pH-Sensitive Flocculation: Settling Rates and Sediment Densities

George V. Franks, Carola V. Sepulveda, and Graeme J. Jameson
Centre for Multiphase Processes, The University of Newcastle, Callaghan NSW 2308, Australia

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The polyelectrolytes chitosan and polyacrylic acid have been used to flocculate alumina, silica, and zircon suspensions. The flocculant concentrations and pH were such as to cause attractive interaction forces between particles, resulting in rapid sedimentation. Initial settling rates were typically on the order of 0.1 to 5 m/hr. After the formation of a sediment bed, the pH was changed to establish repulsive forces between the particles; additional sediment consolidation was seen to occur. By creating repulsion between the particles in the sediment, the volume of sediments could be reduced by between 10 to 50% compared to attractive flocculation only. For each case, increasing the molecular weight of the flocculant increased the settling rate and improved the supernatant clarity, but decreased the density of sediments. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2774–2782, 2006

Keywords: flocculation, sedimentation, sediment density, chitosan, polyacrylic acid, stimulant sensitive polymers

Introduction

Suspended colloidal particles are constantly and randomly bombarded from all sides by molecules of the liquid, making them move in a zigzag path. This type of movement is known as Brownian motion and increases in significance as particle size decreases. Since the mass of a colloidal particle is also small, its settling rate under the influence of gravity is slow. When the effect of Brownian motion dominates, it becomes very difficult and slow to separate the particles from the liquid by gravity sedimentation.[1-3] Finely divided solids and colloidal particles, which cannot be removed from a liquid by sedimentation within a short period of time (less than a few hours), are typically converted into aggregates by coagulation and/or flocculation. The larger aggregates have more mass and the influence of gravity dominates over Brownian motion so that sedimentation occurs in a relatively short time. Flocculation, sedimentation, and dispersion of colloidal suspensions play an important role in many industrial processes, as they are related to the recovery of solids particles from liquid media and to the transport and fate of contaminants in aquatic environments. One of the most common methods of inducing aggregation is bridging flocculation with polyelectrolytes. Bridging flocculation is extremely important in wastewater treatment[4] and mineral tailings disposal.[5]

Polymeric flocculants are known to produce large and rapid settling aggregates by bridging. Bridging occurs when segments of a polymer chain adsorb on different particles and help the particles agglomerate into larger particles. Most modern industrial flocculants are polyelectrolytes based on polyacrylamide.[6] Anionic functionality is created by substituting some or all of the amide groups with acid groups. When all of the groups are acid, the polymer is polyacrylic acid (PAA). Cationic functionality is achieved in commercially available flocculants by replacing some or all of the amide groups on polyacrylamide with quatrinized amines. Typically, polyelectrolytes with opposite charge to that on the particles surface are found to be suitable bridging flocculants at low polymer doses (when the particles surfaces are only partially covered by polymer). At higher doses the polyelectrolyte acts as a dispersant by creating an electro-steric repulsion when the particles surfaces are completely covered by the adsorbed polyelectrolyte.

Correspondence concerning this article should be addressed to G. Franks at gvfranks@unimelb.edu.au.

Table 1. Colloidal Material Properties

Alumina: α-Al_2O_3	Silica: SiO_2	Zircon: $ZrSiO_4$
AKP-15 Sumitomo Corp., Japan	Nyasil 20 (95 wt % metal oxide)	Opacfine Australia—
Density: 3.98 g/cm^3	Density: 2.20 g/cm^3	Density: 4.40 g/cm^3
Particle size (d_{50}): 0.6 μm*	Particle size (d_{50}): 1.4 μm*	Particle size (d_{50}): 2.6 μm*
Isoelectric point: pH 9.0$^+$	Isoelectric point: pH 2-3$^+$	Isoelectric point: pH 3.8$^+$

*Particle sizing with Malvern Mastersizer.
$^+$Zeta potentials measured with Colloidal Dynamics Acoustosizer.

PAA is an anionic flocculant typically used to aggregate a positively charged suspension, such as hematite[7,8], and sterically stabilized polystyrene latex.[9] Another interesting natural polyelectrolyte receiving attention recently is the cationic polysaccharide chitosan. It has been used as a flocculant for treating oily waste streams,[10] mineral colloids,[11] cellular suspensions,[12] river silt,[13] and kaolinite.[14] These applications focus on flocculating negatively charged colloids, at pH values below 7 where the chitosan is soluble.

The charge on a weak polyelectrolyte is created by reaction of ionizable sites on the polymer with acid or base in the aqueous solution. The pH where 50% of the charged sites are neutral is known as the pK of the polyelectrolyte. The pK of polyacrylic acid is 6.[15] At pH below about 3, PAA is neutral and becomes negatively charged as pH is increased. On the other hand, chitosan has a pK around 6.5.[16] Chitosan becomes positively charged at pH below this value and becomes neutral at pH greater than about 7.5. The charge on these polyelectrolytes is important in making them soluble in aqueous solutions.[11,17] Typically, uncharged high molecular weight polymers are relatively insoluble in water. The development of charge increases the solubility of the polymer through favorable interactions between the charged sites and the polar water molecules.

The primary factors to consider when designing a thickener for solid/liquid separations by traditional methods[18,19] are the solids flux as a function of concentration and the free settling rate of the suspended solids. The free settling rate must exceed the withdrawal rate of the overflow to avoid solids reporting to the overflow. Typical conventional thickeners require free settling rates on the order of 2 to 10 m/hr or more to be deemed useful in industrial applications.[20,21] More modern thickener design[22] requires information about suspension compressibility and permeability over a wide range of solids concentrations.

The density of the sediment bed is also important in determining the effectiveness of a solid/liquid separation since it determines the amount of water contained in the solids rich sediment. Repulsive particles remain stable for extended periods of time, but will eventually settle. (Long settling times under gravity usually make the removal of well-dispersed colloidal particles uneconomical for industrial purposes.) However, when the particles do eventually settle, the resulting sediment bed is quite dense. These suspensions consolidate to relatively high volume fractions of solids (low moisture contents) even at low applied consolidation pressures.[23,24] On the other hand, there are attractive forces between particles that have been flocculated so the particles are pulled together to form aggregates that rapidly settle. The sediment beds that form, unfortunately, are of relatively low density and contain high residual moisture contents. These suspensions require high pressures to consolidate to higher volume fractions when compared to the same particles interacting with repulsive forces.[23,24]

Recently, a new paradigm in solid/liquid separation has been disclosed that enables both rapid sedimentation and low moisture sediments by controlling particle interaction forces during each stage of the dewatering process. The concept relies on developing attraction between particles during the settling phase and then using a stimulus to switch the particle interaction to repulsive during the consolidation phase.[25,26] The weight of the particles within the sediment is sufficient to produce a significant consolidation pressure.

The polyelectrolyte chosen for this new paradigm should have the ability to act as both a dispersant and a flocculant. In order to induce attraction between the particles, the charge on the polyelectrolyte is turned off by adjusting the pH to a value where the polymer is not charged. Either bridging or hydrophobic attraction between the polymer-coated particles will cause the particles to aggregate, allowing them to be rapidly separated from most of the liquid. The pH can then be adjusted back to a value where the polymer is highly charged so that a repulsive electro-steric force is re-established between the particles to allow for additional consolidation.

The focus of this article is to make quantitative measurements of the free settling rates of suspensions while the attraction is present and to compare the final sediment volumes of the flocculated only suspensions to those where repulsion was re-established. This information will be valuable in justifying additional measurements of suspension compressibility and permeability in order to determine the suitability of the stimulant sensitive approach in applied solid/liquid separation processes.

Experimental Procedures

Materials

Three different colloidal materials (alumina, silica, and zircon) were investigated in this study. Their properties are found

Table 2. Polymer Properties

PAA—Polyacrylic Acid [-$CH_2CH(CO_2H)$-]$_n$	Chitosan (1,4)[2-amino-2-deoxy-β-δ-glucopyranan]
Low molecular weight—Mw: 250000	Low molecular weight—Mw: 150000
Aldrich Chemical Company—35 wt % solution	Fluka Biochemika—flake
Medium molecular weight—Mw: 750000	High molecular weight—Mw: 600000
Aldrich Chemical Company—Powder	Fluka Biochemika—flake
pK = 6	pK = 6.5

Table 3. Combinations of Colloid and Polymer Investigated

Colloid	Polymer	Solids Content (wt %)
Alumina	250,000 PAA	10
Alumina	750,000 PAA	10
Alumina	150,000 chitosan	5
Alumina	600,000 chitosan	5
Silica	150,000 chitosan	6
Silica	600,000 chitosan	6
Zircon	150,000 chitosan	5
Zircon	600,000 chitosan	5

in Table 1. Two different polymers (polyacrylic acid (PAA) and chitosan) were used in this investigation. The details of the polymers are shown in Table 2. PAA is anionic and chitosan is cationic.

Method

Polymers Solutions. Flocculants solutions are difficult to prepare as highly concentrated solutions because they are usually very viscous. In industrial practice a 0.1%-1% solution is usually used for testing purposes and is stable for a few weeks. Some changes occur over a period of time, primarily the first 24 hours.[27]

Low and medium molecular weight polyacrylic acid solutions were dissolved as a 0.4 wt % solution in distilled water at pH 8.0. The solution was allowed to dissolve overnight. The PAA solutions were used for a period of time between 24 hours and 14 days after preparation. Polyacrylic acid is negatively charged at high pH, while at low pH it becomes neutral. Low and high molecular weight chitosan solutions were dissolved as a 1 wt % solution in an approximately 1 mole/liter acetic acid solution in distilled water with pH adjusted to 4.0 with HCl. The chitosan was allowed to dissolve for more than 2 days. The chitosan solutions were used for a period of time between 48 hours and 14 days after preparation. Chitosan is positively charged at low pH, but loses its charge as pH is increased above neutral. When it loses its charge, it becomes hydrophobic and is only sparingly soluble in water.[17]

Colloidal suspensions

The matrix of tests shown in Table 3 was devised in order to demonstrate that the method is useful for colloidal materials with different isoelectric points, that both cationic and anionic polyelectrolytes are useful, and to determine if there was an effect of polymer molecular weight in the range about 10^5 to 10^6. The solids content was chosen between 5 and 10 wt % so that a final sediment bed height of between about 2 and 10 cm was obtained in a settling column with 25 cm initial suspension height.

Colloidal suspensions were prepared by slowly adding the powder to distilled water at the appropriate pH, then slowly tumbling for 16 to 24 hours. The concentration of solids in the suspension was somewhat (usually about 20%) greater than that indicated in Table 3, so that after addition of the polymer solution the final solids content was as indicated in Table 3.

Table 4. Concentration and pH Used to Produce Stable Suspensions

	Chitosan	PAA
Alumina	1 wt %, pH 5	0.4 wt %, pH 8
Silica	2 wt %, pH 4.5	
Zircon	1 wt %, pH 5	

Table 5. Conditions Used to Induce Flocculation

	Polymer	pH for Flocculation
Alumina	0.4 wt %, PAA	2.8
Alumina	1.0 wt %, chitosan	10
Silica	2 wt %, chitosan	8.5
Zircon	1 wt %, chitosan	7.8

Initially, the polymer concentration and pH were determined for each combination of polymer and particle that produced a stable repulsive particle suspension. Typically about 0.5 to 1.5 wt % polymer by weight of solid is required to produce well-dispersed suspensions by the steric repulsion mechanism. The polymer concentrations and pH values that were found to produce stable dispersions and chosen for further investigation are shown in Table 4.

The guiding criteria for choosing these conditions were that the pH was chosen so that the polymer was well charged and soluble and had opposite charge to the particles' surface. An exception occurred with alumina with chitosan at pH 5, where both polymer and particle are positively charged. The conditions indicated in Table 4 are not the only combinations of polymer concentration and pH that produced stable dispersions. They are chosen only as typical conditions that fall within a range of both polymer concentration and pH that produced stable dispersions. It should be noted that at very small additions of polymer (typically around 0.04 to 0.1 wt %), traditional bridging flocculation was found to occur, resulting in rapid sedimentation, but producing turbid supernatants.

Sedimentation tests

The suspensions prepared as described above remained stable (did not form a clear supernatant and well defined sediment bed) for over 24 hours. Flocculation was induced by adjusting the pH of the suspension so that the polymer was uncharged and rendered only sparingly soluble. For PAA this is at a pH

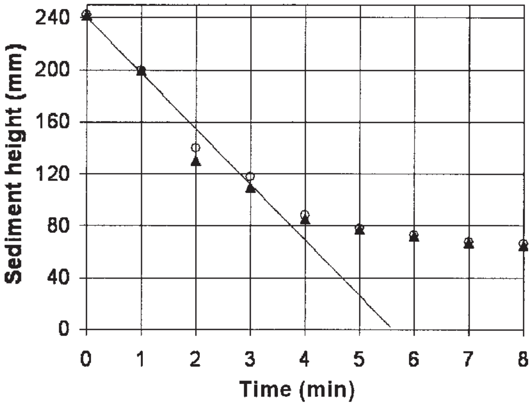

Figure 1. Estimation of initial settling rate from initial slope of the sediment height versus time plot for 5 wt % alumina with 1 wt % low MW chitosan at pH 10.

The open circles and black triangles represent two different experiments under the same conditions.

Table 6. Initial Settling Rates and Solids Fluxes

Suspension	Polymer	pH	Initial Settling Rate (mm/min)	Initial Settling Rate (m/h)	Solids Flux (kg/m^2 · min)
10% alumina	0.4% PAA Low mw	2.8	5.4	0.32	0.54
10% alumina	0.4% PAA Medium mw	2.8	82	5.0	8.20
5% alumina	1% Chitosan Low mw	10	42.5	2.5	2.125
5% alumina	1% Chitosan High mw	10	56.8	3.4	2.84
6% silica	2% Chitosan Low mw	8.5	1.2	0.07	0.072
6% silica	2% Chitosan High mw	8.5	3.3	0.20	0.198
5% zircon	1% Chitosan Low mw	7	44.3	2.7	2.215
5% zircon	1% Chitosan High mw	7	64	3.8	3.20

near 3, while for chitosan the relevant pH is above about 7. Flocculation was found to occur over a limited range of pH for PAA from about 3 to 2.5 (the lowest pH investigated), but for a wider range of pH for chitosan, from about 7.5 to 10.5 (the highest pH investigated). Preliminary investigations indicated that clear supernatants and rapid sedimentation occurred for each of the systems investigated, as indicated in Table 5.

Rapid aggregation and sedimentation occurred once the pH was changed. The clarities of the supernatants were quite good for the conditions presented in this article. It should be noted that poor clarity supernatant will result if the polymer dose or the pH is not carefully chosen.

Three test samples of 250 ml of suspension (25 cm tall columns) were prepared for each of the four combinations of colloid and polymer listed in Tables 4 and 5. One of the three samples was maintained at the pH resulting in stability, and the other two were adjusted to the pH to induce flocculation. The three test samples were shaken vigorously (in the corked columns) for approximately 30 seconds and placed onto a bench to allow the particles to settle. Photographs were taken at frequent time intervals over the next few hours. After the sedimentation rate of the flocculated samples appeared to be reaching a plateau (usually 30 to 90 minutes), the pH of one of the samples, where flocculation was initially induced, was changed to that which produced a stable suspension. This was carried out by first removing all but 10 ml of the supernatant above the top of the sediment. Then, either acid or alkali was added to obtain the required pH. Slow stirring was applied in order to ensure the pH change was uniform throughout the entire sediment bed. (In other preliminary tests, when the pH of the supernatant only was changed, the behavior of the sediment was such as to suggest that the acid or alkali did not fully penetrate the sediment bed.) In order to keep the experimental control conditions the same, slow stirring was also applied to those samples where the pH was not changed. Photographs of the sediments were taken for a period of time up to between 5 and 72 hours. The height of the top of the sediment (solid phase) was recorded at regular intervals for each settling column using the photographs.

Results

Initial settling rate

The sediment height (interface between clear supernatant and top of the settling bed) was measured as a function of time. A typical curve is shown in Figure 1 for 5 wt % alumina suspensions flocculated with 1 wt % low MW chitosan at pH 10. The gradient of the height versus time curve is an indication of the initial settling rate. In all cases there was an initial constant settling rate period that accounts for the majority of the settling. Table 6 shows the initial settling rates for the flocculated samples and the corresponding solids fluxes calculated from the weight fraction of solids in suspension and the solids densities. With the exception of the silica, these rates and solids fluxes approach those typically found to be economically viable in industrial practice.[20,21] On the other hand, the samples that were maintained in a dispersed condition (as in Table 4)

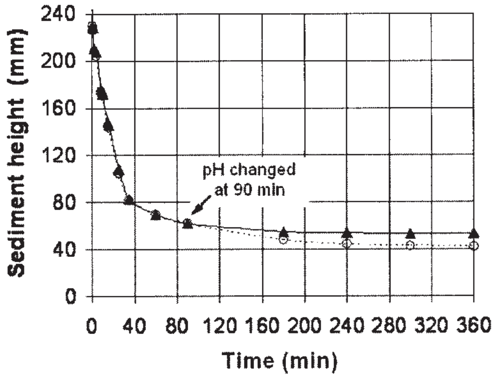

Figure 2. Height of interface between sediment and clarified supernatant as a function of time for 10 wt % alumina suspensions with 0.4 wt % low MW PAA.

Solid triangles represent the suspension flocculated at pH 2.8; open circles represent the suspension flocculated at pH 2.8 for 90 minutes, then pH adjusted to 8. Both suspensions were gently stirred for about 30 seconds after 90 minutes.

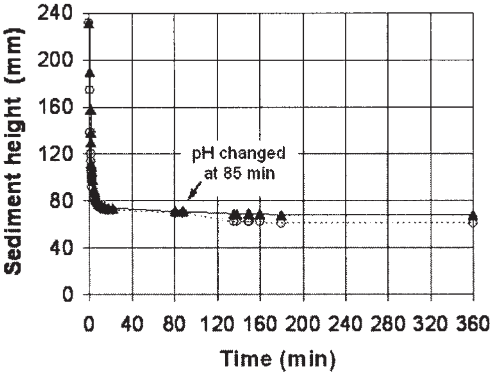

Figure 3. Height of interface between sediment and clarified supernatant as a function of time for 10 wt % alumina suspensions with 0.4 wt % medium MW PAA.

Solid triangles represent the suspension flocculated at pH 2.8; open circles represent the suspension flocculated at pH 2.8 for 85 minutes, then pH adjusted to 8. Both suspensions were gently stirred for about 30 seconds after 85 minutes.

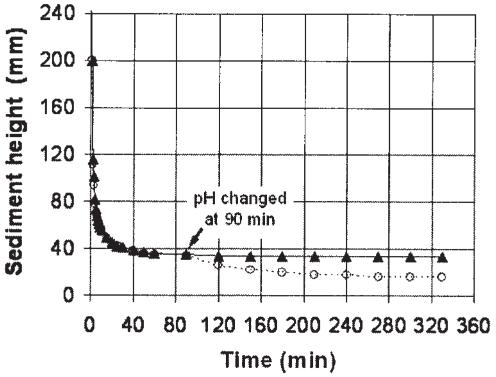

Figure 5. Height of interface between sediment and clarified supernatant as a function of time for 5 wt % alumina suspensions with 1.0 wt % high MW chitosan.

Solid triangles represent the suspension flocculated at pH 10; open circles represent the suspension flocculated at pH 10 for 90 minutes, then adjusted to pH 5. Both suspensions were gently stirred for about 30 seconds after 90 minutes.

did not separate into a clarified liquid phase and a solids rich sediment phase for a period of over 24 hours.

Sediment densities

As the settling proceeded, the sediment bed increased in height. After a period of time, the top of the free settling suspension met the rising sediment bed, and the settling rate decreased and approached zero. Additional consolidation of the sediment bed of the flocculated suspensions was relatively minor after this time. The transition between the fast, linear, free settling period and the slow, consolidation period can be seen in Figures 2-9 for the eight different combinations of colloid and polymer that were investigated. At approximately the end of the free settling period, all but 10 ml of the supernatant was removed and the sediment bed was gently stirred for 30 seconds. If the flocculated sediment was stirred only (but kept at the pH for flocculation as in Table 5), the sediment did not continue to increase in density with increasing time. If the pH of the sediment was changed to that indicated in Table 4 to re-establish repulsion between particles in the suspension, the suspension continued to consolidate to higher densities over a period of additional time, as indicated in Figures 2-9.

After an additional period of time, the additional consolidation of the samples where repulsion was re-established appeared to reach a plateau. At this time, the experiment was deemed to have been completed. The final volume of the sediment was recorded and is presented in Table 7 as well as the percent reduction in sediment volume of the suspension when repulsion was re-established compared to suspensions left at constant pH. Figures 10-12 are some of the photographs of three of the experiments. The images indicate the levels of the sediment at various times, either just before the pH was

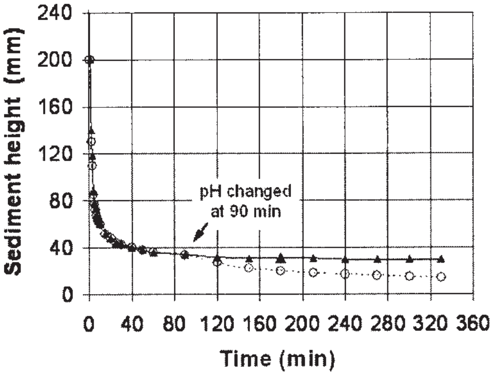

Figure 4. Height of interface between sediment and clarified supernatant as a function of time for 5 wt % alumina suspensions with 1.0 wt % low MW chitosan.

Solid triangles represent the suspension flocculated at pH 10; open circles represent the suspension flocculated at pH 10 for 90 minutes, then adjusted to pH 5. Both suspensions were gently stirred for about 30 seconds after 90 minutes.

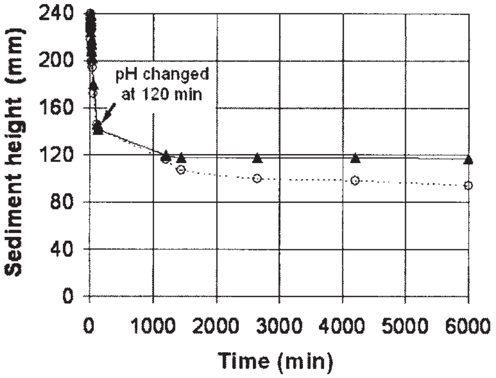

Figure 6. Height of interface between sediment and clarified supernatant as a function of time for 6 wt % silica suspensions with 2.0 wt % low MW chitosan.

Solid triangles represent the suspension flocculated at pH 8.5; open circles represent the suspension flocculated at pH 8.5 for 120 minutes, then adjusted to pH 4.5. Both suspensions were gently stirred for about 30 seconds after 120 minutes.

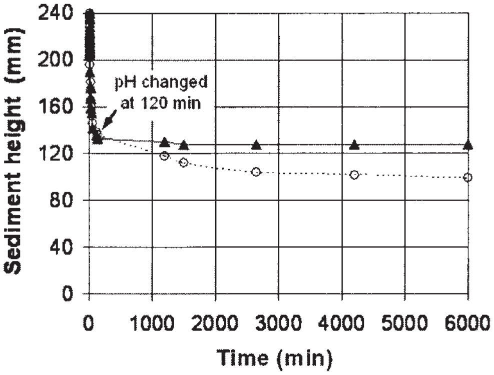

Figure 7. Height of interface between sediment and clarified supernatant as a function of time for 6 wt % silica suspensions with 2.0 wt % high MW chitosan.

Solid triangles represent the suspension flocculated at pH 8.5; open circles represent the suspension flocculated at pH 8.5 for 120 minutes, then adjusted to pH 4.5. Both suspensions were gently stirred for about 30 seconds after 120 minutes.

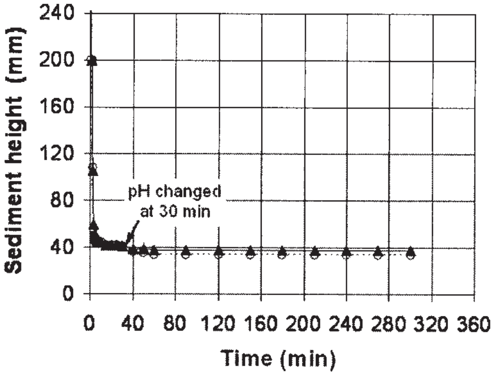

Figure 9. Height of interface between sediment and clarified supernatant as a function of time for 5 wt % zircon suspensions with 1.0 wt % high MW chitosan.

Solid triangles represent the suspension flocculated at pH 7.8; open circles represent the suspension flocculated at pH 7.8 for 30 minutes, then adjusted to pH 5. Both suspensions were gently stirred for about 30 seconds after 30 minutes.

adjusted or at the end of the completed experiment. The white arrows in the photographs indicate the position of the top of the sediment bed. These photographs provide direct visual confirmation of the reduction in sediment volume and the typical supernatant clarity.

Discussion

Consolidation

The results suggest an interesting effect of the pH. When the pH was such that the forces between particles were always attractive, the sediment height reached a plateau that was always greater than in the cases where the pH was adjusted to create repulsive forces between particles. The additional consolidation occurs because the repulsion between particles within the sediment bed allows them to rearrange into a more efficient packing structure compared to attractive particles at the same consolidation pressure.[23,24] In other words, the compressive yield stress of the repulsive particles is less than that of the attractive particles.[28,29] Although we stirred the sediments slightly to mix in the acid or base used to change the pH, and it is possible that shearing the sediment may cause it to consolidate slightly, the additional consolidation we observed is primarily due to the change in inter-particle interaction rather than to shearing the sediment. In earlier work,[26] additional consolidation was observed when the pH of the supernatant was changed without stirring the sediment. Under these circumstances, the additional consolidation required more time (24 hours compared to about 3 when stirring was used) due to the long time required for the acid or base to penetrate into the sediment bed. Furthermore, in the present work, stirring was applied to both the flocculated sediment that had its pH changed and the sediment that was maintained at the same pH. By carefully observing Figures 2- 9, one can observe the slight decrease in sediment volume associated with the stirring in the sediment that was maintained at the same pH compared to the significant decrease in sediment volume that occurs when the sediment pH is changed back to a value that produces repulsion between the particles.

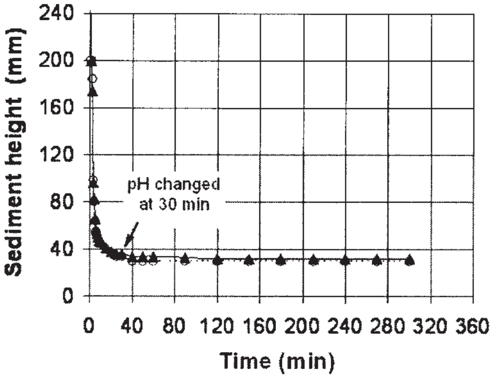

Figure 8. Height of interface between sediment and clarified supernatant as a function of time for 5 wt % zircon suspensions with 1.0 wt % low MW chitosan.

Solid triangles represent the suspension flocculated at pH 7.8; open circles represent the suspension flocculated at pH 7.8 for 30 minutes, then adjusted to pH 5. Both suspensions were gently stirred for about 30 seconds after 30 minutes.

Thus, by controlling the inter-particle interaction so that attraction dominates only when settling is required, and repulsion dominates once the sediment has formed, improved dewatering is possible, at least under the conditions investigated. The free settling rates and solids fluxes are comparable to those usually encountered in conventional solid/liquid separation in the minerals industry using thickeners. The resulting sediments can be up to 50% more compact than those produced when attraction only is present between the particles.

The improvement in sediment density is the most notable for the particles of least mass (alumina) and least notable for those of greatest mass (zircon). Mass is simply calculated from the particle radius and density. This trend can be explained by the diminished role of the inter-particle forces relative to the gravitational force that increases with increasing mass.

Table 7. Final Sediment Volumes (ml)

Suspension	Polymer	Time	Flocculation Only	Flocculation Then Repulsion	% Reduction
10% alumina	0.4% PAA Low mw	6 hrs.	53 ml	43 ml	19
10% alumina	0.4% PAA Medium mw	6 hrs.	68 ml	61 ml	10
5% alumina	1% Chitosan Low mw	5 hrs.	30 ml	15 ml	50
5% alumina	1% Chitosan High mw	5 hrs.	34 ml	16 ml	53
6% silica	2% Chitosan Low mw	72 hrs.	118 ml	98 ml	17
6% silica	2% Chitosan High mw	72 hrs.	128 ml	102 ml	20
5% zircon	1% Chitosan Low mw	5 hrs.	32 ml	30 ml	6
5% zircon	1% Chitosan High mw	5 hrs.	38 ml	34 ml	11

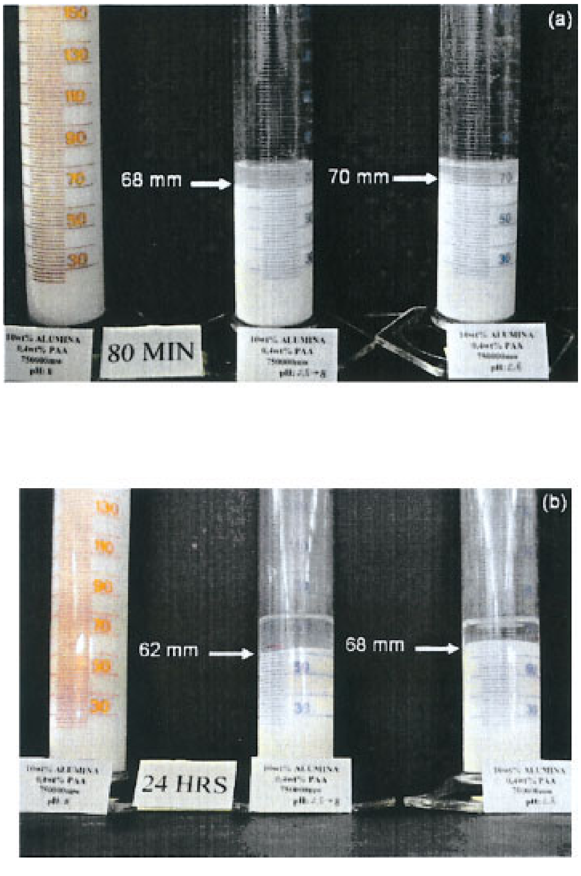

Figure 10. Photographs of 10 wt % alumina suspensions with 0.4 wt % medium MW PAA.

(a) The suspension in the cylinder on the left was at pH 8 (dispersed), and the suspensions in the middle and right side columns were at pH 2.8 (flocculated). This photo taken at 80 minutes shows the sediment height when the flocculation had reached a plateau. (b) After 85 minutes the pH of the suspension in the column in the middle was changed to 8. The photo taken after 24 hours shows that the sediment in the middle column consolidated to a greater extent than the suspension in the column at the right. The stable suspension at the left side did not settle even after the 24 hour period. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

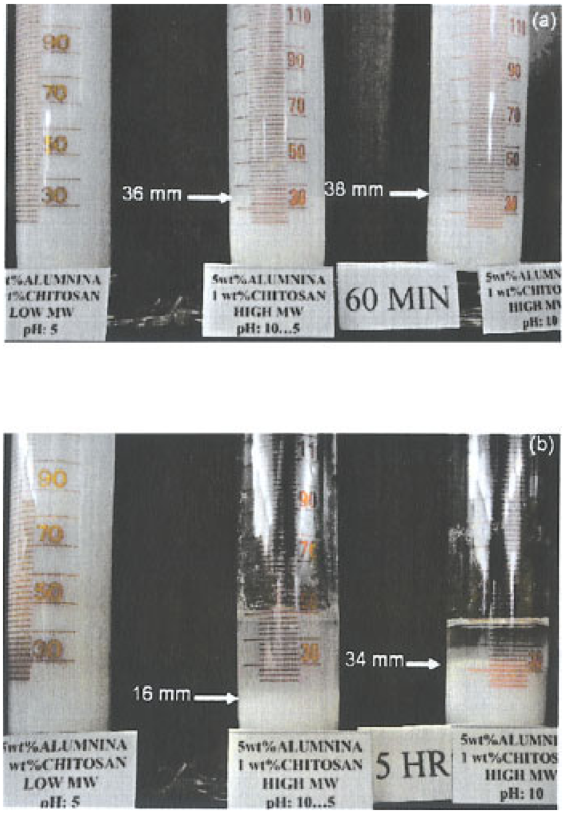

Figure 11. Photographs of 5 wt % alumina suspensions with 1.0 wt % high MW chitosan.

(a) The suspension in the cylinder on the left was at pH 5 (dispersed), and the suspensions in the middle and right side columns were at pH 10 (flocculated). This photo taken at 60 minutes shows the sediment height when the flocculation had nearly reached a plateau. (b) After 90 minutes the pH of the suspension in the column in the middle was changed to 5. The photo taken after 5 hours shows that the sediment in the middle column consolidated to a greater extent than the suspension in the column at the right. The stable suspension at the left side did not settle even after the 5 hour period. (Note: The label of the column on the left is incorrect. The word "LOW" should be "HIGH.") [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

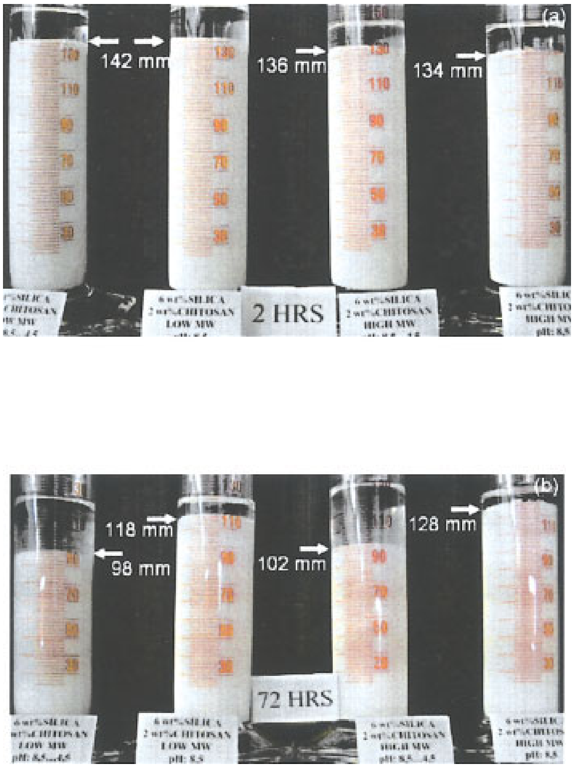

Figure 12. Photographs of 6 wt % silica suspensions with 2.0 wt % chitosan.

The two suspensions in the cylinders on the left had low MW chitosan, and the two on the right had high MW chitosan. (a) This photo shows the sediment height after 120 minutes of sedimentation when the pH of the suspensions was at 8.5 (flocculated). (b) After 120 minutes the pH of the first and third suspensions was adjusted to pH 4.5 (dispersed), and the second and fourth suspensions were maintained at pH 8.5 (flocculated). This photo taken after 72 hours shows that the sediment in the first and third columns consolidated to a greater extent than the suspensions in the second and fourth columns. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of polymer MW

In all cases, when other factors were maintained constant, the higher molecular weight polymer produced faster initial settling rates. The ratio of the settling rates of the high to low molecular weight polymers varied significantly from less than 2 to more than 10, depending on the polymer and particle types (see Table 6). Although no quantitative measurements were performed, it appeared that the higher molecular weight polymers produced supernatants that were clearer than when low molecular weight polymers were used. It was also observed that the high molecular weight polymers produced larger volume sediment beds than the lower molecular weight polymers. The effect was more pronounced in the suspensions that were flocculated only, but was present to a lesser extent in the suspensions that were made repulsive after a period of flocculation. These observations are consistent with the premise that larger aggregates are produced from the higher molecular weight polymers. The literature[30] also supports the notion that larger molecular weight polymers produce larger aggregates.

Conclusions

Weak polyelectrolytes are useful pH-sensitive polymers that can be used alternately as flocculants and dispersants. By adjusting the pH so that the polymer is not charged and poorly soluble, flocculation and rapid sedimentation results. Once a sediment bed has formed, the pH can be adjusted so that the polymer becomes charged and creates repulsion between the particles. The sediment will then continue to consolidate under the influence of gravity compared to the flocculated only sediments. Denser sediments and additional liquid recovery are possible using the described method. The technique has been demonstrated for a range of colloidal materials and both anionic and cationic polyelectrolytes. The concept of stimulant sensitive flocculation and consolidation has the potential for significant improvements in solid liquid separations, and further development of polymeric flocculants that respond to stimuli such as pH and temperature should be undertaken to refine the technology for industrial practice.

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