Effect of Molecular Weight of Poly(*N*-isopropyl acrylamide) Temperature-Sensitive Flocculants on Dewatering

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The influence of molecular weight (MW) and dose of Poly(N-isopropyl acrylamide) (PNIPAM) (temperature-sensitive flocculant) on sedimentation rate, sediment density, and supernatant clarity of silica suspensions was investigated. The addition of PNIPAM resulted in rapid sedimentation ($T >$ critical solution temperature, CST) and low sediment moisture ($T <$ CST). Higher MW polymers resulted in more effective flocculation and sediment consolidation. At 10 ppm, PNIPAM (3.6 million Da) produced 20 m/h settling rate and 48 vol % solids sediment density, whereas 0.23 million Da polymer produced 0.1 m/h settling rate. PNIPAM produces effective flocculation and consolidation by cycling the interparticle interactions between repulsion and attraction as temperature is cycled around the CST. The change in temperature produces a hydrophilic/hydrophobic transition of the polymer, influencing adsorption onto the surface and the inter-particle forces. Conventional polyacrylamide flocculants (not influenced by temperature), cannot be used to produce both rapid sedimentation and dense sediments. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2070–2080, 2009
Keywords: flocculation, temperature-sensitive polymer, solid–liquid separation, solids dewatering

Introduction

Solids settling and sediment consolidation are two important steps in solid/liquid separation practice in mineral tailings treatment. They usually take place in a thickener and a settling pond, respectively.[1,2] In the thickener, the fine solid particles are flocculated and settle down quickly where most of the liquid is removed. The thickened solid sediments are then further consolidated in the settling pond to minimize the liquid content over a longer period of time. Efficient liquid removal by the thickener requires a rapid solid settling rate that is dependent on the solid aggregate size and density. Also, efficient consolidation of the sediment bed is related to the compressive yield strength of the bed that depends on interparticle forces.[1,3–5] The challenge faced by the mineral industry is how to effectively and economically treat tailings containing large amount of colloidal solid particles. These particles are stabilized by interparticle repulsive forces in liquids and settle extremely slowly under the influence of gravity alone. Thus it is very difficult for these fine solids to be removed from liquids by gravity sedimentation, therefore resulting in poor efficiency of solids dewatering. In most cases, some polymeric flocculant, such as polyacrylamide (PAM), is used to induce attractive forces between fine particles to form large size flocs that can settle down quickly for efficient solids dewatering.[6–8] The most common action mechanism of PAM as flocculant is the adsorption of large molecular weight (MW) polymer onto multiple particle surfaces, which results in the formation of large and loose flocs via polymer bridging attraction.[9,10] The flocculation

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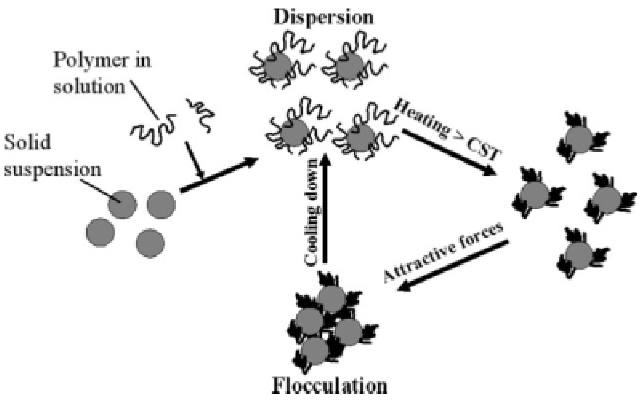

Figure 1. Schematic illustration of how PNIPAM is used in controlling aggregation (attractive forces) and dispersion (repulsive forces) of mineral suspensions.

behavior is strongly dependent on the physiochemical properties of the polymer such as functional groups, charge density, and MW.[9–12] The flocs formed by this type of flocculant are hydrophilic in their surface properties. The strong bridging force created by conventional PAM flocculants results in high compressive yield stresses and hinders the consolidation of sediments and underflows. As a result, a large amount of water is trapped in the flocs. This has an adverse effect on the water release during the stage of sediment consolidation.

The development of novel flocculants with better performance than PAM would be useful in managing tailings dewatering. One class of new flocculants are stimuli-sensitive polymers,[13,14] such as chitosan and Polyacrylicacid (pH-sensitive polymers),[15] methylcellulose (a low MW temperature-sensitive polymer),[14] and poly(*N*-isopropyl acrylamide) (PNIPAM) (a temperature-sensitive polymer).[2,13,16–19] These polymers have been tested in flocculating for example, TiO_2 with a 2×10^5 Da MW (weight average MW) PNIPAM,[17] kaolin with a 3.95×10^6 Da MW (number or weight average not specified) PNIPAM,[18] zircon with an 86,000 Da MW (approximately according to the manufacturer) methylcellulose,[14] and kaolinite with 3.2×10^6 Da M_n (number average MW) PNIPAM.[19] In these cases, the flocculation is induced at temperature above the (CST) of the polymer where the polymer becomes hydrophobic and poorly soluble in aqueous solution.

The role of PNIPAM as a flocculant has been extended by Franks and coworkers[13,14] to also include a role as a consolidation aid when the temperature is reduced to below the CST after sediment formation. With this concept, both rapid solid sedimentation and low sediment moisture are possible for much more efficient solids dewatering.[13,14] Unlike conventional PAM polymers, that have no response to stimuli, the stimuli-sensitive polymers can be used to manipulate the interparticle forces corresponding to a change of stimuli conditions, such as from repulsive to attractive (See Figure 1). First the appropriate amount of PNIPAM is added into the slurry and mixed with the solid suspension at room temperature which produces repulsion between the particles keeping them dispersed. At a temperature higher than the CST, the PNIPAM produces attraction between particles and induces aggregation of the solid suspension. By cooling the suspension below the CST, the repulsion between particles can be re-established. As illustrated in Figure 2, the approach can be used to form hydrophobic solid aggregates which settle rapidly at high temperature. After settling is finished, the temperature is reduced to create repulsion between particles to break up the flocs and to induce more water release from the sediment.[13,14] Thus, using this type of stimuli-sensitive polymer as a novel flocculant would lead to the development of a novel strategy/process technology for improving the entire solids dewatering process including both solid settling and sediment consolidation.

This article presents results of the application of the temperature-sensitive polymer, PNIPAM as a flocculant in solids dewatering. The focus is on the effect of PNIPAM MW and dose on the sedimentation rates and sediment consolidation of a silica suspension. The aims of the current study are to find the optimal PNIPAM MW and dosage range for rapid and efficient solids dewatering. In addition, we compare a conventional PAM flocculant with the PNIPAM flocculants.

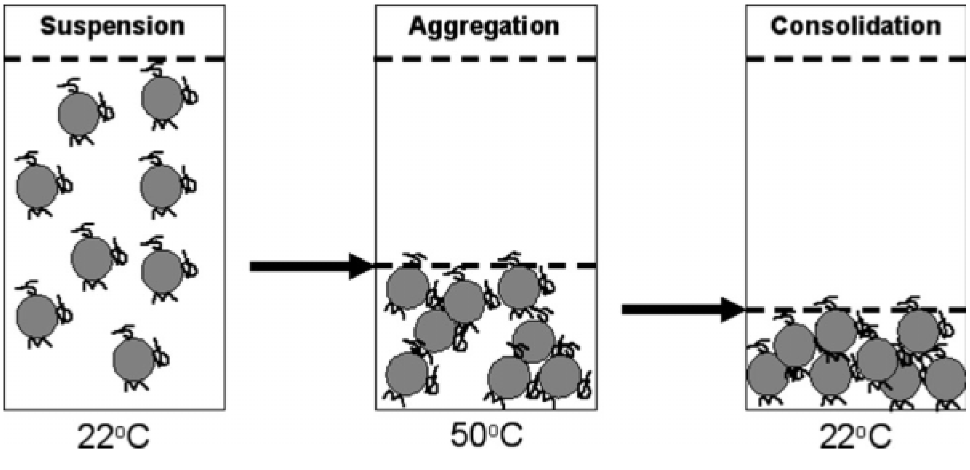

Figure 2. Schematic illustration of the use of temperature responsive flocculation in aggregation (sedimentation) and sediment consolidation.

Experimental

Materials

A silica powder (Silica 400G) was obtained from Unimin Australia Limited. It has a density of 2.64 g/cm^3. The particle size distribution is 80% minus 20 micron, 53% minus 10 micron, and 30% minus 5 micron. The BET surface area of the powder is 1.7 m^2/g. The silica powder contains 99.6% silica and traces of alumina, ferric oxide, titania, and lime.

Temperature-sensitive polymers, poly(*N*-isopropyl acrylamide) (PNIPAM), with four MWs were investigated. PNIPAM is nonionic. A PNIPAM with low MW of 0.23×10^6 Da MW (weight average MW) was purchased from Sigma-Aldrich, Australia. Two PNIPAMs with medium and high MWs, 0.71×10^6 and 2.00×10^6 Da MW, were purchased from Polymer Source, Canada. PNIPAMs with the highest MWs of 1.32×10^6, 1.80×10^6, 3.60×10^6, and 4.50×10^6 Da MW were synthesized in our lab as described in detail elsewhere.[20] The weight average MWs of the polymers were determined by Gel Permeation Chromatography with online light-scattering using a Shimadzu instrument as described elsewhere.[20] The polymers were dissolved in distilled reverse osmosis-treated water at room temperature at pH = 6.0 as a 0.1 wt % flocculant solution. PNIPAM has a CST of 32°C,[18] below which the polymer is soluble in water but becomes insoluble above it. This phase transition is reversible. A cationic PAM flocculant, Zetag7570 with medium MW (approximately about 5 to 8 million Da), was obtained from Ciba Specialty Chemicals. It was prepared in a 0.1 wt % flocculant solution in distilled reverse osmosis treated water at pH = 6.0.

Settling tests

Settling tests were carried out in 100 mL glass cylinders at a number of combinations of polymer MW, dosage, and temperature. For each settling test, the solid suspension was prepared with 5 g silica and distilled reverse osmosis-treated water containing 0.01 M $NaNO_3$. Appropriate volume of polymer solution (0.1 wt %) was added to make a final suspension concentration of 5 wt % solids. The pH value of the suspension was measured at 6.0 ± 0.2. After the suspension was filled in the cylinder, it was sealed with a parafilm wax film and gently shaken upside down several times to mix the suspension and polymer solution. The cylinder was placed on a flat solid surface and the settling test began; no further disturbances were allowed. The descent of the solids/liquid interface (mudline) was carefully observed and recorded as a function of settling time. The slope of the settling curve at time zero was obtained as the initial settling rate. Each settling test was conducted at two temperatures, (22°C) below and (50°C) above the PNIPAM critical transition temperature (CST = 32°C). To maintain the required temperature at 50°C, a water bath was used. After the polymer solution was mixed into the suspension, the cylinder was immersed into the water bath controlled at 50°C for 5 min to warm up. Then the cylinder was gently shaken upside down several times and was put back into the water bath and the settling test started immediately. The turbidity of the supernatants was measured with a HACH 2100 AN turbidity meter after a specified period of sedimentation.

Sediment consolidation tests

After 2 h of settling at 50°C, the sediment volume reached an apparent equilibrium and showed no more variation; the sediment volume was recorded. The cylinder was taken out from the water bath and allowed to cool down to room temperature. The height of the sediment/solution interface was monitored for 24 h until another apparent equilibrium was noticed where no additional consolidation was observed. This sediment volume was also recorded. The final sediment density (volume fraction of solids) was determined by conservation of mass based on the relationship:

$$\phi_{\text{init}} h_{\text{init}} = \phi_{\text{fin}} h_{\text{fin}} \tag{1}$$

where ϕ_{init} and h_{init} are the initial volume fraction of solids and suspension height and ϕ_{fin} and h_{fin} are the final volume fraction of solids and suspension height. To evaluate the polymer performance on sediment consolidation, the water release percentage was calculated based on the sediment volume changes recorded at 50°C and 22°C.

$$\text{Water Release} = \frac{(V_{50} - V_{22})}{V_{50}} \times 100 \tag{2}$$

where, V_{50} is the sediment volume at 50°C and V_{22} is the volume at 22°C.

PNIPAM adsorption measurements

PNIPAM adsorption on to silica surfaces was investigated with the depletion technique. This method involves equilibrating a polymer dosed silica suspension at the desired conditions, centrifuging the suspension to separate the solid from the supernatant then extracting and analyzing the supernatant.[20] The concentration of polymer remaining in the supernatant is measured by determining the total organic carbon (TOC) in the supernatant and comparing the value to a known calibration standard. The difference between the concentration of the polymer as dosed and that found in the supernatant corresponds to the amount of PNIPAM adsorbed onto the silica. Using this information and the surface area of the silica, the adsorption isotherms can be determined. For each MW of PNIPAM, the mixtures of PNIPAM and solid suspension (5 wt %) were allowed to equilibrate at 25 and 65°C, respectively. Both of the mixtures were allowed to stand for 2 days until adsorption equilibrium was reached. A third set of experiments was conducted with equilibration at 65°C for 24 h followed by equilibration at 22°C for 24 h to investigate desorption of the polymer. A more detailed description can be found elsewhere.[20]

Results

Effect of PNIPAM MW on the flocculation of fine solids

Figure 3a shows an example of the typical sediment mudline vs. time data for silica suspensions with 10 ppm PNIPAM as a function of MW at room temperature (22°C). At 10 ppm, PNIPAM is not an effective flocculant for silica for any of the MWs investigated at room temperature. Figure 3b

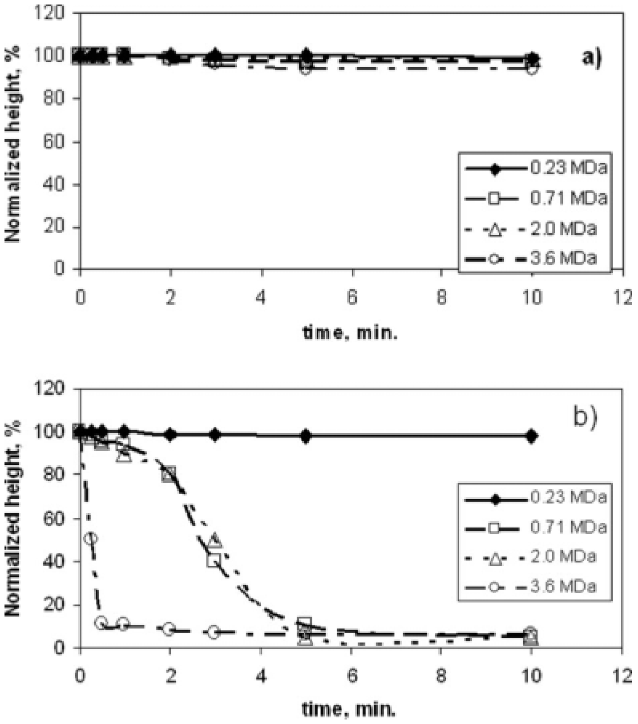

Figure 3. Height of mudline vs. time for 5 wt % silica in 0.01 M $NaNO_3$ solution flocculated with 10 ppm various MW PNIPAMs at, (a) 22°C and (b) 50°C.

is an example of the settling behavior under the same conditions except at 50°C. In this case, the PNIPAM of sufficiently high MW acts as a flocculant and the influence of MW is clear.

Figure 4a shows the settling rate of silica suspensions at room temperature as a function of PNIPAM MW and dose. At a room temperature, PNIPAM is not an effective flocculant. Well dispersed suspensions were obtained at most conditions. The highest MW polymers (2.0 and 3.6 million Da) produce a weak bridging flocculation at doses around 4 to 5 ppm as demonstrated by the maximum in sedimentation rate (2–3.5 m/h) at those dosages. Figure 4b presents the results of initial settling rate at 50°C against the dosage of PNIPAM for the four MWs investigated. It clearly displays that silica aggregation (settling) is much improved at 50°C (compared to 22°C) and strongly dependent on the PNIPAM MW and dosage.

Without any PNIPAM addition, the solids settling rate at 50°C is very low (near zero), indicating that changing temperature alone did not change the dispersion state of solid suspension. At low PNIPAM dosage of 4 ppm, only the PNIPAMs having high MWs (2 and 3.6 million Da) induced observable silica aggregation with settling rates of 1.6 and 8.9 m/h, respectively. These results imply that larger and denser aggregates were formed by higher MW PNIPAM. On the other hand, no significant flocculation occurred with the PNIPAMs with low MWs (0.23 and 0.71 million Da) as their settling rates are smaller than 0.1 m/h. To allow these low MW PNIPAMs to induce aggregation, higher PNIPAM dosage is required. At a moderate PNIPAM dosage of 10 ppm, the PNIPAM with 0.71 million Da induced aggregation at a settling rate of 1.10 m/h. The PNIPAM with 0.23 million Da still did not produce flocculation even at 10 ppm dose. At the same dose, the PNIPAM with 3.6 million Da produced a settling rate as high as 19.90 m/h. The high MW PNIPAM is more effective in inducing effective silica aggregation at a low PNIPAM dosage. Once the PNIPAM dosage was increased to 20 ppm, the PNIPAMs with low MW started to induce observable solid aggregation. The 0.23 million Da PNIPAM induced a 2.1 m/h settling rate and 5.1 m/h for a 0.71 million Da PNIPAM. Comparatively, the other two PNIPAMs having high MWs induced very quick solid settling (both near 20 m/h). The PNIPAM with the highest MW of 3.6 million Da seems to have reached its maximum aggregating ability because the settling rate did not increase as dose was increased above 10 ppm. All results clearly demonstrate that the ability for a PNIPAM to perform efficient solids aggregation is determined by its MW and dosage. The PNIPAM having higher MW has stronger aggregating ability than that with lower MW, less dosage is needed for the high MW polymer to induce effective solid aggregation.

It was also observed during the settling tests that the PNIPAM MW has an effect on the supernatant clarity. Figures 5a–c are photos showing the supernatant clarity as a function of the PNIPAM MW and dose after settling for 2 h at 50°C. It can be observed that the PNIPAM with higher MW produced clearer supernatant. The 3.6 million MW PNIPAM

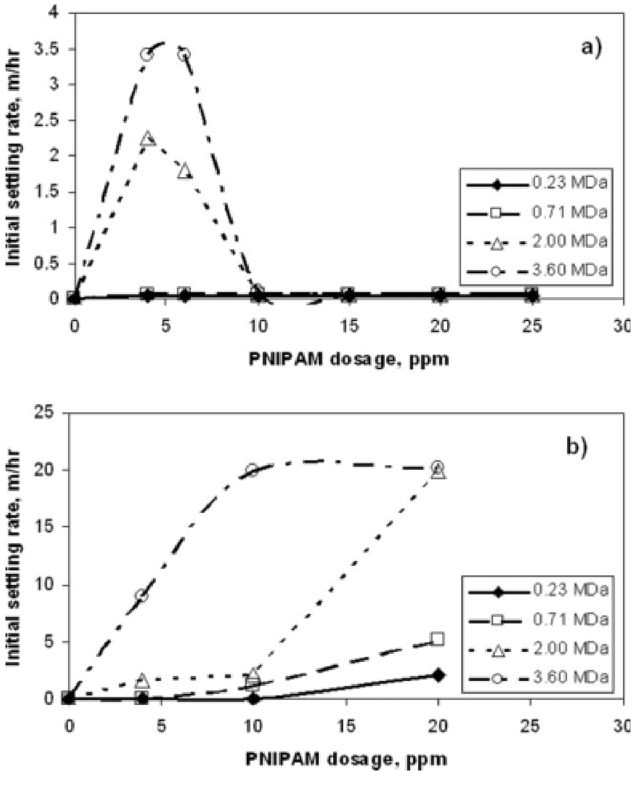

Figure 4. Initial settling rates of 5 wt % silica in 0.01 M $NaNO_3$ solution flocculated with PNIPAM at various MWs and dosage at, (a) 22°C and (b) 50°C.

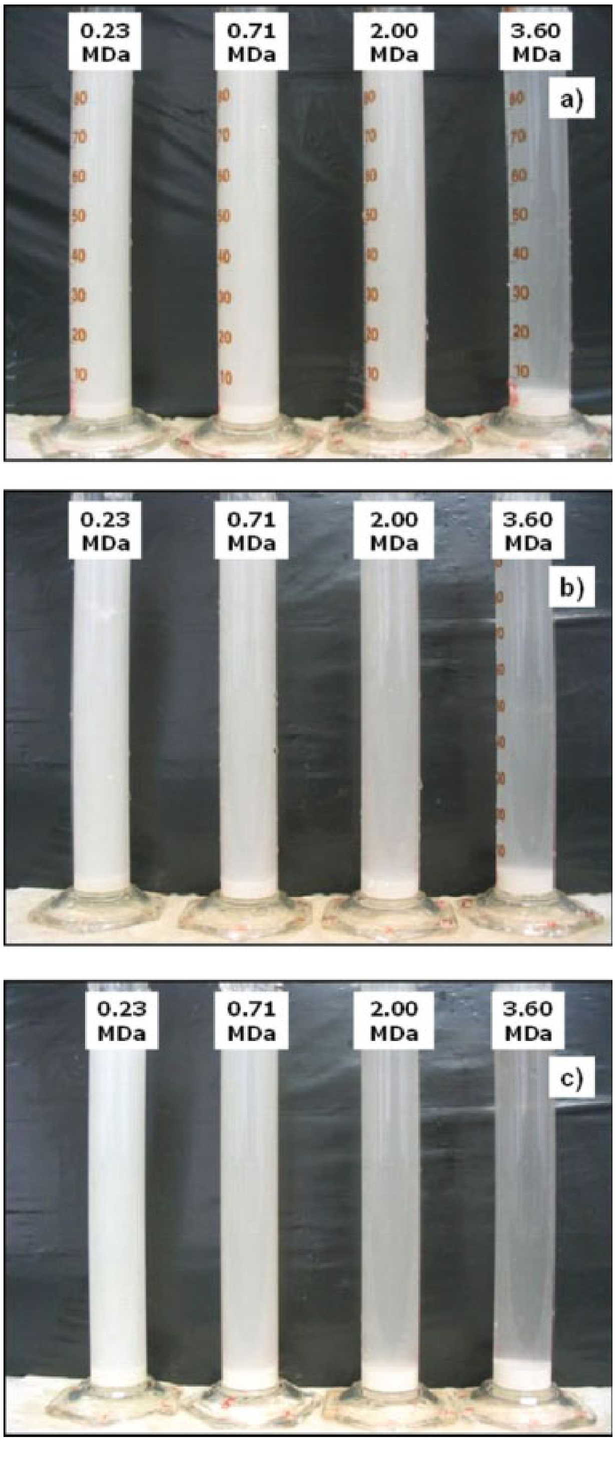

Figure 5. Photos showing the effect of PNIPAM MW and dosage on supernatant clarity at 50°C after 2 h of sedimentation [PNIPAM dose: (a) 4 ppm, (b) 10 ppm, and (c) 20 ppm].

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

produced an almost clear supernatant. However, the PNIPAMs with low MWs are not able to produce such clear supernatant and the situation with the 0.23 million Da MW PNIPAM appears to be the worst as the supernatant is almost opaque. Figure 6 shows the turbidity of the supernatant of 5 wt % silica suspensions aggregated at 50°C with 5, 10, and 20 ppm, of 0.23×10^6, 1.8×10^6, and 4.5×10^6 Da PNIPAMs after 2 h settling as a function of polymer dose and MW. These observations reflect the same PNIPAM MW-dependent performance as the settling tests. These phenomena can be explained by the knowledge that PNIPAMs with low MW do not produce interparticle attractive forces that are strong enough to induce efficient solids aggregation. Perhaps it would be possible to produce a strong attraction with low MW PNIMAM at a larger dose of PNIPAM than investigated here, but it would be less practical for industrial application.

Considering the results of both silica settling rate and supernatant clarity induced by the four PNIPAMs at 50°C, it was found that the PNIPAM with the highest MW (3.6 million Da) achieved the best flocculation performance when compared with the lower MW polymers. Based on the results of initial settling rates against PNIPAM dosage, the recommended optimum PNIPAM dosage for flocculation of this silica with the 3.6 MDa PNIPAM was between 10 and 20 ppm.

Effect of PNIPAM MW on sediment consolidation

Figure 7a shows the equilibrium solids volume fractions after 2 h sedimentation time at 50°C as a function of polymer dose and MW. The larger MW polymers which produce the faster sedimentation rates also produced the least dense sediments. This result is consistent with the behavior observed with conventional flocculants, where strong attraction produced both large rapidly settling aggregates and difficult to densify sediments.[10,21] After the silica aggregation and settling step (induced by PNIPAM at 50°C) which has resulted in the final sediment densities shown in Figure 7a, the temperature was then reduced below the PNIPAM CST to change the interparticle interactions from attractive to repulsive. Strong attractive forces between particles result in aggregated particle networks that are difficult to consolidate because the adhesive bond holding individual particles together, needs to be broken for consolidation and rearrangement to occur.[3,4,14,22] Repulsive interactions lead to much higher solids volume fraction during consolidation because

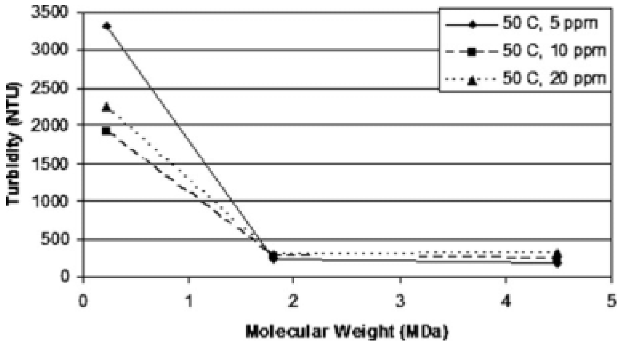

Figure 6. Turbidity (Nephelometric Turbidity Units (NTU)) of supernatants after 2 h settling for 5 wt % silica suspensions flocculated with PNIPAM at 50°C at various doses and MWs.

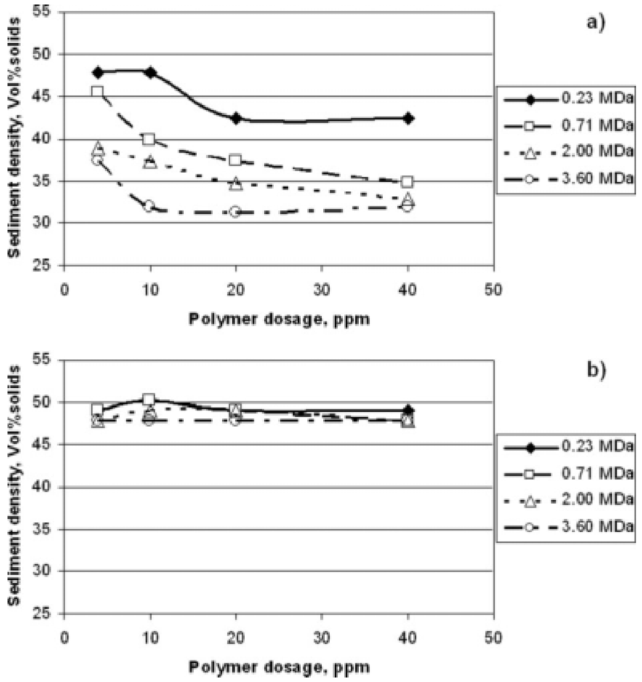

Figure 7. Density of sediment (in volume % solids) as a function of PNIPAM MW and dose (a) after 2 h at 50°C and (b) after 2 h at 50°C followed by 24 h at 22°C.

the particles are not stuck together. They are free to rearrange into more dense packing configurations under the applied consolidation pressure.[3,4,14,22] In the case of the sediment beds investigated in the current work, the weight of the particles themselves result in the consolidation pressure driving the densification process. The change in particle interaction from attraction to repulsion results in more water release and sediment consolidation over a period of time. The final sediment solids volume fractions after sediment consolidation tests conducted at 22°C for 24 h are presented in Figure 7b. In this case, the sediments for all polymer doses and MWs consolidate between 47 and 50 vol % solids. The highly dense sediments are a result of the repulsion between particles at room temperature which leads to sediments that are easy to consolidate.

The additional water released during consolidation is shown in Figure 8. The sediment releases more water with increased PNIPAM MW and dosage. This is primarily because the sediment with high polymer MW and high dose produced the least dense sediments during the 50°C sedimentation step. In fact, as shown in Figure 7b after consolidation at 22°C, all the sediments reach a final solid concentration of between 47 and 50 vol % solids. The advantage of using the high MW polymer is that it can produce a fast sedimentation rate and clear supernatant. Thus solid/liquid separation can be conducted both rapidly and efficiently. From the results of both settling rates (Figures 3 and 4) and sediment consolidation (Figures 7 and 8), it can be concluded that the preferred PNIPAM to achieve satisfactory solid settling and sediment consolidation is to use a high MW polymer at a low to moderate dosage. Therefore, the

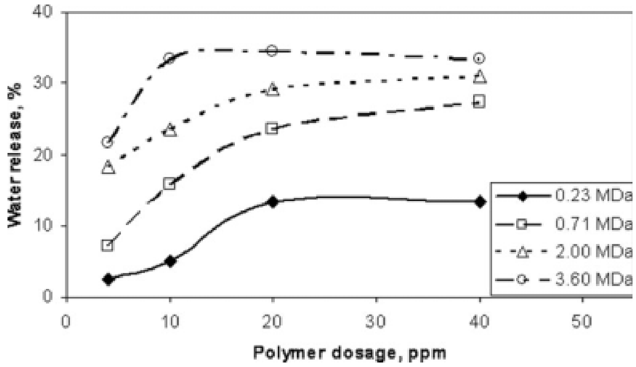

Figure 8. Effect of PNIPAM MW and dosage on sediment water released when temperature is reduced from 50°C to 22°C.

PNIPAM with 3.6 million Da MW should be recommended for practical application.

Comparison between PNIPAM and PAM

The results presented above clearly demonstrate that the temperature-sensitive polymer PNIPAM can play a dual-role in promoting both solids aggregation (settling) and sediment consolidation. The performance of PNIPAM has also been compared with a conventional PAM flocculant. Comparison tests between PNIPAMs and a PAM (MW about 5 to 8 MDa and cationic) were conducted. Settling tests were carried out at both 22 and 50°C. Sediment consolidation tests were conducted by keeping the suspension at 50°C for 2 h than decreasing the temperature to 22°C for 24 h. The settling rates and sediment bed volumes were recorded and sediment density was calculated based on sediment volumes.

The comparison of settling rates between PNIPAM and a PAM are presented in Table 1. It can be seen that both PNIPAM and PAM induced solids aggregation at 50°C. The PNIPAM with 3.6 million MW produced a 19.90 m/h settling rate at 10 ppm addition. In the case of PAM, the sedimentation rate produced was 17.2 m/h, which is a little lower than that with high MW PNIPAM but higher than that with other three low MW PNIPAMs. At room temperature, only the conventional PAM polymer produced good sedimentation rates.

Figure 9 presents photos taken at the end of the settling and consolidation tests of the PNIPAM (3.6 million Da MW) and PAM. These photos compare the sediment volumes produced by PAM and PNIPAM. In the case of settling at 50°C, the PAM produced a 12 mL sediment as seen from Figure 9a, whereas a 6 mL sediment was formed by the PNIPAM (Figure 9b). After consolidation at 22°C, the PAM was not found to produce any further water release from the sediment as the same volume (12 mL) sediment

Table 1. Initial Settling Rates of Suspensions Flocculated with Conventional PAM and PNIPAM

	22°C	50°C
No polymer	<0.01 m/h	<0.01 m/h
PAM, 10 ppm	17.70 m/h	17.20 m/h
3.6 M Da PNIPAM, 10 ppm	0.11 m/h	19.90 m/h

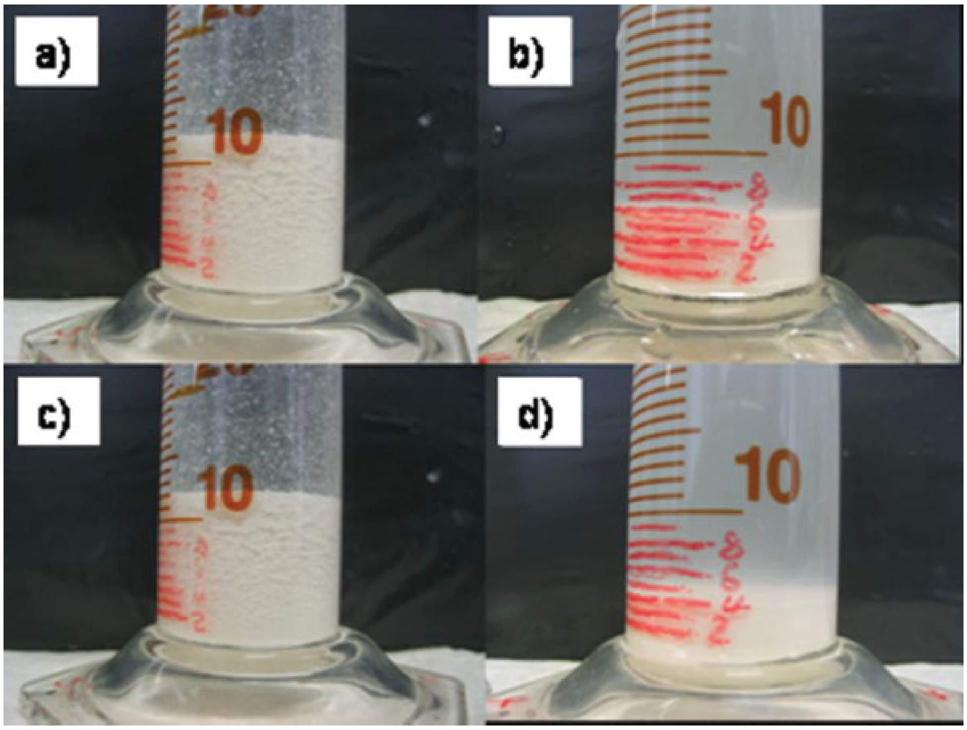

Figure 9. Comparison of sediment volumes after 2 h at 50°C [(a) and (b)] and after consolidation for 24 h additional time at 22°C [(c) and (d)] for conventional PAM [(a) and (c)] and 3.6 million MW PNIPAM [(b) and (d)] at 10 ppm dosage each.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bed was observed in Figure 9c. However, the sediment volume was further reduced by the PNIPAM to a lower value of 4 mL after 22°C consolidation as seen in Figure 9d, meaning more water was released during sediment consolidation. When compared with PAM, the final sediment volume induced by PNIPAM and thermal cycling is only one third of that induced by PAM. Consequently, the two polymers produced sediments with significantly different volume fractions (densities) as shown in Figure 10. The sediment solids concentrations were found to be 16 vol % for PAM vs. 31 vol % for PNIPAM after settling at 50°C. After consolidation at 22°C, the PAM sediment remained at 16 vol %, whereas the PNIPAM sediment consolidated to 47 vol %. Obviously, PNIPAM has an advantage over PAM because it produces denser sediments and slightly faster settling. Therefore, more water can be recovered, although the consolidation stage will take some time (typically 3 h or less).[15] The only disadvantages of using PNIPAM are that the supernatant clarity is not as good as conventional PAM and the cost of PNIPAM may be more than conventional polymeric flocculants. Perhaps MW even higher than 3.6 million Da PNIPAM will improve supernatant clarity and production costs of PNIPAM will decrease with increasing production volumes. If the temperature of the suspension needs to be significantly increased to implement the use of temperature responsive flocculation and consolidation, it is likely that the capital and operating costs will be prohibitively expensive. It is likely that the new processing concept will be most useful in processes where there is already an inherent temperature change in the process. Examples of processes where the suspension requiring solid–liquid separation is at elevated temperatures (around 50 to 90°C) early in the process and later naturally cool to ambient temperature include red mud from the Bayer process and leach residues such as from nickel laterite processing.

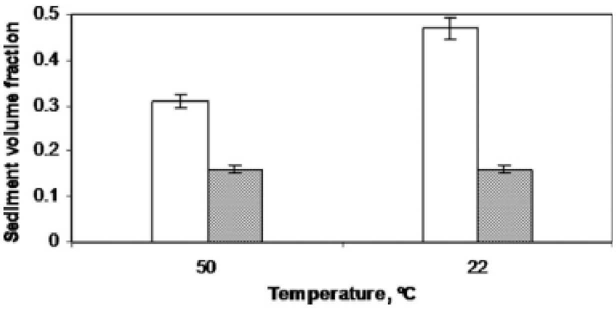

Figure 10. Comparison of sediment densities in volume fraction solids after 2 h at 50°C and after consolidation for 24 h additional time at 22°C for conventional PAM (textured gray bar) and 3.6 million MW PNIPAM (white bar) at 10 ppm dosage each.

PNIPAM adsorption onto solids surfaces

The effect of PNIPAM MW and temperature on the adsorption of polymer onto silica surfaces is shown in the adsorption isotherms presented in Figure 11. In this set of experiments, PNIPAMs of 1.32 and 4.52 million Da were

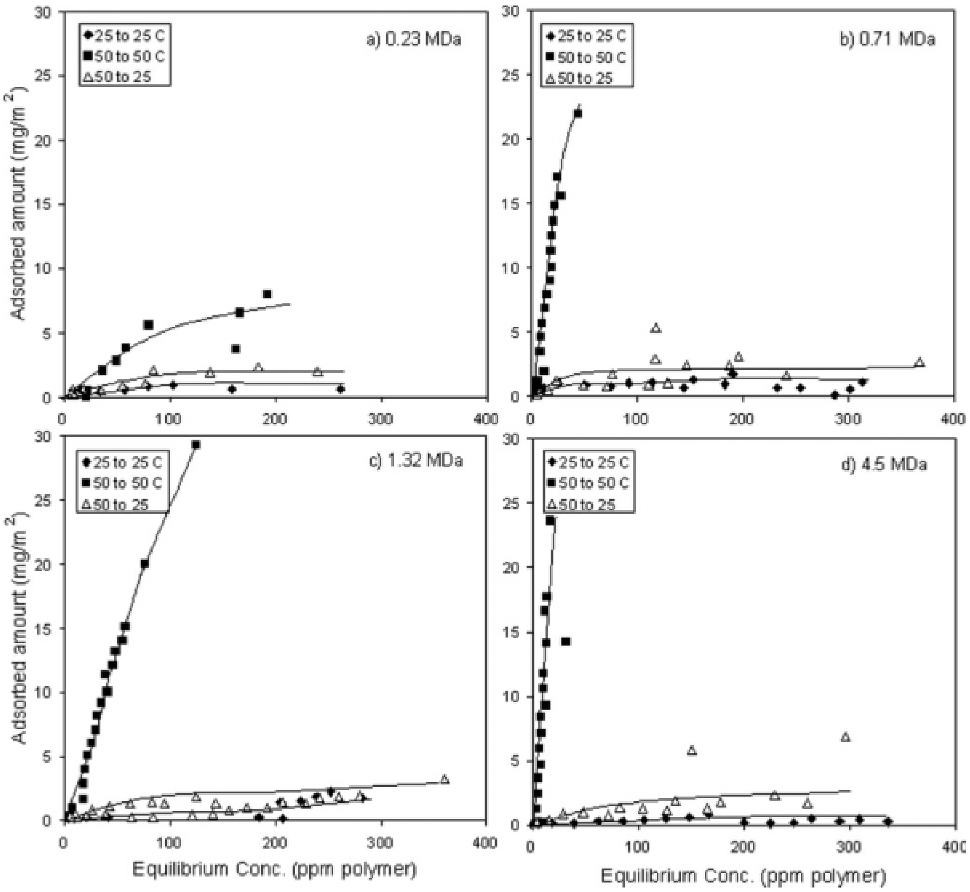

Figure 11. Adsorption isotherms [adsorbed amount (mg/m^2) vs. equilibrium concentration (ppm) of polymer] of PNIPAM on to silica equilibrated 48 h at 25°C, 50°C, and after 24 h at 50°C followed by 24 h at 25°C for: (a) 0.23 M Da, (b) 0.71 M Da, (c) 1.32 M Da, and (d) 4.5 M Da MWs.

used in place of the 2.0 and 3.6 million Da polymers used in previous experiments due to lack of sufficient quantity. At 22°C, it can be seen from Figure 11 that the adsorbed amounts are relatively low and that there is no obvious difference between PNIPAMs with different MWs. However, the amounts of PNIPAM adsorped were dramatically increased at 65°C, although there is still no clear trend with different MWs. Another important finding from the adsorption measurements is that the PNIPAM adsorption is largely reversible. That is, most of the polymer adsorbed at 65°C desorbs form the silica surface when the temperature is reduced to 22°C.

Discussion

PNIPAM role in promoting solids dewatering

The test results presented above clearly demonstrate that PNIPAM has better performance than PAM in both solids settling and sediment consolidation. Differences in the molecular structure of the two polymers (See Figure 12) account for their performance difference. The molecular structure of PNIPAM leads to the unique property that PAM does not have, that is, PNIPAM is sensitive to the changes of temperature of the aqueous solution.[18,23] At temperature below the CST, the hydrogen atoms of the amide groups and the oxygen atoms of the carbonyl groups will be hydrogen bonded to water molecules. At temperature above the CST, the thermal energy is sufficient to break the H-bonds between polymer groups and water; instead, hydrogen bonds

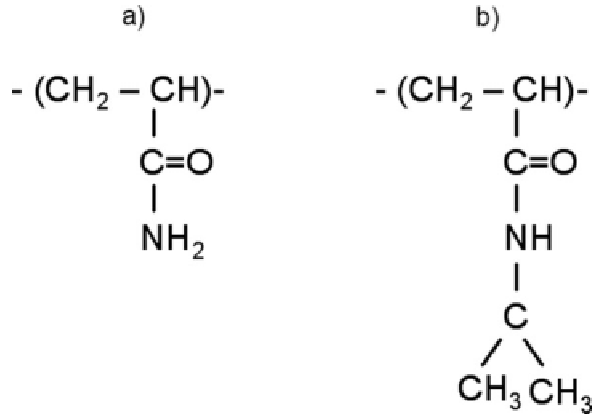

Figure 12. Molecular structures of (a) Polyacrylamide (PAM) and (b) Poly(*N*-isopropyl acrylamide) (PNIPAM).

between carbonyl oxygen atoms and the hydrogen on the amide groups are favored. These result in intra- and intermolecular hydrogen bonding which causes the polymer to change its conformation in solution such that the hydrophobic backbone and methyl groups of the PNIPAM are exposed to the solution, whereas the hydrophilic amide and carbonyl groups are wrapped up in the polymer core. The presentation of hydrophobic groups to the aqueous solution, the intermolecular hydrogen bonding, and entropic reasons cause the PNIPAM molecules to aggregate and precipitate out of solution at temperature above the CST.

At room temperature, the adsorption of PAM and PNIPAM onto mineral surfaces is controlled by similar mechanisms. At room temperature, the PAM and PNIPAM are adsorbed to mineral surfaces by a combination of hydrogen bonding and van der Waals interactions.[24] The adsorption of PAM is not influenced significantly by temperature of aqueous solution. On the other hand, the strong adsorption of PNIPAM at temperature above the CST is driven by the highly unfavorable interaction between the polymer molecule (in its high temperature conformation) and water. To get out of the water, the polymer will adsorb on the nearest surface heterogeneously rather than precipitate homogeneously from solution as in the case of solution without suspended solids.

The temperature dependant adsorption of PNIPAM on solid surfaces makes it possible to manipulate the interparticle interactions to be repulsive or attractive via changing temperature. When the surfaces of mineral particles are covered with PNIPAM at temperature above the CST, the particle surface becomes hydrophobic. The hydrophobic surface of the particles results in attraction between particles[18,25] and aggregation results. The primary mechanism of PNIPAM in promoting solids dewatering is now clear. PNIPAM possess the ability to modify the particle surface hydrophilic/hydrophobic properties and in turn to manipulate interparticle repulsive/attractive force when temperature is used as a switch to stimulate PNIPAM. In contrast, the PAM molecules play their role in solids flocculation mainly via bridging[10,24] which does not depend strongly on temperature.

Also it was found that the MW of PNIPAM plays an important role in determining the dewatering behavior of suspensions. The importance of polymer MW suggests that the mechanism for attraction between particles is not purely due to a hydrophobic attraction. Hydrophobic attraction would not be expected to be dependent on polymer MW. The strong dependence of aggregation on MW suggests that the polymer bridging mechanism also plays a role. Perhaps subtle differences in the surface coverage, layer thickness, or nanoscale topography of the adsorbed layer (which may depend upon the MW of the polymer) are responsible for the MW dependence of the flocculation behavior. Initial preliminary results indicate that increasing the temperature to a greater extent above the CST tends to improve the settling rate and supernatant clarity.

Influence of polymer addition and shear during aggregation

The results presented here appear to differ somewhat from the results found recently in a similar study by Li et al.,[19] concerning the use of PNIPAM as a flocculant. In their study, a maximum settling rate of only about 2 m/h was found at high temperature, whereas we have found settling rates approaching 20 m/h (for 3.6 MDa PNIPAM). To produce the maximum settling rate, we used only 10 ppm (for 3.6 MDa PNIPAM), whereas Li et al.[19] required 500 ppm. Some of the key differences in the studies are as follows. The study of Li et al.[19] is on kaolinite. Although the particle size is not presented in the publication, dispersed kaolinite particles are typically sub micron in size. Our work is on silica with average particle size of about 10 microns. A substantial difference in settling rate would be expected for the two different size particles. In this study, the polymer MW is 3.6×10^6 Da, on a weight average basis, whereas the PNIPAM used by Li et al.[19] was 3.2×10^6 Da, on a number average basis. The difference between number average and weight average measurements means that our polymer had significantly higher MW, which we have shown is important in determining settling rate. Also, our tests were conducted at 50°C, whereas those of Li et al.[19] were at 40°C. Although no results are presented here, in preliminary studies, we have found that increasing temperature (over the range 40–50°C) improves both sedimentation rate and supernatant clarity. Finally, and most importantly, we believe that both the method of mixing the polymer solution into the suspension and the shear conditions during the temperature increase are important in determining the aggregate properties. It is known that the mixing and shear conditions during aggregation with conventional PAM flocculants strongly influence the aggregate size and density which influences the settling rate and supernatant clarity.[26–28] It is not unusual for different flocculation procedures to produce settling rates that vary by more than an order of magnitude.[28] In both the current work and the work of Li at al.,[19] the polymer solution was added to the suspension at room temperature. In our work, the polymer was mixed into the solution by inverting the cylinder several times then the suspension was warmed to

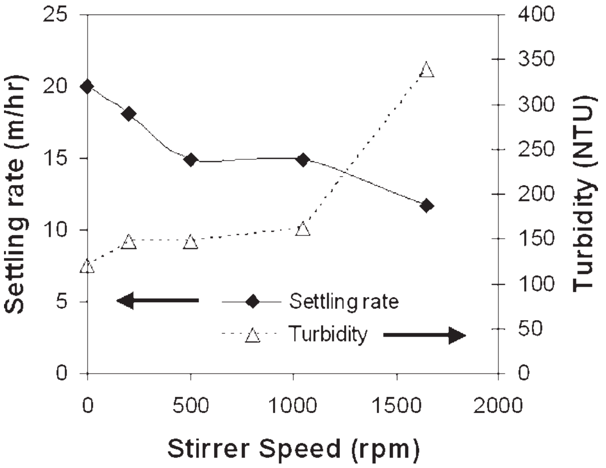

Figure 13. Initial settling rates and turbidity [Nephelometric Turbidity Units (NTU)] of supernatants after 30 min for 5 wt % silica suspensions flocculated at 50°C with 20 ppm, 2×10^6 Da PNIPAM as a function of mixing impeller rotation speed (3 min mixing).

50°C without being disturbed. Then the cylinder was inverted a few times again before the settling test began. Li et al.[19] instead heated the suspension to 40°C while stirring at 1000 rpm. Figure 13 shows results of settling rates and supernatant clarity of 5 wt % silica suspensions aggregated at 50°C with 20 ppm, 2×10^6 Da PNIPAM as a function of shear during aggregation measured in our lab. The suspension was heated to 50°C then subject to stirring at the rate indicated in Figure 13 for 3 min. The suspension was poured into a cylinder then left for 2 min to rest at 50°C. The cylinder was inverted 5 times and the settling tests initiated. The results clearly indicate that the increased shear produces lower sedimentation rates and more turbid supernatants. This is consistent with the breaking down of aggregates which occurs for conventional polymeric flocculation during shear.[26–28] This evidence suggests that the vigorous mixing during heating the suspension used by Li et al.[19] produced aggregates of smaller size resulting in slower settling. We also recently reported[29] that reduced sedimentation rates are observed when the polymer solution is added to suspensions which are already at temperature above the CST. Therefore, it is very important how the suspension is handled during addition of polymer solution and increasing of temperature.

Conclusions

The temperature-sensitive polymer, PNIPAM, was found to play a dual-role in fine solids aggregation and sediment consolidation of silica suspensions by cycling the temperature around the CST. Rapid sedimentation was observed above the CST and dense sediments resulted below the CST. The conventional flocculant, PAM, does not have the same ability. The highest MW PNIPAM (3.6 MDa) produced the fastest settling rates (up to 19.9 m/h) and clearest supernatants at 50°C and only required 10 ppm dosage. After consolidation at 22°C, the final sediment density was between 47 and 50 vol % solids, independent of polymer MW although only the high MW polymers (>1 MDa) produced rapid sedimentation. The action mechanism of PNIPAM in playing the dual-role (flocculant and consolidation aid) is to manipulate the interparticle forces (repulsive/attractive) via a hydrophilic/hydrophobic polymer transition when the temperature is cycled below/above the CST. The methods of both addition of the polymer and raising the temperature are critical in controlling the sedimentation behavior and supernatant clarity. Potentially, PNIPAM-based flocculants could be used in industry as a replacement for conventional PAM flocculants to enable more efficient solids dewatering for processes where temperature change is inherent in the process.

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