpm agitation and decreased linearly to 0.21 cm/s at 1250 rpm. Measurement of the average settling rate versus the rate of addition of the polymer solution gave a maximum average settling rate of 4.6 cm/s for the addition of 10 mL of the polymer solution for 60 s.

With Copolymers MeAM-co-AM-2b to -4 and Control PAM

The initial average, average to compaction, and average settling rates determined for the floccu-

Table I Selection of Detailed Flocculation Results for the New Copolymers and Control PAM

Flocculant Origin	Feedstock AM Content (mol %)	Initial Average Settling Rate ^a (cm/s)	Average to Compaction Settling Rate ^b (cm/s)	Average Settling Rate ^c (cm/s)	Sediment Volume (mL)	Supernatant Turbidity, 3.0 Min (NTU)	Capillary Suction Time (s)
3% Na-kaolinite no flocculant	n/a ^d	0.095	0.094	0.086	130	1167	54.7
MeAM-co-AM-2b	80	0.118	0.113	0.102	110	25.5	28.0
MeAM-co-AM-3	60	0.096	0.084	0.079	146	80.3	38.9
MeAM-co-AM-4	40	0.062	0.053	0.053	168	124.2	42.7
Control-6 PAM	100	0.187	0.174	0.157	102	9.45	27.2

Conditions: 3% by weight hydrated Na-kaolinite in water, polymer dosage of 700 ppm, polymer solution addition rate of 10 mL for 60 s, and agitation at 1000 rpm.

^a Initial average settling rates were measured between 290- and 250-mL volume increments.

^b Average to compaction settling rates were measured between 290- and 170-mL volume increments.

^c Average settling rates were measured between 290- and 90-mL volume increments.

^d n/a, not applicable.

lation tests which used PAM from control-6 (complementary to MeAM-co-AM-6) were much greater than were those for the copolymers from MeAM-co-AM-2b to -4 and decreased as the content of AM in the copolymer decreased (Table I). The settling performance of 3% Na-kaolinite without polymer addition was only slightly different from that found for flocculation tests which used the copolymers MeAM-co-AM-3 and -4.

The copolymer MeAM-co-AM-2b and PAM were the only polymers which gave sediment volumes which were less than those obtained for the 3% Na-kaolinite blank tests. The sediment volume, 30-min supernatant turbidity, and capillary suction times decreased as the proportion of PAM in the copolymers increased. From this group of polymers, PAM gave the best values for these parameters.

By Commercial PAM and Control PAM

The average settling rates showed the greatest increase for PAM from control-6 (complementary to MeAM-co-AM-6, 5E+06 to 10E+06 MW) and commercial PAM from Polysciences (5E+05 MW) between the 0 and 100 ppm polymer dosages [Fig. 1(a)]. This increase was much greater for the tests which used control PAM than for those using commercial PAM. The initial average and average to compaction results paralleled the average settling rates for both polymers [Fig. 1(b)].

Flocculation performance was hardly affected by the polymer dosage in the 25–800-ppm dose

range in the 30-min-sediment volume versus polymer dosage test [Fig. 1(b)]. However, control PAM produced 30-min supernatant turbidities that were significantly lower than were those of commercial PAM and at lower polymer dosages [Fig. 2(a)]. Commercial PAM gave a slight increase in the average capillary suction time as the polymer dosage increased, whereas control PAM gave a slight decrease [Fig. 2(b)].

Flocculation Performance with 1% Na-Kaolinite Suspensions

Effect of Agitation Rate and Polymer Addition Rate Using Control PAM

With tests of agitation rates using control PAM, 1000-rpm agitation gave the highest average settling rates and the lowest 30-min supernatant turbidities (Fig. 3). The average settling rates increased with the polymer concentration for dosages of 25, 50, and 100 ppm for all three agitation rates.

For control PAM, a polymer addition rate of 10 mL for 60 s gave the highest average settling rates, 0.6 cm/s, and the lowest supernatant turbidities, 130 NTU, compared to the values obtained from polymer addition during 30 or 90 s. For polymer addition rates in the 0–100 ppm range, the average settling rates increased and the supernatant turbidities decreased with the polymer dosage.

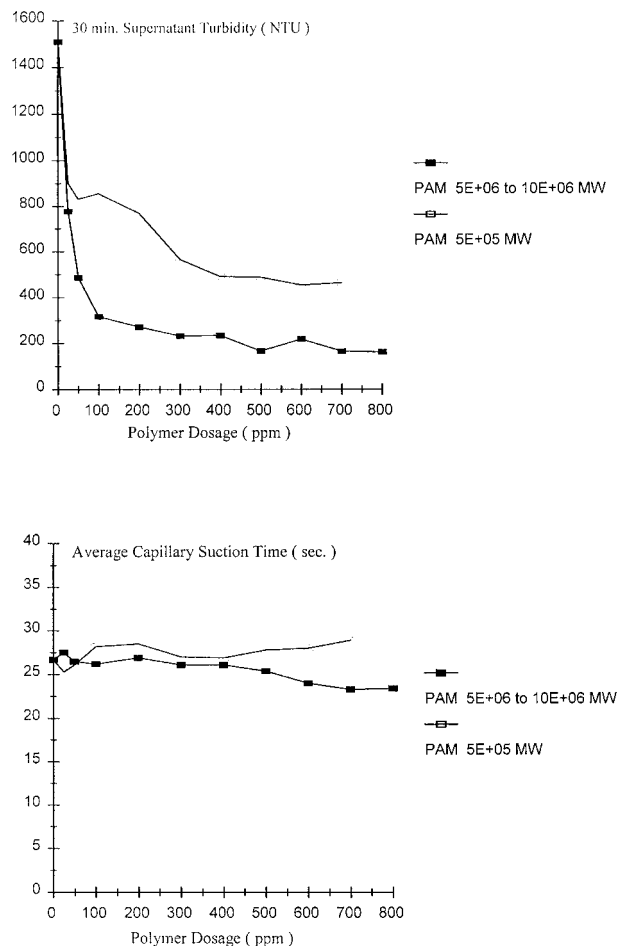


Figure 2 (a) Thirty-minute supernatant turbidities versus polymer dose for flocculation of 3% Na-kaolinite using control PAM ($5E+06$ to $10E+06$ MW) or PAM ($5E+05$ MW, Polysciences). (b) Average capillary suction time versus polymer dosage for flocculation of 3% Na-kaolinite using control PAM ($5E+06$ to $10E+06$ MW) of PAM ($5E+05$ MW, Polysciences). Conditions: as for (a).

By the Copolymers from DMA-co-AM-3 to -5 and Control PAM

Low solubility restricted the flocculation tests to the copolymers from DMA-co-AM-3 to -5. These copolymers gave average settling rates which were greater than those for PAM from control-6 (complementary to DMA-co-AM-6) and increased as the content of DMA in the copolymers decreased [Fig. 4(a)]. Thirty-minute supernatant turbidities obtained for these copolymers were lower than were those for PAM and also decreased as the content of DMA in the copolymer decreased [Fig. 5(a)].

By the Copolymers from MeAM-co-AM-2b to -5 and Control PAM

The average settling rates obtained for the copolymers from MeAM-co-AM-2b to -5 were less than were those for PAM from control-6 (complementary to MeAM-co-AM-6) and decreased as the content of MeAM in the copolymers increased [Fig. 4(b)]. Lower 30-min supernatant turbidities were obtained for PAM than for the tests which used the copolymers from MeAM-co-AM-2b to -5 and decreased as the MeAM content decreased [Fig. 5(b)].

By the Copolymers NTBAM-co-AM and Control PAM

The copolymers from NTBAM-co-AM-1b (cloudy layer), -1b (clear layer), and -2 (dialyzed fraction) gave lower average settling rates [Fig. 6(a)] and higher supernatant turbidities than those of PAM from control-6 (complementary to MeAM-co-AM-6), which reflected the lower settling performance [Fig. 7(a)]. Settling performance improved with an increase in the polymer dose from 25 to 100 ppm. The average settling rates decreased and the supernatant turbidities increased as the content of NTBAM in the copolymers increased.

By the Cationic Derivatives of the Copolymers

The purified cationic derivative of the DMA-co-AM-7 copolymer gave the highest average settling rates of the newly prepared cationic derivatives of DMA-co-AM-7, MeAM-co-AM-2, NTBAM-co-AM-1b (cloudy layer), and control PAM [Fig. 6(b)]. The average settling rates for a 100-ppm dosage of the nonionic copolymers were greater than were those obtained for the same dosages of their cationic derivatives, except for nonionic MeAM-co-AM-2b and its cationic derivative (Figs. 6 and 7). Also, the average settling rate for nonionic PAM from control-6 (of MeAM-co-AM-6) was greater than that of any of the new cationic derivatives.

For 30-min supernatant turbidity tests which exceeded the 2000 NTU limit of the turbidimeter, turbidities were brought to within range by diluting the 20-mL aliquot of the supernatant with deionized water. The equivalent turbidities of the undiluted supernatant were calculated by assuming the relationship given by eq. (5):

$$\text{Equivalent NTU} = \text{diluted NTU} \times \text{diluted volume}/20 \text{ mL} \quad (5)$$

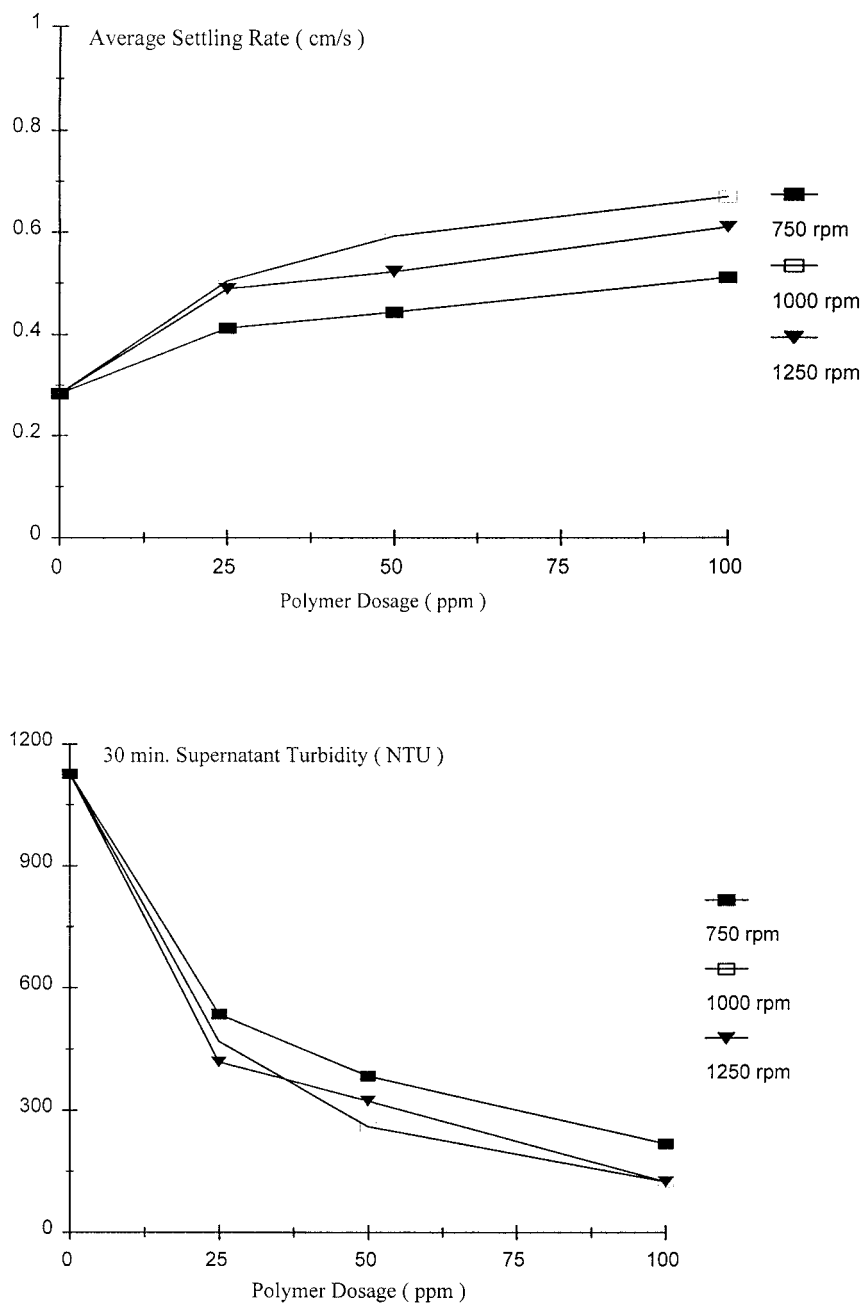


Figure 3 (a) Average settling rate versus polymer dosage and agitation rate for flocculation of 1% Na-kaolinite using control PAM. Conditions: a polymer solution addition rate of 10 mL per 60 s. (b) Thirty-minute supernatant turbidity versus polymer dosage for flocculation of 1% Na-kaolinite using control PAM. Conditions: as for (a).

where equivalent NTU is the approximate turbidity outside the 0–2000 NTU range, diluted NTU is the turbidity of the diluted supernatant brought within the 0–2000 NTU range, and the diluted volume is the total volume of the diluted 20-mL supernatant sample.

The lowest 30-min supernatant turbidities were obtained for the cationic derivative of the

copolymer from DMA-co-AM-7 (Table II). At a polymer dosage of 100 ppm, the 30-min supernatant turbidity produced by the nonionic copolymer from DMA-co-AM-7 was about the same as that produced by its cationic derivative. At 100-ppm dose rates, the nonionic copolymers from MeAM-co-AM-2b and NTBAM-co-AM-1b (cloudy layer) and control PAM all gave 30-min superna-

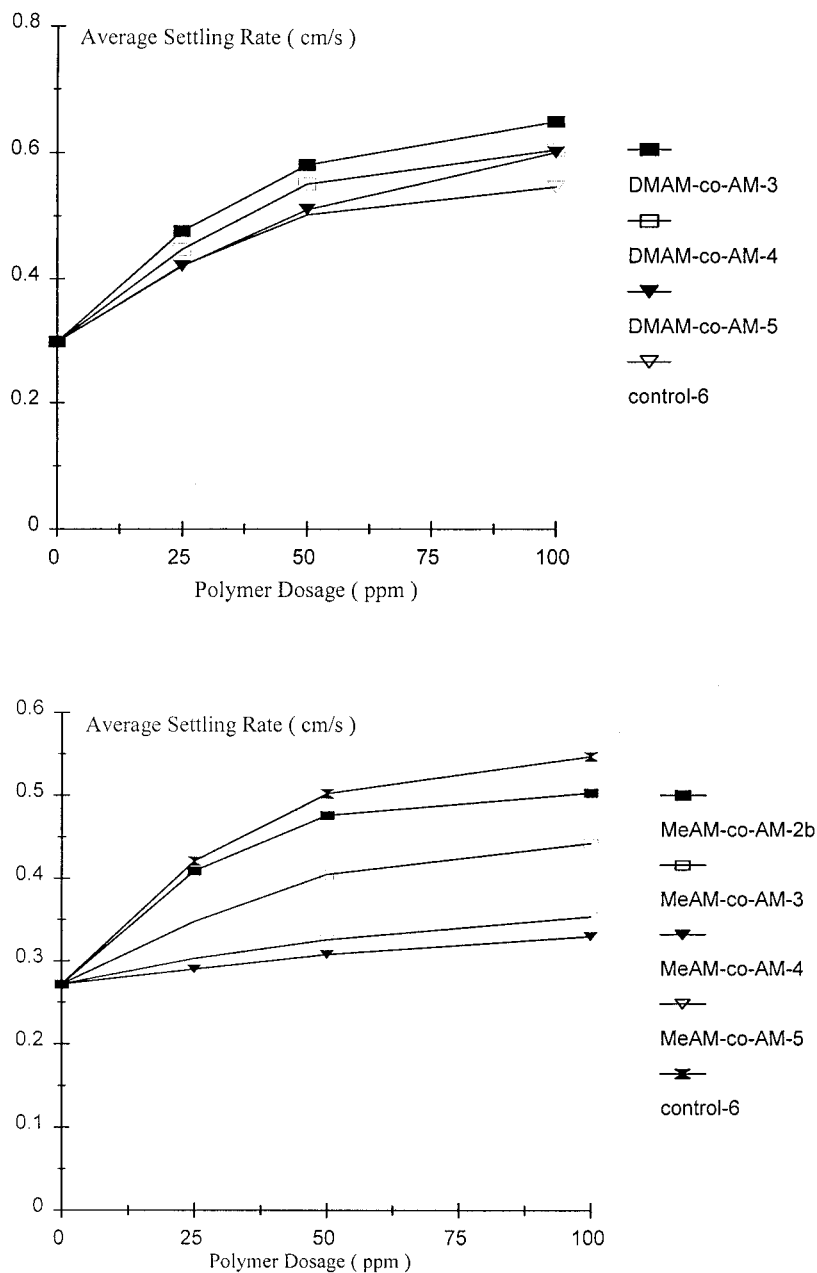


Figure 4 (a) Average settling rate versus dosage for flocculation of 1% Na-kaolinite using the copolymers DMAM-co-AM3 to -5 and PAM from control-6. Conditions: 1000 rpm agitation, addition of 10 mL of polymer solution over 60 s. (b) Average settling rate versus dosage for flocculation of 1% Na-kaolinite using the copolymers MeAM-co-AM-2b to -5 and PAM from control-6. Conditions: as for (a).

tant turbidities, which were lower than were those produced by their cationic derivatives.

By Commercial Percol 351, Percol 721, and Percol E-24 and Control PAM

The commercial polymers all gave higher average settling rates than those of PAM from control-6

(of MeAM-co-AM-6) (Fig. 8). Percol 721 gave the highest average settling rate at 100 ppm.

All the commercial polymers gave lower and comparable 30-min supernatant turbidities than those of control PAM [Fig. 7(b)]. Again, at 100 ppm, Percol 721 gave the lowest 30-min supernatant turbidity by a small margin.

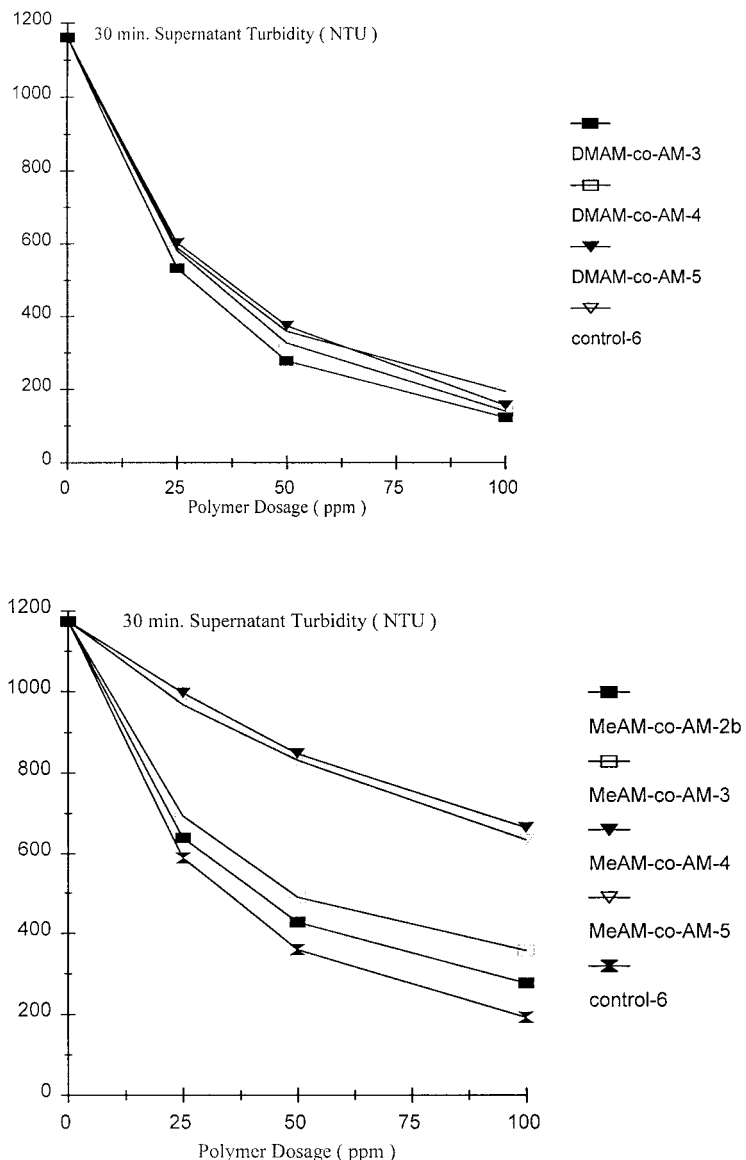


Figure 5 (a) Thirty-minute supernatant turbidity versus polymer dosage for flocculation of 1% Na-kaolinite for the copolymers DMAM-co-AM3 to -5 and PAM from control-6. Conditions: 1000 rpm agitation and addition of 10 mL of polymer solution over 60 s. (b) Thirty-minute supernatant turbidity versus polymer dosage for flocculation of 1% Na-kaolinite for the copolymers MeAM-co-AM-2b to -5 and PAM from control-6. Conditions: as for (a).

Overall Performance Comparison

The highest average settling rates and lowest supernatant turbidities were obtained for the new copolymers from DMA-co-AM-3, MeAM-co-AM-2b, NTBAM-co-AM-1b (cloudy layer), and PAM from control-6 (of MeAM-co-AM-6). However, the commercial polymers did give higher average set-

ling rates and lower 30-min supernatant turbidities (Figs. 7 and 8). The largest differences in average settling rates were observed at 100 ppm. The copolymer from DMA-co-AM-3 at 25- and 50-ppm dosages gave average settling rates equivalent to those of Percol 721, and at 100 ppm, gave a nearly equivalent 30-min supernatant turbidity.

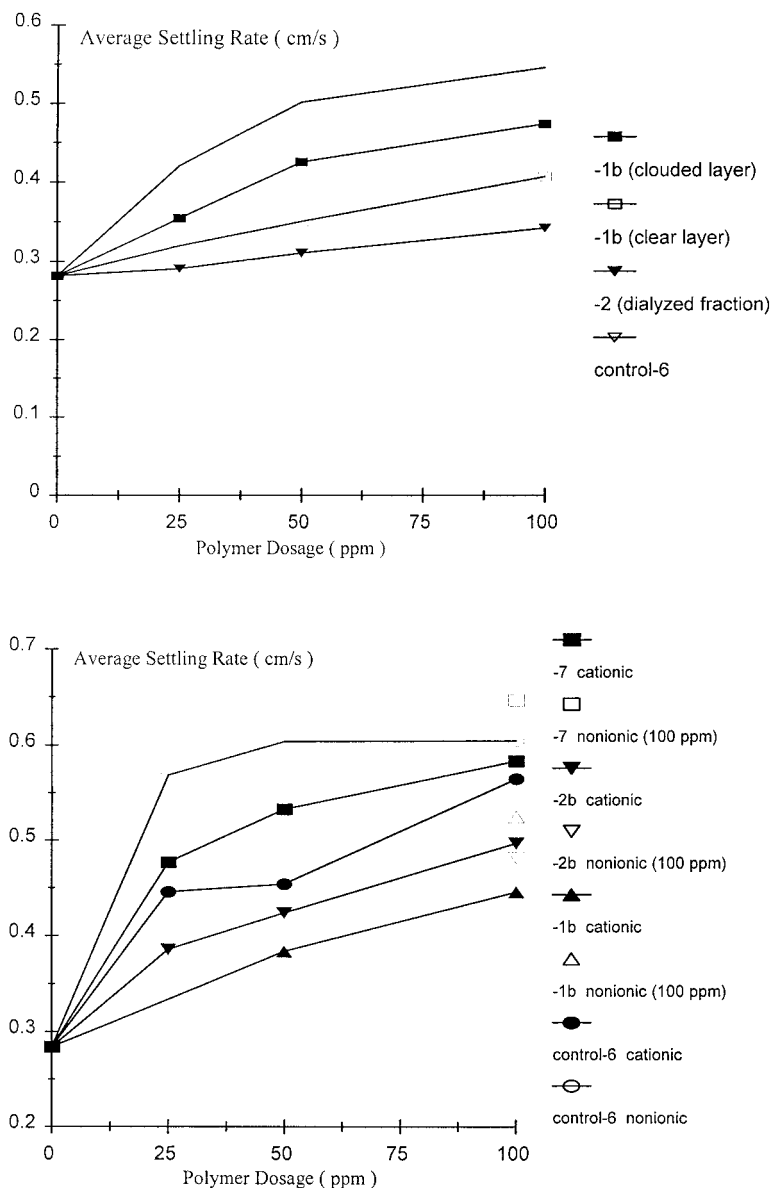


Figure 6 (a) Average settling rate versus polymer dosage for flocculation of 1% Na-kaolinite for the copolymers NTBAM-co-AM-1b (cloudy layer), -1b (clear layer), and -2 (dialyzed fraction) and control PAM. Conditions: 1000 rpm agitation, addition of 10 mL of polymer solution over 60 s. (b) Average settling rate versus polymer dosage for flocculation of 1% Na-kaolinite using the purified cationic polymers from DMAN-co-AM-7, MeAM-co-AM-2b, NTBAM-co-AM-1b (cloudy layer), control PAM, and their nonionic polymer substrates. Conditions: as for (b).

DISCUSSION

Flocculation Test Medium

A reproducible test procedure was developed to evaluate the performance of the acrylamide-based polymers as flocculants and to link this performance to their solution behavior. Kaolinite is a

preferred flocculation test medium^{30,31} since its chemistry in aqueous suspensions is well understood.³²⁻³⁴ It is the most common clay mineral of the kaolin group and has the 1:1 layered structure common to this group, comprising a layer of silicon oxygen tetrahedra joined by one of the four oxygen atoms of each tetrahedron, or joined by a

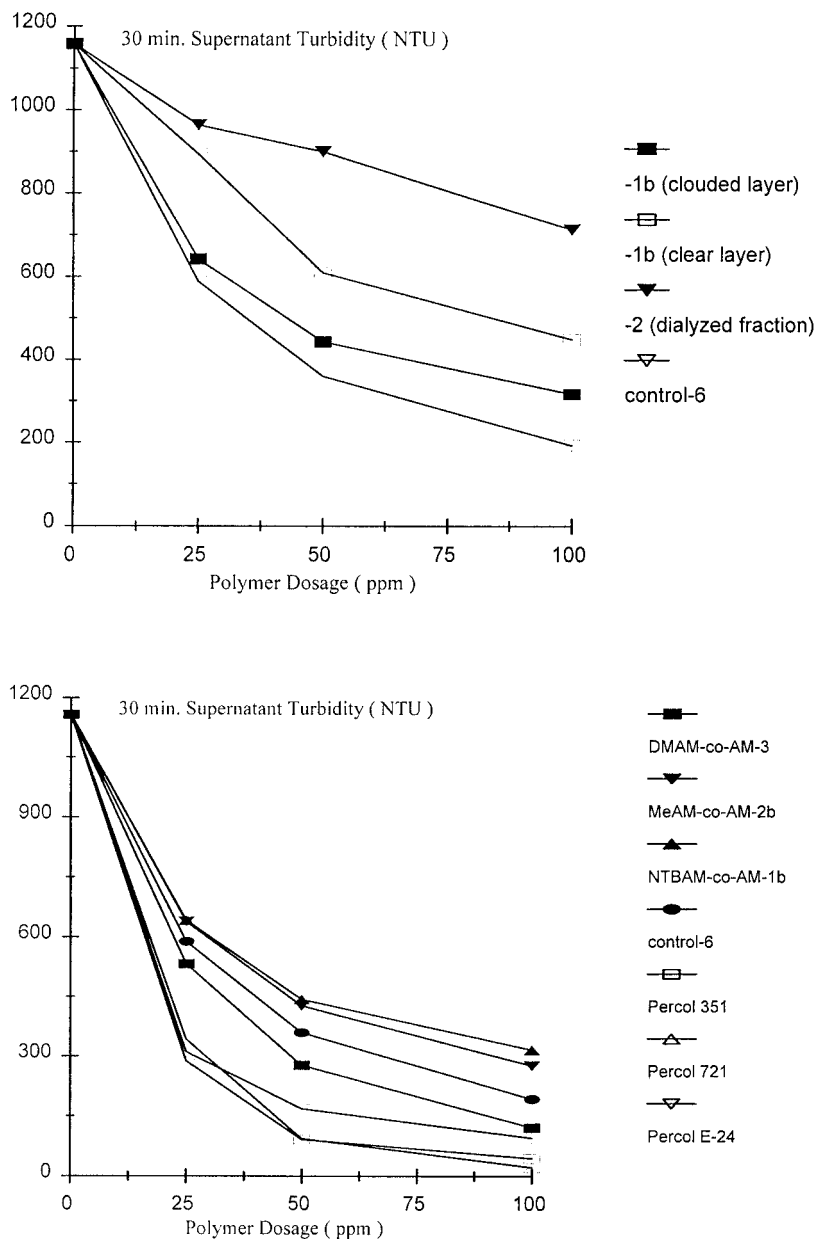


Figure 7 (a) Thirty-minute supernatant turbidity versus polymer dosage for flocculation of 1% Na-kaolinite for the copolymers from NTBAM-co-AM-1b (cloudy layer), -1b (clear layer), and -2 (dialyzed fraction) and control PAM. Conditions: 1000 rpm agitation, addition of 10 mL of polymer solution over 60 s. (b) Thirty-minute supernatant turbidity versus polymer dosage for flocculation of 1% Na-kaolinite for Percol 351, Percol 721, and Percol E-24, the copolymers from DMAM-co-AM-3, MeAM-co-AM-2b, NTBAM-co-AM-1b (cloudy layer), and control PAM. Conditions: as for (a).

hydroxyl group, to a layer of aluminum oxygen-hydroxyl octahedra. Van der Waals attraction, electrostatic interactions, and hydrogen bonding bind together several 1:1 aluminosilicate layers. Crude kaolinite contains counterions such as Al^{3+} , Fe^{2+} , or Mg^{2+} , which can cause ion ex-

change with the hydrogen atoms involved in intramolecular hydrogen bonding, which does not happen with Na^+ .³¹ For this reason, the heteroionic kaolinite was converted to the sodium form (Na-kaolinite) prior to use. The NaCl concentration in the supernatant of the converted slurry

Table II Comparison of Flocculation Results for the Nonionic Polymers and Their Purified Cationic Derivatives with PAM from Control-6

Flocculant	Polymer Dosage (ppm)	30-min Supernatant Turbidity (NTU) ^a
Blank (1% Na-kaolinite)	0	9792
Nonionic DMAM- <i>co</i> -AM (DMAM- <i>co</i> -AM-7)	100	222
Cationic DMAM- <i>co</i> -AM (DMAM- <i>co</i> -AM-7)	25	2636
	50	1182
	100	215
Nonionic MeAM- <i>co</i> -AM (MeAM- <i>co</i> -AM-2b)	100	1169
Cationic MeAM- <i>co</i> -AM (MeAM- <i>co</i> -AM-2b)	25	9696
	50	2862
	100	1305
Nonionic NTBAM- <i>co</i> -AM (NTBAM- <i>co</i> -AM-1b, clouded layer)	100	1040
Cationic NTBAM- <i>co</i> -AM (NTBAM- <i>co</i> -AM-1b, clouded layer)	25	9360
	50	2738
	100	1370
Nonionic PAM (control-6) ^b	25	4335
	50	940
	100	491
Cationic PAM (control-6)	25	5448
	50	1820
	100	746

Conditions: 1% by weight Na-kaolinite in water, 1000 rpm agitation rate, and a polymer solution addition rate of 10 mL for 60 s.

^a Turbidities exceeding 2000 NTU were approximated using eq. (5).

^b Control-6 was prepared under equivalent experimental conditions to those used to prepare MeAM-*co*-AM-6.

was reduced to 1.138×10^{-4} M by washing, to minimize adsorption of Na⁺ on the basal face A and to prevent hydrolysis in an aqueous medium.³¹ This also isolated the edges of the Na-kaolinite particles as the test sites for polymer-clay interactions.

Suitability of 3% Na-Kaolinite for Bridging Flocculation

The initial test medium used was 3% (w/w) Na-kaolinite in deionized water, the pH of which was 7.0 ± 0.2 . This could cause the edges of the clay particles to be prone to intramolecular hydrogen bonding, which could hinder bridging flocculation, but, at the same time, should enhance test sensitivity to polymer structure and chain extension. The isoelectronic point of the Na-kaolinite used here (pH 2.7) and the low concentration of elec-

trolyte present should minimize contributions from face-face or edge-face agglomeration.^{20,31}

The average plate diameter of the Na-kaolinite used was assumed to be similar to the Na-kaolinite which originated from Kaolin des Charantes, from the agreement between the respective BET surface areas.²⁷ Having estimates of the average plate diameter (0.21 μ m) and edge thickness (0.04 μ m), and assuming a double layer thickness of 100 nm,^{9,12} polymer loops or trains would have to extend 200 nm for bridging flocculation to occur. Thus, many of the nonionic, acrylamide-based polymers prepared had sufficiently high average polymer chain extensions to permit this.

The number of Na-kaolinite particles and the volume per particle in the test medium were calculated by assuming the platelet dimensions of

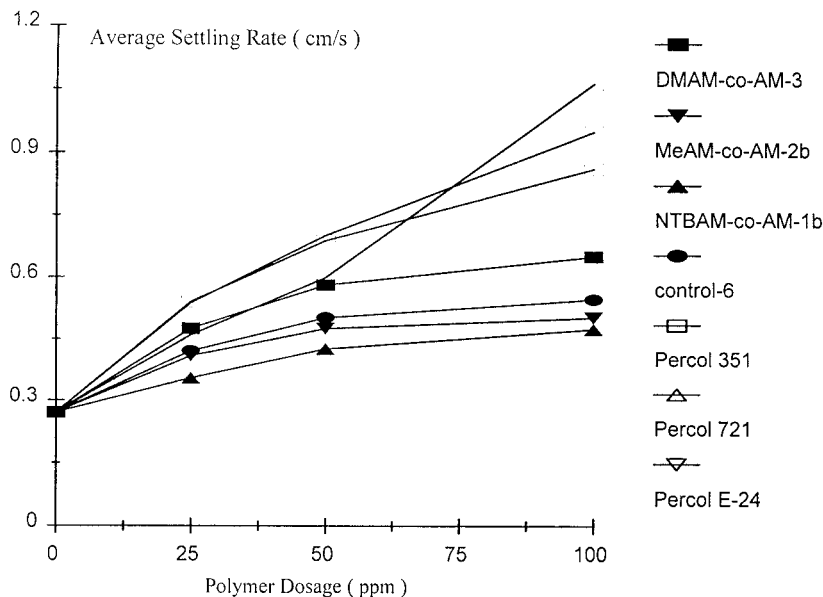


Figure 8 Average settling rate versus polymer dosage for flocculation of 1% Na-kaolinite for Percol 351, Percol 721, and Percol E-24 and the nonionic copolymers from DMAM-*co*-AM-3, MeAM-*co*-AM-2b, and NTBAM-*co*-AM-1b (cloudy layer) and control PAM. Conditions: 1000 rpm agitation, addition of 10 mL of polymer solution over 60 s.

the Na-kaolinite from Kaolin des Charentes and a perfect hexagon shape. This established that the 3% Na-kaolinite test medium was sufficiently dilute to accommodate even the theoretical high limit of double-layer thickness without complications.

Equipment

The ASTM standard flocculation test (D2035-80) requires instantaneous addition of the flocculant to a stirred test medium, and the ISO/CD standard test (10086-1) uses instantaneous addition of the flocculant to a stationary test medium followed by mixing. However, Hogg et al. showed that good mixing *and* flocculant addition during a prescribed time decreases the probability of surface saturation of colloidal particles.³⁰ A mixing tank was constructed to meet these requirements and to match the fluid dynamics described by Holland and Chapman.²¹ Polymer solutions were kept to 10^{-4} to 10^{-3} g/mL concentrations to minimize polymer chain entanglement and 10-mL volumes to keep the ratio of additive to treated volume low.

The 3% Na-Kaolinite Flocculation Tests

The 10-L volume of the test medium prepared for these tests ensured substrate consistency

throughout.^{30,35} Polyacrylamide (PAM, from control-6, MeAM-*co*-AM-6) was used as a control reagent, initially using 1000-rpm agitation and flocculant addition for 60 s.

Test Variables

The average settling rate was expected to increase with increasing polymer dosage to a maximum value and then decrease with further increases in polymer dosage. However, this was not observed (Fig. 7), perhaps because the dose range used was too narrow.

The effect of agitation at 500, 750, 1000, and 1250 rpm during the time of flocculant addition was tested. The highest average settling rates were obtained at 500 rpm, which would be expected, since agitation once some flocculant addition has occurred mainly causes degradation of the floc.^{22,30}

Flocculant addition for 30 or 90 s produced lower average settling rates than did addition for 60 s. This is attributed to a less even polymer distribution for flocculant addition for 30 s and greater floc degradation from agitation-induced shear for addition for 90 s. Subsequent tests all used flocculant addition for 60 s.

Sensitivity to Polymer Chain Extension

The average settling rates, supernatant turbidities, and capillary suction times obtained were consistent with test sensitivity to polymer chain extension and bridging flocculation (Table I). The lower average settling rates observed for the copolymers from MeAM-co-AM-3 and -4 than for 3% Na-kaolinite without flocculant were attributed to the insufficient polymer chain extension of these materials. The greater chain extension of MeAM-co-AM-2b and PAM from control-6 probably contributed to the observed improvement in the settling rate.

To remove the copolymer composition variable from these tests, PAM (5E+05 MW, Polysciences) and PAM from control-6 (of MeAM-co-AM-6, 5E+06 to 10E+06 MW) were tested at 0–1000 ppm using a 1% Na-kaolinite suspension. This did not lower the average settling rates for higher polymer concentrations beyond the maximum average settling rate (Fig. 3), perhaps because an insufficient range of polymer concentrations was tested. However, the large differences in the average settling rates and supernatant turbidities recorded for polymer dosages between 0 and 100 ppm for each polymer tested is consistent with a sensitivity of the test procedure to polymer chain extension and polymer dosage (Figs. 1 and 2).

Influence of Flocculant on Settling Rate

During these flocculation tests, there was generally an initial period of a high settling rate, followed by a constant rate period and then, as the sediment compression point was reached, a decreased settling rate. So, to begin with, the initial average, average to compaction, and overall average settling rates were recorded. However, as the results were compiled, the overall average settling rate was clearly sufficient to define the performance of each flocculating system and, therefore, became the only settling value recorded.

Average settling rates for the PAM-treated (control PAM) suspension and 1% Na-kaolinite without flocculant were reproducible since these all gave respective means within $\leq 5\%$ for tests performed up to several days apart. The percentage difference between means only increased to nearly 15% when conducted months apart, probably from aging effects of the Na-kaolinite test medium, including some clay hydrolysis.

Supernatant Turbidity

The supernatant turbidities are relative results, rather than absolute, since they were not mea-

sured against a standard. Unlike higher average settling rates, which are generally related to floc size, lower supernatant turbidities are generally related to floc density.^{16,22} Like average settling rates, the supernatant turbidities were reproducible as long as the measurements were taken within a few days of each other.

Sediment Volume

Increased floc density would be expected to favor a lower sediment volume, whereas increased floc size would be expected to favor a larger sediment volume. It was found that the sedimented volume of a flocculated suspension was always greater than that obtained without using a flocculant. Consequently, sediment volumes were only recorded in preliminary tests.

Capillary Suction Time

Capillary suction time (CST) is a measure of the filterability of a slurry and can also provide a measure of floc strength.^{23,36} The filterability, in turn, can be related to the floc size and floc density. Increased floc size would be expected to favor a lower capillary suction time, whereas increased floc density would be expected to favor a higher capillary suction time. An exact volume of flocculated slurry was not required to measure the capillary suction times because the hydrostatic pressure exerted by the slurry added to the instrument reservoir was only 2.5% of the capillary suction pressure of Whatman No. 17 absorbent paper.²³

Normally, capillary suction time and average settling rate information complement one another. Erratic capillary suction times were obtained, probably because of the thin filter cake obtained from the low percentage of solids in the flocculated slurry. For a thin filter cake, CST measurements are said to be a better indication of blocking filtration rather than is filter cake permeability.^{36,37} For these reasons, CST measurements were only used for preliminary tests.

One Percent Na-Kaolinite Flocculation Tests

Average settling rates and supernatant turbidities have now been established to be sensitive to polymer dosage and to the difference in the average polymer chain extension between PAM (5×10^5 g/mol) and PAM (5×10^6 , to 10×10^6 g/mol) with 3% Na-kaolinite suspensions (Figs. 1 and 2).

So, the same conditions were used with 1% Na-kaolinite suspensions.

Newly Synthesized Nonionic Polymers

Average Settling Rates

The decline in the average settling rate observed for greater average polymer chain extensions in the copolymers from DMA-*co*-AM-3 to -5 was probably due to hindered hydrogen bonding, since the polymer chain extension also increased with a greater proportion of DMA¹ [Fig. 4(a)]. Evidently, the hindered hydrogen bonding was less important than was enhanced bridging since the higher average polymer chain extensions of the copolymers from DMA-*co*-AM-3 to -5 gave greater average settling rates than those of control PAM.

The decline in average settling rates [Fig. 4(b)] observed for a greater proportion of MeAM in the copolymers from MeAM-*co*-AM-2b to -5 is attributed to decreased average polymer chain extensions² and, therefore, decreased bridging capability. The greater average settling rate obtained by using PAM can be explained by both the higher-average polymer chain extension and the less hindered hydrogen bonding of PAM.

A greater proportion of NTBAM in the copolymers from NTBAM-*co*-AM-1b (cloudy layer), -1b (clear layer), and -2 (dialyzed fraction) caused a decline in the average settling rate [Fig. 6(a)]. Hindered hydrogen bonding and, therefore, more difficult adsorption, probably contributed to this. The average polymer chain extensions of these polymers were nearly equivalent,³ so the bridging ability of the copolymers was not a variable. As with the MeAM copolymers, the higher average settling rates obtained by using PAM (control 6) are attributed to the higher average polymer chain extension and unhindered hydrogen bonding of PAM.

Supernatant Turbidity

The lower supernatant turbidities observed from tests with the DMA copolymers, than from tests which used PAM from control-6 (from MeAM-*co*-AM-6), suggests that both flocculation efficiency and lower supernatant turbidity are promoted by the greater average polymer chain extension of these copolymers [Fig. 5(a)]. The lower supernatant turbidities observed for the tests which used PAM, rather than the MeAM copolymers or NTBAM, are attributed to the greater average polymer chain extension and the unhindered hydrogen bonding of PAM [Figs. 5(b) and 7(a)].

New Nonionic Polymers Compared to Their Cationic Derivatives

Typically, flocculation of a charged test suspension by an oppositely charged polyelectrolyte proceeds by a bridging mechanism for polymers having a high polymer chain extension and a low charge density and by a charge neutralization mechanism for polymers having a low polymer chain extension and a high charge density.^{8,10,14-16} Since the cationic derivative having the greatest chain extension and the highest percentage cationicity gave the highest settling rate, flocculation could have developed from bridging, or charge neutralization, or a combination of these mechanisms. It is possible to test this, since charge neutralization involves reversible adsorption of the polyelectrolyte, whereas adsorption is irreversible for the bridging mechanism.^{8,17} The flocculated slurry was exposed to high shear agitation for several minutes and then allowed to stand. The flocculated slurry reformed, which qualitatively supports the charge-neutralization mechanism.

Lower average settling rates and higher supernatant turbidities were recorded for the flocculation tests which used the cationic derivatives than for tests which used the nonionic polymer substrates (Fig. 6). It is possible that the high average polymer chain extensions of the cationic derivatives⁴ covered a significant proportion of the particle surface which hindered particle-particle interaction.

New Nonionic Polymers Compared to Commercial Polymers

The higher average settling rates and lower supernatant turbidities observed for flocculation tests which used the commercial polymers than those observed for the newly synthesized polymers are attributed to the greater average polymer chain extensions and, therefore, greater bridging abilities of the commercial polymers [Figs. 6(b) and 8]. This can probably be explained by the low charge density of Percol 721 (cationic PAM) helping to favor the bridging mechanism over charge neutralization.

The highest average settling rates and lowest supernatant turbidities were observed for tests which used Percol 721 [Figs. 7(b) and 8]. Unhindered adsorption to the oppositely charged surface of Na-kaolinite particles and superior polymer chain extension probably contributed to this result. Flocculation performances comparable to

that obtained using Percol 721 indicate that polymer–clay hydrogen bonding prevailed over intramolecular hydrogen bonding of the clay particles.

The copolymer from DMA-*co*-AM-3 gave a flocculation performance comparable to that of the commercial polymers and, at the same time, a solution conformation which was insensitive to changes in solution pH and the presence of electrolytes. This suggests that a potential application for this type of copolymer could be for the effective treatment of variable pH aqueous streams which might also contain electrolytes.

CONCLUSIONS

A reproducible flocculation test procedure was developed using Na–kaolinite suspensions in water which was sensitive to the average polymer chain extension and the structure of acrylamide-based polymers. Using this procedure, the average settling rate decreased and the radius of gyration, $\langle r_g \rangle$, increased as the proportion of DMA in the DMA-*co*-AM copolymers increased. These results are explained by hindered hydrogen bonding for these copolymers.

Both the settling rates and $\langle r_g \rangle$ decreased as the proportion of MeAM in the MeAM-*co*-AM copolymers increased. These results are attributed to the diminished bridging ability of the copolymers from decreased polymer extension. The decrease in average settling rates observed for an increased proportion of NTBAM in the NTBAM-*co*-AM copolymers is credited to both hindered hydrogen bonding and the diminished bridging ability of the copolymers.

Supernatant turbidity was found to be influenced mainly by the bridging ability of the copolymers and, therefore, the floc size. The lowest values obtained for supernatant turbidity coincided with the highest average settling rates. No clear distinction could be made between floc size and floc density with the low percent solids test media used.

Greater chain extensions were found for the cationic derivatives prepared from the nonionic copolymers than for their nonionic precursors. However, flocculation tests using the new cationic derivatives gave lower average settling rates and higher supernatant turbidities relative to those of the commercial polyelectrolytes, probably due to their higher charge densities. The higher average settling rates and lower supernatant turbidities

observed for tests using Percol 721 (cationic PAM), in particular, are attributed to the low charge density, greater $\langle r_g \rangle$, and, therefore, greater bridging ability of Percol 721.

The greater M_w and $\langle r_g \rangle$ values of the commercial polymers than those of the newly synthesized copolymers explains the higher average settling rates and lower supernatant turbidities obtained for commercial polymers. However, for a similar M_w and a slightly lower $\langle r_g \rangle$, the copolymer from DMA-*co*-AM-3 gave settling rates and supernatant turbidities comparable to those of the commercial polymers. This performance, plus the resistance to conformation change with pH or the presence of an electrolyte, suggests that these copolymers could have broader applications than have the current commercial polyelectrolytes. Procedures developed here also confirm that AM copolymerization with the tested substituted acrylamides is possible to produce M_w 's and $\langle r_g \rangle$'s which are adequate for flocculant applications.

Energy Mines and Resources, Devon, Alberta, are thanked by the authors for the provision of support and facilities, without which this research would not have been possible. The Government of British Columbia and the University of Victoria are also thanked by the authors for support (K. A. K.) of this research. The authors are also grateful to Laurier Schramm, of the Petroleum Recovery Institute (Calgary), for conducting a particle-size analysis and for measuring the isoelectric point of the prepared homoionic Na–kaolinite.

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