Controlling Thickener Underflow Rheology Using a Temperature Responsive Flocculant

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*Continuous solid–liquid separations with the temperature responsive flocculant poly (*N-*isopropylacrylamide) (PNIPAM) were conducted in a pilot-scale thickener for the first time, using fine quartz as the feed slurry. The performance in continuous operation was compared to batch sedimentation. The increase in sediment consolidation on cooling in batch sedimentation was less significant in the continuous operation due to kinetic limitations of the deeper sediment bed and shorter residence times in the pilot-scale thickener. The reduction in underflow rheology which results when using the temperature responsive polymer as flocculant is significant. Paste-like behavior results when underflow is discharged at 50°C, whereas low viscosity, near Newtonian behavior results when the underflow is discharged at 20°C. Compared to conventional polyacrylamide-based flocculants, PNIPAM produces higher concentration underflow but lower clarity overflow and most importantly, significantly reduced underflow rheology (viscosity and yield stress). Temperature responsive flocculants have significant potential to reduce underflow pumping energy and cost for mineral tailings.* © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2940–2948, 2014

Keywords: thermosensitive polymer, stimulant responsive flocculation, poly (N-isopropylacrylamide), solid–liquid separation, thickening, dewatering

Introduction

Gravity thickening is commonly used to separate solid particles from liquids to produce a liquid rich phase which exits the device at the top (overflow) substantially free of solid particles and a concentrated suspension rich in solid particles which exits the device at the bottom (underflow).[1–3] The underflow suspensions usually have to be pumped to another unit operation or waste facility.[4–6] Although in many operations the performance of the thickener and underflow density is adequate for the needs of the process flow sheet, improvements in throughput, and separation efficiency (increasing solids concentration in the underflow and decreasing solids in the overflow) are usually desirable.[1–3] Reduction of the viscosity of the underflow (at constant solids concentration) will reduce the pumping energy requirements and cost.[4–6] In many mineral processing operations management of the tailings is a significant environmental issue. Improving solid-liquid separation efficiency while reducing the underflow rheology will improve the sustainability of the industry and minimise impact on the environment.[4,5] In most cases, rapid sedimentation and high solids concentration of the underflow are desirable as this improves throughput and efficiency of the thickener.[1–3]

Many mineral tailings contain a sufficient fraction of fine colloidal particles (low mass) which do not settle sufficiently rapidly to be viably removed from the liquid by gravity sedimentation. In these cases, the fine particles are typically aggregated by adding an agent which induces attraction[7,8] between the individual fine particles to produce flocs (aggregates) which have sufficient mass and size to sediment under the influence of gravity at sufficient rate to be viably removed in a thickener.[1,9] The most commonly used agents to induce attraction between fine mineral tailing particles are synthetic polyacrylamide-(PAM) based flocculants of very high-molecular weight[9] which we refer to as conventional flocculants in this article. These polymers typically adsorb onto multiple particles creating strong bonds between the particles primarily by bridging attraction.[10,11] The resulting flocs have sufficiently large mass and size to induce sedimentation at a rate much faster than the individual particles making solid–liquid separations in a gravity thickener viable.[1] Unfortunately, consolidation to high density in the consolidation zone and low viscosity underflow is difficult to achieve when conventional flocculants are used, because the conditions which produce rapid sedimentation (attraction between particle) are usually mutually exclusive from those conditions that produce high-density particle packing and low viscosity (repulsion between particles).[7,8,12–14] The conventional synthetic PAM-based flocculant promotes strong attraction between particles in both the settling and consolidation zones of the thickener as well as within the underflow pipeline. Although the strong attraction produced by bridging

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polymers produces large flocs which settle rapidly, the persistence of the attraction between particles during the consolidation stage leads to difficulty in producing high density during consolidation and low viscosity during pumping of underflow.[10]

The development of temperature responsive flocculants has led to a variety of polymers which can be reversibly used to turn flocculation on and off.[15–17] The aim of this work has primarily been to enable both rapid sedimentation and consolidation (dense underflow).[17]The focus of the early work[15,16] was on controlling sedimentation or stability of suspensions. These researchers pioneered the use of poly (*N*-isopropylacrylamide) (PNIPAM) in this application. PNIPAM has a lower critical solution temperature (LCST) around 32°C such that the polymer is soluble in aqueous solution at temperature below 32°C and poorly soluble at temperature above 32°C.[18,19] The change of solubility of polymer adsorbed onto particles surfaces changes the action of the polymer from a dispersant at T < the LCST (steric repulsion between particles due to polymer brushes extending into good solvent[20]) to a flocculant at T > the LCST (attraction between particles due to adsorbed polymer in a poor solvent[21]). Sakohara and coworkers[22–24] have adopted a slightly different approach where they aim to improve dewatering by using both the change in solubility of the polymer and mechanical force to squeeze the water out of the flocculated suspension. In this approach, the polymer is used to stabilize the suspension by steric repulsion (polymer brushes extend into solution, keeping particles from contacting each other)[20] at room temperature. Then, the suspension is heated to induce a change from hydrophilic to hydrophobic nature of the polymer to induce flocculation. Additional consolidation results due to rearrangement of particles in the flocs induced via a plunger type apparatus.[22–24] Xu and coworkers,[25] use the change in conformation of the polymer from extended at room temperature to coiled at high temperature to pull the particles together and induce flocculation. The change in conformation of the polymer to the coiled state on heating is believed to be the mechanism for reduced water content in the final sediment.[25] This work also showed a direct link between increased adhesion between particles and increased initial sedimentation rate. Kuznik and coworkers[26,27] have studied the size of the flocs produced with PNIPAM-based flocculants. They also explain why reversible flocculation only occurs when the polymer dosage is sufficiently high to induce suspensions stabilized by steric mechanism.[26] The concept of temperature responsive flocculation has also been investigated using other polymers such as methycellulose[17] and pullulan[28] as well as poly (N-vinyl caprolactam).[29,30] In addition, PNIPAM has been found to be a useful flotation reagent for fine particles as it acts both as a flocculant and collector.[31–33]

The approach our group has taken is similar to that used by Guillet and coworkers[15,16] where the particle interaction is changed between attraction and repulsion, but in addition, we further realized that by reversing the stimuli within the sediment bed (or consolidation zone of the thickener), additional consolidation could improve the solid–liquid separations[17] and decrease the rheological behavior of the suspensions.[34] Our group also investigated the influence of polymer architecture including molecular weight[35,36] and both charged random[37] and block[38] copolymers of PNIPAM. To date the work of all these research groups has been conducted on the bench scale in small batch sedimentation jar tests. The aim of this article is to investigate solid–liquid separations in a continuous pilot-scale thickener using PNIPAM as a temperature responsive flocculant. The underflow density, overflow clarity, and underflow rheology are the key parameters investigated. The use of high-molecular weight PNIPAM is compared to conventional commercial PAM-based flocculants.

Experimental

Materials

A fine quartz powder obtained from UNIMIN Australia Limited (Silica 400G) was used as the solids to be investigated. The silica powder contained 99.6% silica and traces of alumina, ferric oxide, titania, and lime. The particle-size distribution of the silica particles was measured using light scattering, and was determined to have a D_{80} of 20 μm, a D_{50} of 8 μm, and a D_{30} of 5 μm. The density of the silica particles is 2670 kg/m^3. It was chosen as a substrate because it has particle size and surface chemistry typical of mineral tailings in many operations which have quartz as primary gangue component. The PNIPAM homopolymer used in this work had the molecular weight of 6 MDa. This polymer was synthesized by aqueous free radical polymerisation initiated by redox couple ammonium persulfate/sodium metabisulfite as described elsewhere.[36] To make 10 g quantities, three necked flasks were used rather than Shlenk tubes. Two conventional commercial PAM flocculants were trialled and compared to the PNIPAM. Magnafloc 351 is a nonionic PAM with high-molecular weight and Zetag 7530 is believed to be a high-molecular weight moderately charged cationic PAM. Both polymers were obtained from Ciba Specialty Chemicals which has subsequently become part of BASF. The polymers were added to the suspensions as aqueous solutions which were prepared between 24 and 48 h prior to the start of the experiment. PNIPAM was prepared as 0.6 wt % solution, the Magnafloc 351 as 0.134 wt % solution, and the Zetag 7530 as 0.16 wt % solution. Preliminary bench scale jar tests indicated the minimum dosage to produce visibly clarified supernatant for PNIPAM was 720 g/tonne and for Magnafloc 351, 445 g/tonne. As such these were the dosages used in the continuous pilot thickener tests. For Zetag 7530, the minimum dosage to produce visibly clarified supernatant was 445 g/tonne. This dosage was doubled to 890 g/tonne for the continuous pilot thickener tests to investigate the influence of larger flocs and better clarity supernatant.

Pilot-scale thickener

A continuous pilot-scale thickener rig has been designed and fabricated as introduced elsewhere.[39] The cylindrical transparent Perspex column is about 1.5 m tall and 30 cm in diameter. The bottom of the column is fitted with a cone, that is, 20 cm in height to allow underflow discharge. The schematic representation of the column as well as a column photograph are presented in Figure 1a, b. The feed suspension (50 wt % solids) is mixed in a tank with predissolved polymer. An overhead Rushton turbine mixer and a pump to circulate the suspension help to minimise sedimentation within the feed tank. The column feed is composed of a combination of two streams; a concentrated feed stream from the feed tank and a fresh tap water stream. By adjusting the respective flow rates of these two streams the feed

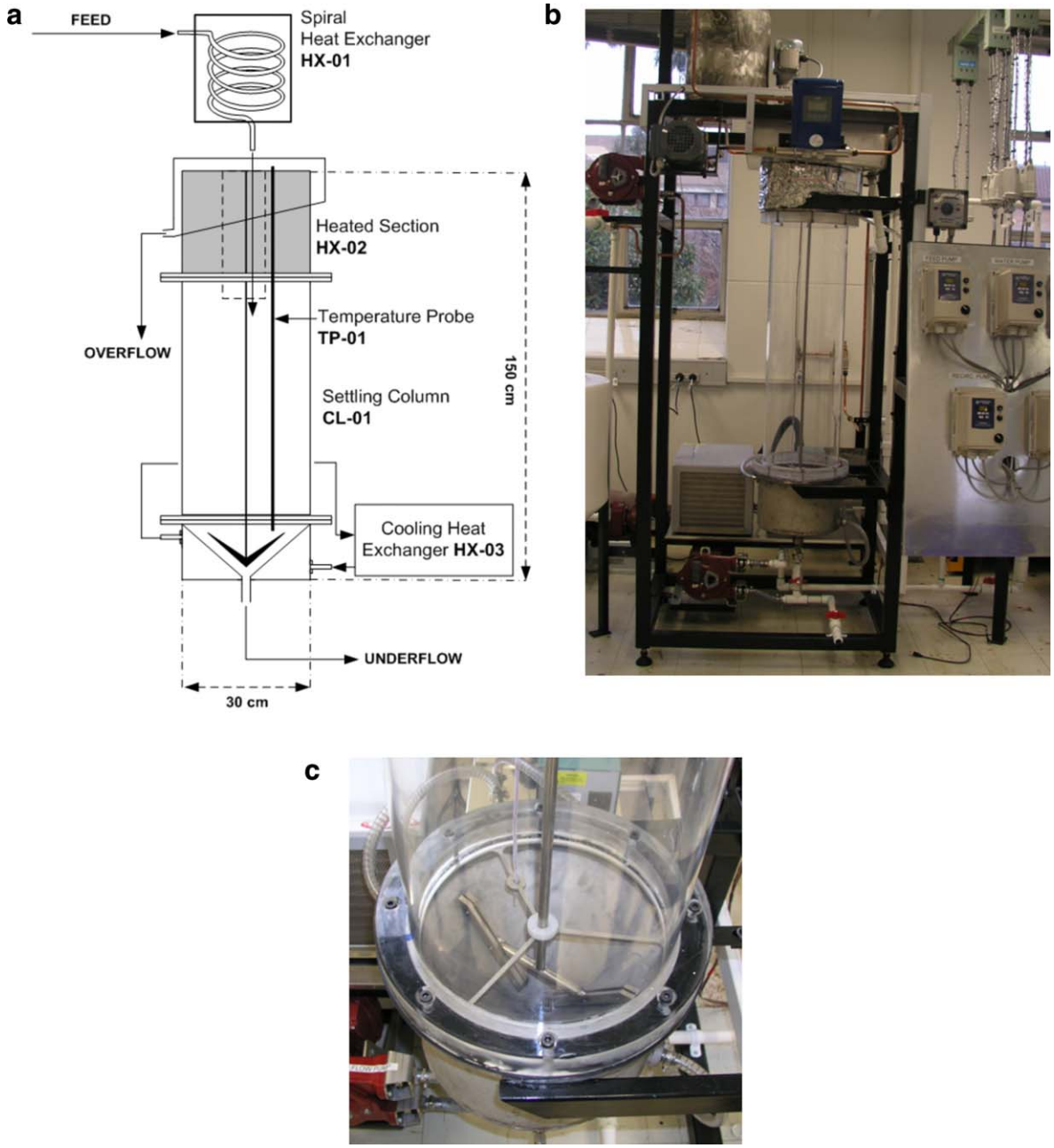

Figure 1. (a) Schematic representation of the pilot-scale thickener column.

(b) Photo of the column. (c) Detail of the cone scraper at bottom of column. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

composition was controlled to be 8.5 wt % solids. The feed is pumped through a heat exchanger (HX-01) to heat the suspension to about 50°C to activate the PNIPAM as flocculant. HX-01 consists of a copper pipe (7 m long by 10 mm ID) which is coiled in a cylindrical hot water bath. The suspension is pumped through the coiled copper pipe. The hot suspension is fed to the feedwell (10 cm in diameter and 40 cm in length) at the top of the column (indicated by dashed line at top of Figure 1a). This allows for the addition of the column feed at a level well below that of the column overflow and assists in obtaining improved overflow clarity. The temperature at the top of the column is controlled to temperature above the LCST (typically 50°C) with resistive heating tape (HX-02). The clarified overflow passes over a weir and is gravity fed to a drain. The temperature of the underflow is controlled by a jacketed conical section (HX-03) at the bottom of the column. Either hot or cold water is pumped through the jacket on the cone to control the underflow to either 50 or 20°C. The conical section of the column is also fitted with a cone scraper (see Figure 1c) rotated at 0.33 RPM to prevent the formation of dead zones and channels through the sediment bed. Although raking with picketed rakes has significant influence on underflow solids concentration,[2,40,41] this type of apparatus has been avoided in this work which instead of investigating influence of rake geometry, focuses on the influence of temperature of the discharge as a mechanism to switch the particle interaction force from attractive to repulsive. The underflow is continuously

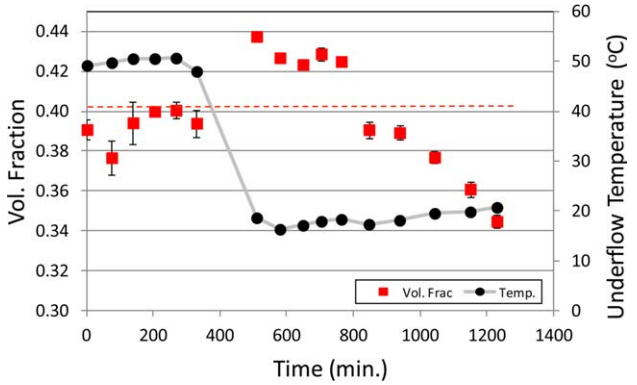

Figure 2. Typical underflow solids concentration as a function of time and temperature for a silica suspension flocculated with 720 g/tonne PNIPAM (Data shown is from Run 2 which is similar to Run 1).

The filled black circles are the data for the temperature (right side y axis) and the filled red squares are the volume fraction of solids in the underflow (left side y axis). The error bars indicate the range of the three measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pumped out of the bottom of the column into a storage tank. The temperature profile is measured by a temperature probe (TP-01) that has 10 different thermocouples in a bundle located at 15 cm intervals from the top of the column to a location about 2 cm above the cone scraper. Positive displacement pumps are used to transport the feed and underflow suspensions.

Continuous solid–liquid separation tests

In the case of experiments with PNIPAM, the feed tank was filled up to 50 L with tap water. 12 L of 0.6 wt % PNIPAM polymer solution was added to the feed tank (72 g total polymer). KCl of 302 g, predissolved in 4.5 L of water was added to feed tank. Silica of 100 kg was then slowly added to the feed tank over about 30 min. 33.5 L tap water was added to the mixing tank to bring the solution up to 100 L total. The feed was allowed to mix for 30 min to 1 h. The suspension in the feed tank consists of 50 wt % solids suspension (suspension density = 1450 kg/m^3) with 720 g/tonne PNIPAM in 0.04 M concentration of KCl. The suspension was kept mixed by continuously pumping from the bottom apex of the tank through a vertical loop and back into the top of the tank as well as by an overhead stirrer (Rushton turbine). The natural pH of the suspension was between pH 5 and 6; no adjustment was made.

The column was filled with 2.5 $\times$ 10^{-3} M KCl aqueous solution at 50°C and the top and bottom of the column were maintained at 50°C with heat exchangers HX-02 and HX-03. The utility water in heat exchanger HX-01 was maintained at 55–60°C. A small pump transferred 4 L/h of the 50 wt % suspension (5.8 kg/hr suspension) in the feed tank from a T junction in the feed tank recirculation loop into HX-01. Before entering HX-01, the feed was diluted to 8.5 wt % solids by addition of tap water with another pump (28.3 L/h dilution water added). The diluted feed passed through a flow rate measurement device before entering the copper coil in heat exchanger HX-01. The feed entering HX-01 (and the feedwell) contained 8.5 wt % solids, 720 g/tonne solid of PNIPAM, and 2.5 $\times$ 10^{-3} M KCl. The total feed rate to HX-01 (and the feed well) was 32.3 L/h suspension corresponding to a mass flow rate of 2.9 kg solid per hour. The feed exiting HX-01 was found to be between 48 and 54°C and large flocs were observed. The flocs settled through the feedwell down through the column and began to form a sediment bed. The cone scraper was rotated at 0.33 RPM. The clarified overflow ran over the weir and into a drain. After about 4 h the sediment bed had increased to about 15 to 20 cm above the bottom of the cylindrical section of the thickener. The underflow pump was turned on and the flow rate adjusted over the next couple of hours to maintain a steady-state height of the top of the sediment bed. Two runs (Run 1 and Run 2) were conducted with PNIPAM where the bottom of the column was initially kept at 50°C for about 6 h, (after steady state is reached) then cooling the bottom of the column to 20°C and running for another 15 or 18 h. Samples of the underflow and overflow were taken at regular intervals typically every 60 to 90 min. The underflow sample was taken through a T junction, small pipe and valve attached to the underflow just under the apex of the bottom of the column. The overflow sample is taken just before it enters the drain. Three samples were taken and averaged for the measurement of solids in the underflow and overflow.

In the case of the experiments with the conventional flocculants, a similar procedure was followed except for the following differences. The entire column and HX-01 were maintained at ambient room temperature (20°C) for the whole experiment. No polymer was added to the feed tank. The polymer was added via a metering pump and a T junction into the 10 mm ID feed pipe 9.2 m before the feed pipe enters the feedwell. In Run 3, the Magnafloc 351 was dosed at a rate of 0.96 L/h of 0.134 wt % polymer solution (1.3 g polymer/h corresponding to 445 g/tonne solid). In Run 4, the Zetag 7530 was dosed at a rate of 1.567L/h of 0.164 wt % polymer solution (2.57 g polymer/h corresponding to 890 g/tonne of solid. A final experiment was conducted where PNIPAM was combined with Zetag 7530 (Run 5). In this case, the experiment was conducted as for the other experiments with PNIPAM, except that an additional small dosage of

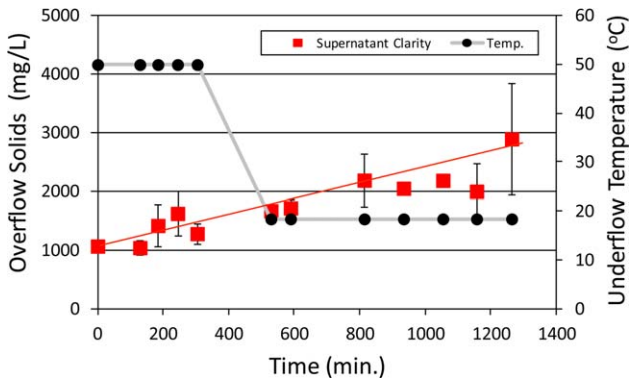

Figure 3. Typical concentration of solids in the overflow as a function of time and temperature for a silica suspension flocculated with 720 g/tonne PNIPAM (Data shown is from Run 1 which is similar to Run 2).

The filled black circles are the data for the temperature (right side y axis) and the filled red squares are the volume fraction of solids in the underflow (left side y axis). The error bars indicate the range of the three measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

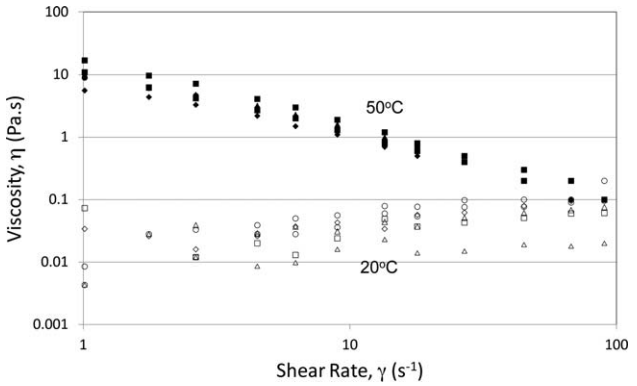

Figure 4. Comparison of underflow rheology of silica suspensions flocculated with 720 g/tonne PNIPAM discharged at 50°C (filled symbols are from the first 330 min of the run) and 20°C (unfilled symbols are from 500 to 1200 min of the run; Data from Run 2 shown here is similar to Run 1).

Zetag 7530 was added to the hot suspension 9.2 m before entering the feed well. In this case, the Zetag 7530 was added at a rate of 0.96 L/h of 0.034 wt % solution (0.33 g polymer /h corresponding to 115 g/tonne solid).

Samples of the feed, underflow, and overflow were taken regularly, typically every 60 to 90 min. The solids content of the samples was measured by weight loss on drying. Three samples were taken and the average and range of the samples recorded. The viscosity of the underflow was measured as a function of shear rate with a Hakke VT550 Rheometer. The viscosity measurements were conducted within a few minutes of sampling and the samples taken at 50°C discharge temperature were stored in sealed containers at 50°C for these few minutes. The measurements were made using a Couette (concentric cylinders) geometry, (profiled cup ID = 42 mm, profiled cylinder OD = 40 mm, $L = 60$ mm, recessed ends, gap = 1.0 mm). The data presented are those taken for increasing shear rate. The shear yield stress was measured with the Hakke VT550 using the vane technique.[42,43]

Results

Separations with PNIPAM at 50 and 20°C

The pilot-scale thickener could be controlled to produce steady-state operation for extended periods up to 18 to 24 h at which point the feed was exhausted (total run times 24 to 30 h including start up and approach to steady state). The steady-state condition was maintained by slightly adjusting the underflow pump flow rate to maintain a constant depth of sludge blanket (sediment bed). Figure 2 shows typical results for the volume fraction of solids of the underflow as a function of time and temperature for the 8 μm average diameter silica suspension fed to the pilot thickener at concentration of 8.5 wt % solids flocculated with 720 g PNIPAM per tonne of solid. During the first 5 h of steady-state operation, the temperature of the underflow was maintained at 48 to 50°C. The concentration of the underflow was found to be in the range of 38 to 40 volume percent solids when discharged at 48 to 50°C. After 5 h the bottom of the thickener was cooled to between 16 and 18°C. Even after cooling the bottom of the thickener, the top part of the consolidation zone remained at temperature above 45°C. Only the lowest thermocouple (just at the top of the conical discharge section, within the middle of the sediment bed) registered a temperature of 30°C, so the majority of the sediment bed was at temperature above the LCST. Three hours after the temperature change it appears steady state was achieved in the new condition. For the first few hours of the "cold" discharge part of the run, the underflow density increased slightly to between 42 and 44 volume percent solids. When observed for a longer period of time, (12 or 13 h) the concentration of the solids in the underflow steadily decreased as a function of time. This unexpected trend was observed in both Runs 1 and 2. As shown in Figure 3, the concentration of solids in the overflow increased steadily and approximate linearly as a function of time, regardless of the change in temperature.

The rheological behavior of the underflow is a very strong function of the discharge temperature. As shown in Figure 4, when discharged at nominally 50°C the suspension behaved like a paste with high and shear thinning viscosity. The discharge during this "hot" period of the run was also found to have a shear yield stress in the range about 15 to 20 Pa, as measured by the vane technique.[42,43] This behavior is typical of strongly flocculated suspensions.[13,44,45] Conversely, the suspensions discharged at nominally 18°C displayed nearly Newtonian and low viscosity (yield stresses below 0.5 Pa). (The apparent slight shear thickening is likely an artefact of the measurement known as Taylor vortices, which increase the apparent viscosity during measurement in Couette geometry of low viscosity fluids).[46] Such behavior is typical of well dispersed suspensions.[13,44,45]

Comparison with conventional flocculants

To evaluate the performance of PNIPAM as a temperature responsive flocculant for efficient solid–liquid separations and reduced underflow rheology, it is instructive to compare its performance to conventional commercial PAM flocculants.

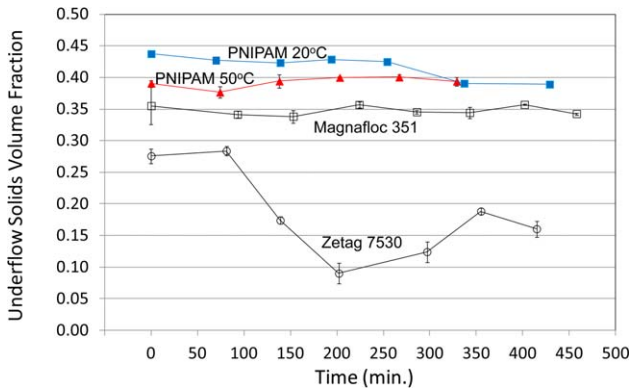

Figure 5. Comparison of underflow solids concentration for silica suspensions flocculated with PNIPAM and conventional flocculants.

Time zero corresponds to the start of steady-state operation (~2 h after the underflow pump was started or the temperature was changed). The filled blue squares are for underflow at 20°C (720 g PNIPAM per tonne of solid). The filled red triangles are for underflow at 50°C (720 g PNIPAM per tonne of solid). The unfilled squares are for underflow at 20°C (445 g Magnafloc 351 per tonne of solid). The unfilled circles are for underflow at 20°C (890 g Zetag 7530 per tonne of solid). The error bars indicate the range of the three measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

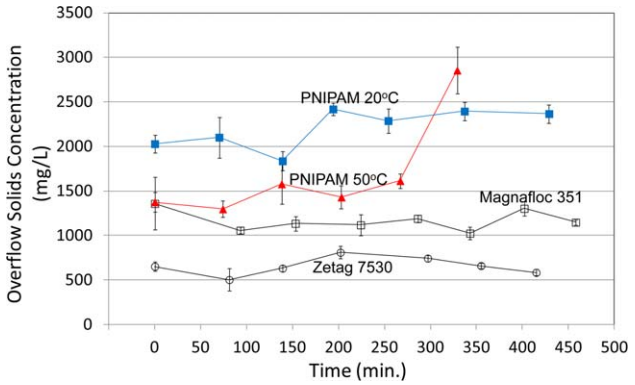

Figure 6. Comparison of solids concentration in the overflow for silica suspensions flocculated with PNIPAM and conventional flocculants.

Time zero corresponds to the start of steady-state operation (~2 h after the underflow pump was started or the temperature was changed.) The filled blue squares are for underflow at 20°C (720 g PNIPAM per tonne of solid). The filled red triangles are for underflow at 50°C (720 g PNIPAM per tonne of solid). The unfilled squares are for underflow at 20°C (445 g Magnafloc 351 per tonne of solid). The unfilled circles are for underflow at 20°C (890 g Zetag 7530 per tonne of solid). The error bars indicate the range of the three measurements. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the underflow solids concentration of the PNIPAM flocculated suspensions discharged at 50 and 20°C in comparison to two conventional flocculants. The highest underflow densities are achieved with PNIPAM when discharged at 20°C while the lowest occurs when Zetag 7530 is used. The Magnafloc 351 produces underflow with concentration around 35 vol % solids while the PNIPAM discharged at 50°C produces underflow slightly higher than the conventional flocculant Magnafloc 351. In terms of underflow density, the PNIPAM discharged at 20°C has the best performance as it produces the highest underflow solids concentration. Figure 6 compares the concentration of particles in the overflow for the temperature responsive and conventional flocculants. The Zetag 7530 flocculant has the best performance in terms of the clarity of the supernatant because it produces the lowest concentration of solids in the overflow. The results show the weakest point of using PNIPAM as a temperature responsive flocculant which is that the overflow clarity is not good for the PNIPAM when discharged at 20°C. As shown in Figure 7, the rheological behavior of the underflow flocculated with PNIPAM at 50°C and the conventional flocculants (Magnafloc 351 and Zetag 7530) was paste-like with high and shear thinning viscosity and yield stress. The yield stress of the Zetag 7530 was the highest in the range 150–200Pa, whereas the Magnafloc 351 had yield stress around 25–35 Pa and the PNIPAM discharged at 50°C had yield stress of between 15 to 20 Pa. Conversely, the underflow discharged at 20°C when PNIPAM was used as flocculant was found to be nearly Newtonian with no significant yield stress.

Discussion

Comparing continuous thickening to batch sedimentation

The increase in underflow solids concentration on discharging the suspension flocculated with PNIPAM at 20°C instead of 50°C is only minor (from about 38 to 43 vol % solids). In fact it could be argued that there is almost no change in underflow solids when a longer period of time is examined as indicated by the dashed red line in Figure 2. The steady decrease in underflow concentration with time (after the discharge temperature was decreased to 20°C) may also be due to a change in the feed as a function of time, such as particle-size distribution perhaps due to sedimentation of large particles. In the previous work, the increase in sediment concentration in batch sedimentation[35] was found to increase from about 32 to 48% for the same powder and similar polymer. The difference between these two situations is because the final sediment density and underflow solids concentration depend on two factors; the compressibility of the suspension (often referred to as the compressive yield stress) and the kinetics of removing the liquid form the suspension.[47,48] The compressive yield stress of the material (an equilibrium material property) is changed when the temperature is changed. This applies to both the continuous separation and the batch sedimentation situations. The change in compressive yield stress is related to the change in particle interaction force from attractive at 50°C to repulsive at 20°C.[17,35,49] But the kinetics of removing the water, which depends on the permeability of the suspension, the path length, and residence time are different in these two situations (P. J. Scales, personal communication) In the earlier batch sedimentation tests, the sediment depth was only about 1 to 2 cm and the residence time for consolidation was 24 h (although most of the consolidation occurred in the first 3 h).[35,36,49,50] In the continuous tests, the flow path from the apex of the discharge cone to the top of the sediment bed was 30 to 35 cm and the residence time of the sediment in the consolidation zone was about 4 to 6 h (depending on the average sediment volume fraction and height of the sediment). It is the much longer path length and shorter residence time in the consolidation zone of the pilot-scale thickener that limits the secondary consolidation of the underflow, as compared to the sediment consolidation during batch settling.

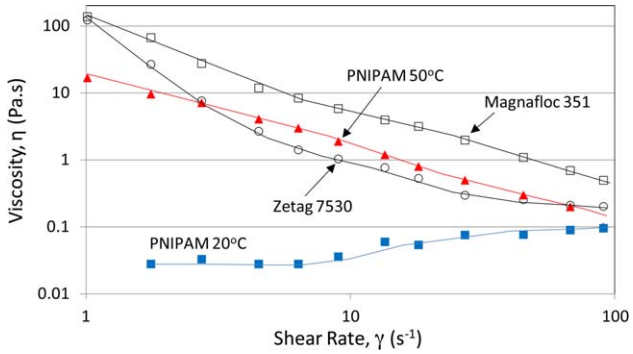

Figure 7. Comparison of typical underflow rheology of silica suspensions flocculated with PNIPAM and conventional flocculants.

The filled blue squares are for underflow at 20°C (720 g PNIPAM per tonne of solid). The filled red triangles are for underflow at 50°C (720 g PNIPAM per tonne of solid). The unfilled squares are for underflow at 20°C (445 g Magnafloc 351 per tonne of solid). The unfilled circles are for underflow at 20°C (890 g Zetag 7530 per tonne of solid). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Comparing PNIPAM to conventional flocculants

The results presented in Figures 5, 6, and 7 are consistent with strong attraction between particles when the conventional flocculants or PNIPAM at 50°C are used and repulsion between particles when PNIPAM is used as flocculant with discharge at 20°C.

First, the underflow solids concentration results (Figure 5) are discussed in terms of the role each type of polymer plays on the particle interaction forces. Magnafloc 351 is a nonionic conventional PAM-based flocculant. It produces underflow discharged at about 35 vol % solids, typical of many conventional flocculants which create bridging flocculation. The Zetag 7530 is a cationic PAM-based flocculant and as such has strong affinity of the negatively charged silica particles surface. In addition, the higher dosage of the Zetag 7530 results in large loose flocs (as observed visually). These conditions produce strong open flocs which resist consolidation and as such the underflow concentration is significantly lower when Zetag 7530 is used. The underflow discharged at 50°C flocculated with PNIPAM has slightly higher solids concentration than when Magnafloc 351 is used. This indicates that the PNIPAM discharged at 50°C creates a slightly weaker attraction than the Magnafloc 351. This is likely due to the lower molecular weight of the PNIPAM, (6 MDa, compared to ~10 to 15 MDa for the Magnafloc 351) and perhaps the different flocculation mechanism of the two polymers (adsorbed polymer brushes in poor solvent for PNIPAM at 50°C[21] and polymer bridging for Magnafloc 351). The high solids concentration underflow discharged at 20°C when PNIPAM is used as flocculant indicates that the PNIPAM acts to create steric repulsion between the particles at room temperature.[21]

The results of the overflow clarity (Figure 6) tell a similar story. The lowest concentration of solids in the overflow was found when Zetag 7530 was used and is consistent with it producing the strongest attraction between particles and collecting the largest fraction of the particles in the flocs. The Magnafloc 351 and the PNIPAM at 50°C perform marginally poorer than the Zetag 7530 (higher concentration of solids in the overflow). This is consistent with the magnitude of the attraction between particles being slightly greater when Zetag 7530 is used. The highest concentration of solids was found in the overflow when the PNIPAM was used as flocculant but discharged at 20°C. It is unlikely that the increased concentration of the solids in the overflow was due to lowering the temperature of the discharge because the entire free settling zone was still at 50°C and the top about half of the consolidation zone was between 45 and 30°C. The gradual monotonic increase in overflow solids concentration shown in Figure 6 is most likely due to a slight change in feed particle-size distribution (greater fraction of small particles as time progresses) rather than due to abrupt change in temperature of the underflow.

The flow properties of the suspensions are consistent with the underflow and overflow solids data and the interaction forces described above. The Magnafloc 351 produces the highest viscosity underflow with yield stress in the range 25 to 35 Pa. This is consistent with suspension behavior of particles interacting by strong bridging attraction at 35 vol % solids. The Zetag 7530 produces an underflow which has yield stress around 150 to 200 Pa but apparent viscosity similar to the Magnafloc 351 at high- and low-shear rates but which dips at intermediate shear rates. Such behavior (reduced viscosity at intermediate shear rates) is typical of high yield stress/very viscous suspensions that slip along the rheological measurement tool surface (concentric cylinders in this case). The slip during rheological measurement results in underestimate of rheological properties. The slip and very high yield stress of the suspension (even at lower solids concentration of 10 to 20 vol % solids) is consistent with the Zetag 7530 producing the strongest attraction between the particles. The viscosity of the underflow when PNIPAM is used as flocculant and discharged at 50°C is paste-like and shear thinning indicative of attractive particle networks. As the viscosity and yield stress (15 to 20 Pa) are slightly lower than that found when Magnafloc 351 is used indicates that the attraction is not as strong between particles when PNIPAM (at 50°C) is used compared to Magnafloc 351. The low and nearly Newtonian viscosity of the underflow when PNIPAM is used as flocculant with discharge at 20°C indicates that the particles in the suspension interact with each other via steric repulsion rather than with attraction.

The data presented for underflow concentration, overflow concentration, and rheology lead to a self consistent conclusion that the strength of attraction between the particles follows the order from strongest to weakest attraction, Zetag 7530 > Magnafloc 351 > PNIPAM 50°C. PNIAPM used at 20°C results in repulsion between particles. The performance of these polymers in terms of flocculation and solid–liquid separation is consistent with this sequence.

Trading off supernatant clarity with *underflow rheology*

Overall the results indicate that PNIPAM could be a useful flocculant to produce efficient solid–liquid separations as well as low viscosity underflow when the free settling zone is maintained at 50°C and the underflow discharge is maintained at 20°C. The primary issue of concern is that the supernatant clarity is not as good with the PNIPAM as with the conventional flocculants. Table 1 compares the overflow solids concentration of the conventional flocculants with PNIPAM. Also shown is data from Run 5 performed using a combination of 720 g/tonne PNIPAM plus 115 g/tonne Zetag 7530. One can see that the PNIPAM does not capture as many of the solid particles as the conventional flocculants at the dosages investigated. Run 5 was conducted to see if a small addition of conventional flocculant (Zetag 7530) in addition to PNIPAM would be useful in improving the supernatant clarity. The data in Table 1 indicate that the combination of PNIPAM with Zetag 7530 was successful in producing the overflow with the highest clarity (lowest concentration of solids in the overflow). The underflow concentration from Run 5 was 43 vol % solids average with standard deviation 1.3% (when discharged at 20°C) which is comparable to the results from Runs 1 and 2 (when PNIPAM only was used). The rheological behavior of the underflow from Run 5 is compared to that from Run 2 in Figure 8. When the underflow is discharged at 50°C (in the flocculated

Table 1. Solids Concentration in the Overflow (mg/L)

	Average Overflow Solids	Standard Deviation
Zetag 7530 (890 g/tonne)	654	101
Magnafloc 351 (445 g/tonne)	1166	115
PNIPAM (20°C, 720 g/tonne)	2206	221
PNIPAM (720 g/tonne) + Zetag 7530 (115 g/tonne)	362	56

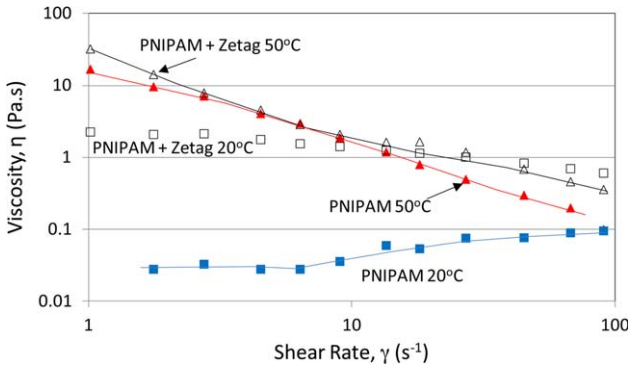

Figure 8. Comparison of typical underflow rheology of silica suspensions flocculated with 720 g PNIPAM only per tonne of solid and 720 g PNIPAM plus 115 g Zetag 7530 per tonne of solid combination.

The filled blue squares are for underflow at 20°C (PNIPAM only). The filled red triangles are for underflow at 50°C (PNIPAM only). The unfilled squares are for underflow at 20°C (PNIPAM plus Zetag 7530). The unfilled triangles are for underflow at 50°C (PNIPAM plus Zetag 7530). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

state for both PNIPAM only and PNIPAM + Zetag 7530) the behavior is paste-like and strong shear thinning is observed. The addition of the Zetag 7530 only slightly increases the viscosity of the underflow. Conversely, when the underflow is discharged at 20°C, the addition of the Zetag 7530 produces a more viscous suspension than when PNIPAM only is discharged at 20°C. These results indicate that is should be possible to tune the performance of the solid–liquid separation to obtain either high clarity overflow or low viscosity underflow, by varying the ratio of the temperature responsive and conventional flocculants. The reduction in viscosity of the underflow which may occur when temperature responsive flocculants are used could result in significant reduction in the energy (and thus cost) of pumping underflow.

Conclusions

PNIPAM has been shown to be an effective temperature responsive flocculant for efficient solid–liquid separations in a continuously operated pilot-scale thickener operated with top of column (feed) at temperature 50°C and bottom of column (underflow) at 20°C.

The underflow solids content in continuous operation (with bottom of the column at 20°C) does not reach as high a value as in sediment beds in batch sedimentation experiments after cooling. This is because the shorter residence times and deeper sediment beds in the continuously operated thickener do not allow the underflow to reach its equilibrium density. The longer pore space path length and shorter residence times within the consolidation zone mean that there is not enough time for the liquid to move through and out of the underflow particle network.

The rheology (viscosity and yield stress) of the underflow is significantly reduced when the underflow is discharged at 20°C as compared to underflow discharge at 50°C. Paste-like shear thinning behavior results when the underflow is maintained at 50°C, typical of flocculated suspensions. Low viscosity nearly Newtonian behavior is observed when underflow discharge is at 20°C, typical of well dispersed suspensions. These rheology results confirm that the particle interaction has been switched from attractive to repulsive by reduction of the temperature within the sediment particle network.

As the change in particle interaction within the consolidation zone is confirmed by the change in underflow viscosity, the lack of underflow densification is clearly attributed to kinetic limitation (permeability) rather than consolidation limitation (compressibility).

Despite the fact that the underflow solids concentration in continuous operation does not reach as high a value as in batch settling, it is still higher when PNIPAM is used as flocculant (discharge at both 20 and 50°C) compared to conventional commercial flocculants. The paste-like underflow rheology results when either conventional flocculants or PNIPAM (at 50°C underflow discharge) is used as the flocculant. When PNIPAM is used as flocculant and the bottom of the column is cooled so that the underflow discharge is at 20°C the rheology of the underflow is significantly decreased compared to the conventional flocculants. The commercial flocculants produce overflow of higher clarity than the PNIPAM. The combination of some conventional flocculant (~11%) with PNIPAM produced intermediate behavior such that overflow clarity can be improved at the expense of slightly increased underflow rheology (underflow discharge at 20°C).

The reduction in underflow viscosity enabled by thickening with PNIPAM discharged at 20°C compared to the underflow viscosity when conventional commercial flocculants are used offers the potential for significant reduction in operating expense in pumping underflow from the thickener to the tailings impoundment.

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