Bridging Flocculation by Polymers

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Abstract

A comprehensive evaluation of flocculation processes is presented with emphasis on physical and engineering aspects. Flocculation by polymer bridging involves three basic sub-processes: mixing of the polymer with the particle suspension, adsorption of the polymer on particle surfaces and the formation and growth of flocs. Each of these is primarily controlled by agitation of the suspension. At the same time, agitation also promotes floc breakage. Since polymer adsorption tends to occur irreversibly, flocculation is a non-equilibrium process and the relative rates of the sub-processes play a critical role. The kinetics of these processes are reviewed and their implications with respect to process design are evaluated. Procedures for controlling the relative rates are shown to provide a basis for the design of efficient flocculation processes in batch systems. Some information on scale-up criteria is presented. Extension of the basic concepts to the design and operation of continuous processes is discussed.

Keywords: polymer adsorption kinetics, destabilization, floc formation and growth, mixing effects, batch flocculation scale-up, continuous flocculation in tanks and in-line mixers

Introduction

The use of polymers for flocculating fine particles is widely practiced in solid-liquid separations. The process can be highly effective, but the results are often quite variable even for very similar systems and conditions. Practical applications generally depend on adsorption of the polymer on the surfaces of suspended particles. The particular arrangement of the adsorbed molecules determines the performance of the process. Variations in performance can usually be attributed to differences in such arrangement, for example, uneven distribution among the particles due to poor mixing of polymer solution and particle suspension.

Polymer-induced flocculation typically proceeds through one or other of two basic mechanisms: charge-patch interaction or particle bridging. Charge-patch interaction results from the adsorption of, usually relatively low molecular weight, polyelectrolyte molecules on oppositely charged particle surfaces. These create a “patch” on the surface that is electrostatically attracted to regions of bare surface on other particles. Bridging flocculation occurs when high molecular weight polymer molecules adsorb simultaneously on more than one particle. Charge-patch flocculation is usually effective and performs consistently, but results only in relatively small flocs. Bridging flocculation, on the other hand, can produce very large flocs but performance can be erratic. This paper focuses on bridging flocculation and presents an evaluation of the causes and solutions to performance variability.

Polymer Adsorption

The polymers used in bridging flocculation are normally high molecular weight linear-chain compounds, commonly based on polyacrylamide. The molecules may be uncharged (nonionic) or partially hydrolyzed as an (anionic) poly-acrylamide/acrylate copolymer. Adsorption is generally considered to result primarily from hydrogen bonding between active groups (amide or hydroxyl) in the polymer chain and

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fully, molecular weights exceed 10 million  which corresponds to more than 100,000 individual  segments each of which is capable of adsorbing on  the surface. It follows that an adsorbed molecule  can be expected to be attached through many such  interactions. While each individual segment probably  undergoes reversible adsorption/desorption steps,  desorption of the molecule as a whole would require  simultaneous desorption of all attached segments  which is exceedingly unlikely. It follows that poly-  mer adsorption is effectively irreversible. Polymer  adsorption generally occurs in two stages – initial at-  traction followed by conformational rearrangement  on the surface. This rearrangement will normally  involve spreading of individual molecules, increasing  the area occupied by each. The process of rearrange-  ment at the surface is considered to be much slower  than the attachment step and is unlikely to contrib-  ute to bridging flocculation.

Adsorption Kinetics

Adsorption rates are determined by particle/  polymer molecule collisions. If particles and (coiled)  molecules can be treated as spheres, classical expres-  sions for collisions due to Brownian motion and/or  shear can be used to estimate collision frequencies.  For particles of diameter $d_s$ and polymer molecules  of effective hydrodynamic size $d_p$, the collision fre-  quency $f_{sp}$ can be estimated from:

$$f_{sp} = K_{sp} n_s n_p$$  \hspace{1cm} (1)$$

where $n_s$ and $n_p$ are the number concentrations of  particles and polymer molecules respectively and $K_{sp}$  is the collision frequency constant. Assuming that  Brownian motion and shear act independently, the  frequency constant, for a combination of the two pro-  cesses, can be approximated by,[5,7]:

$$K_{sp} = rac{2k_B T}{3\mu} \left( 2 + \frac{d_p}{d_s} + \frac{d_s}{d_p} \right) + \frac{G}{6} (d_s + d_p)^3$$  \hspace{1cm} (2)$$

where $k_B$ is Boltzmann’s constant, $T$ is absolute  temperature, $\mu$ is the liquid viscosity, $d_s$ and $d_p$ are,  respectively, the solid particle and effective polymer  molecule diameters and $G$ is the mean shear rate  due to agitation of the suspension.

For soluble polymers, adsorption will be limited by  surface coverage as surface sites become blocked by  adsorbed molecules. If each collision with bare par-  ticle surface results in the removal of one polymer  molecule from suspension, the concentration remain-  ing after time $t$ can be obtained from,

$$\frac{dn_p}{dt} = -K_{sp} n_s n_p (1 - \theta)$$  \hspace{1cm} (3)$$

where $\theta$ is the fractional surface coverage and is  determined by the number and size of adsorbed mol-  ecules. Assuming, for simplification, that the size and  shape of the adsorbed molecules are the same as in  solution, $\theta$ can be estimated using

$$\theta = \frac{n_a}{4n_s} \left( \frac{d_p}{d_s} \right)^2$$  \hspace{1cm} (4)$$

where $n_a$ is the number of adsorbed molecules per  unit volume. The number of adsorbed molecules is  simply

$$n_a = n_{p0} - n_p$$  \hspace{1cm} (5)$$

where $n_{p0}$ is the total amount of polymer added. From  Equations 3, 4 and 5

$$\frac{dn_p}{dt} = -K_{sp} n_s n_p \left[ 1 - \left( \frac{n_{po} - n_p}{4n_s} \right) \left( \frac{d_p}{d_s} \right)^2 \right]$$  \hspace{1cm} (6)$$

or

$$\frac{dn_p}{dt} = -K_{sp} n_s n_p \left[ 1 - \theta_t \left( 1 - \frac{n_p}{n_{p0}} \right) \right]$$  \hspace{1cm} (7)$$

where $\theta_t$ is the fractional surface coverage that  would exist if 100% of the added polymer were ad-  sorbed, i.e.,

$$\theta_t = \frac{n_{p0}}{4n_s} \left( \frac{d_p}{d_s} \right)^2$$  \hspace{1cm} (8)$$

The solution to Equation 7, subject to the initial con-  dition, $n_p = n_{p0}$ at $t = 0$ is

$$\frac{n_p}{n_{p0}} = \left[ 1 - \theta_t \left( 1 - \frac{n_p}{n_{p0}} \right) \right] E$$  \hspace{1cm} (9)$$

where

$$E = \exp \left[ - \left( 1 - \theta_t \right) K_{sp} n_s t \right]$$  \hspace{1cm} (10)$$

Solving for $n_p/n_{p0}$ leads to

$$\frac{n_p}{n_{p0}} = \frac{(1 - \theta_t) E}{(1 - \theta_t E)}$$  \hspace{1cm} (11)$$

Surface Coverage

The fractional surface coverage $\theta$ can be obtained  from Equations 4, 5, 8 and 11 giving,

$$\theta = \frac{\theta_t (1 - E)}{(1 - \theta_t E)}$$  \hspace{1cm} (12)$$

Adsorption Time

A characteristic adsorption time $t_{95}$ i.e., the time for  95% of the polymer to be adsorbed can be calculated
by solving for \( t \) with \( \frac{n_p}{n_{p0}} \) equal to 0.05. From Equation 9

\[
E = \frac{n_p/n_{p0}}{1 - \theta_t(1 - n_p/n_{p0})}
\]  

(13)

When \( t = t_{95} \), \( E = E_{95} \) and, from Equation 13,

\[
E_{95} = \frac{0.05}{1 - 0.95\theta_t}
\]  

(14)

Then, from Equation 12,

\[
t_{95} = \frac{\ln(20(1 - 0.95\theta_t))}{(1 - \theta_t)K_{sp}n_s}
\]  

(15)

It is clear from the above that the adsorption time is determined by the solids concentration, particle size, polymer molecular weight and shear rate due to agitation. For a fixed ratio of polymer to solids concentration (constant \( \theta_j \)), a simple inverse proportionality to solids content can be seen. The more complex effects of the other variables are illustrated in Fig. 1 and 2. Dependence on particle size and polymer molecular weight is shown in Fig. 1. The adsorption time is relatively insensitive to molecular weight but increases significantly with increasing particle size. Increased shear reduces adsorption time, especially for large particles, as seen in Fig. 2 but has relatively minor effects on finer material for which particle/polymer collisions result mostly from Brownian motion.

The calculations indicate that adsorption times can range from more than 2 hours for 0.01% suspensions of 5\( \mu \)m particles agitated at 10 s\(^{-1} \) to as little as 0.02 seconds for 10% suspensions of 0.5\( \mu \)m particles agitated at 1000 s\(^{-1} \). Typical values for practical systems generally fall in the range of a few seconds or less.

**Flocculation**

**Destabilization**

The first step in the flocculation process is destabilization of the suspension by eliminating any repulsive interactions that prevent particles from coming into contact and adhering. Typically, such interactions involve electrical double layers at the surfaces of charged particles or steric effects due to solvation or the presence of protective coatings. Double-layer interactions can generally be suppressed by chemical treatments such as pH control or appropriate electrolyte addition. It has been clearly demonstrated\(^8,9\) that high molecular weight (>10\(^6\)) bridging polymers are inappropriate for destabilization in such applications – they can provide destabilization but only at excessively high dosage with correspondingly high cost. The real benefit of these flocculants is their effectiveness in promoting floc growth following destabilization, and the production of large, shear-resistant flocs appropriate for dewatering by sedimentation or filtration. The strong inter-particle linkages provided by the bridging polymer probably serve to promote growth by enhancing resistance to floc breakage under shear.

Lower molecular weight (< 5.10\(^5\)) polyelectrolytes, on the other hand, can be very effective in dispersion destabilization for both charge- and sterically-stabilized systems. In the case of charge stabilization, however, the simple chemical treatments noted above are usually equally effective and less costly. Unlike the high molecular weight polymers, the low molecular weight reagents do not generally promote the development of large strong flocs. Their use for destabilization is commonly followed by the addition

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**Fig. 1** The effect of particle size on theoretical adsorption times at a slurry concentration of 1% by volume and a mean shear rate of 100 s\(^{-1} \).

**Fig. 2** The effect of shear rate on theoretical adsorption times for a 10 million molecular weight polymer at a slurry concentration of 1% by volume.
of higher polymer flocculants.

An example of the use of polymers for destabilization and floc growth in fine alumina suspensions is given in Fig. 3. It is clear from the figure that the low molecular weight (0.5 million) cationic polymer effectively destabilizes the suspension at low dosage (~0.5 mg/L) but provides only limited floc growth. In contrast, the high molecular weight (15 million) nonionic polymer requires much higher dosage (~5mg/L) to eliminate finer (submicron) particles but can promote growth to much larger sizes.

Floc Growth

Flocculation proceeds through the same basic mechanisms as polymer adsorption – particle/particle collisions due to Brownian motion and shear. The collision frequency between particles of size $d_i$ and $d_j$ can be expressed by a relationship analogous to Equation 2, i.e.,

$$K_{ij} = \left[ \frac{2k_BT}{3\mu} \left( 2 + \frac{d_i}{d_j} + \frac{d_j}{d_i} \right) + \frac{G}{6} \left( d_i + d_j \right)^3 \right]$$

Smoluchowski\(^6\) showed that the reduction due to aggregation in the total number of particles is determined by

$$\frac{dN}{dt} = -\frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} K_{ij} n_i n_j$$

If all collisions are assumed to lead to aggregation and the size distribution of the growing flocs approaches a “self-preserving” form\(^11, 12\), the rate of decrease in the total number $N$ of particles/flocs can be represented by\(^6, 13\):

$$\frac{dN}{dt} = - \left[ K_B N^2 + K_S N \right]$$

where $K_B$ and $K_S$ are effective rate constants for flocculation due to Brownian motion and shear respectively. The constants can be approximated by:

$$K_B = \frac{2k_BT}{3\mu} F_B$$

and

$$K_S = \frac{G\bar{\phi}}{\pi} F_S$$

The factors $F_B$ and $F_S$ are related to the moments of the self-preserving floc size distribution. Their values are estimated to be about 2 and 3 respectively\(^13\).

The solution to Equation 18, subject to the initial condition that $N = N_0$ at $t = 0$, is

$$K_{St} = \ln \left[ \frac{K_B N_0 + K_S (N_0/N)}{K_B N_0 + K_S} \right]$$

A characteristic time $t_{95}$, corresponding to a 95% reduction in the total number of particles, can be estimated by setting $N_0/N$ equal to 20 in Equation 21. Examples of flocculation time estimates are shown in Fig. 4.

**Fig. 3** Floc size distributions resulting from the application to an initially stable alumina suspension (plot a) of a 0.5 million molecular weight cationic polymer (plots c and e) and a 15 million molecular weight nonionic polymer (plots b, d and f). Data of Rattanakawin\(^10\).

**Fig. 4** Characteristic (theoretical) adsorption and flocculation times for suspensions at 1% by volume in the presence of a 10 million molecular weight polymer.
Adsorption times are included for comparison. It can be seen that predicted adsorption rates are higher than those for flocculation except for coarse particles for which the rates are similar. Adsorption times are more dependent on particle size than are flocculation times. It should be recognized, however, that while adsorption is almost complete at 95%, reduction by 95% of the total number of particles represents only an early stage in the flocculation process – for coalescing particles an average floc containing 20 primary particles would correspond to growth by factor of about 2.7 (i.e., $20^{1/3}$) only.

**Batch Flocculation Process**

In the above analysis, polymer adsorption and flocculation have been treated as independent processes. In practice, of course, they occur simultaneously and are mutually interdependent – collision efficiencies in flocculation depend on adsorption and adsorption depends on particle size which changes as a result of flocculation. However, the analysis can provide useful insight into the actual process. For example, if adsorption rates are significantly greater than flocculation rates, the polymer will be distributed over the entire surface area of the particles leading to high polymer consumption at relatively low coverage. Lower adsorption rates can actually control the rate of flocculation and reduce polymer consumption by restricting adsorption to the external surface of growing flocs.

**Mixing**

The analysis described so far also includes the implicit assumption that polymer is instantaneously distributed uniformly over the particle surfaces. This requires that the rate of mixing of the polymer solution with the particle suspension be much higher than the rate of adsorption. Otherwise, extensive local adsorption will occur at the point of initial contact between polymer and particle suspension. The effective irreversibility of polymer adsorption noted above precludes rapid redistribution of the adsorbed polymer resulting in a highly uneven coverage of the particle surfaces.

Experimental studies of the mixing of miscible liquids in agitated vessels can be used to estimate mixing times in flocculation systems. For turbine-agitated baffled tanks, Norwood and Metzner[14] presented a correlation of a mixing factor $f_t$ with the Reynolds number for different tank configurations are available[17].

A comparison of polymer adsorption times and mixing times is shown in Fig. 5. It is clear that, for particles finer than a few micrometers at concentrations of 1% by volume, adsorption occurs much more rapidly than mixing of the polymer with the suspension. It follows that addition of polymer solution un-

$$f_t = n t_m \left(\frac{D_a}{D_t}\right)^2 \left(\frac{D_t}{H}\right)^{1/2} \left(\frac{g}{n^2 D_a}\right)^{1/6}$$

where $t_m$ is the mixing time, $n$ is the agitator rotational speed (rps), $D_a$ is the agitator diameter, $D_t$ and $H$ are the respective tank diameter and liquid depth and $g$ is the acceleration due to gravity. The Norwood and Metzner correlation shows that $f_t$ decreases with increased agitation and becomes approximately constant, at about 5, for Reynolds numbers greater than about 50,000. As a rough approximation for a six-bladed turbine in a baffled tank with $D_t/H = 1$ and $D_a/D_t = 1/3$, at high Reynolds number,

$$t_m \approx 45/n$$

Theoretical adsorption times as determined from Equation 15 also depend on agitation, in this case through the shear rate $G$. For agitated tanks, the latter can be estimated from

$$\bar{G} = \left(\frac{P}{\mu V}\right)^{1/2}$$

where $P$ is the power input, $\mu$ is the liquid viscosity and $V$ is the liquid volume. The power input is given by

$$P = N_p \rho n^3 D_a^5$$

$\rho$ is the liquid density and $N_p$ is the power number for which Reynolds number correlations for different tank configurations are available[17].

![Fig. 5](image-url) Calculated adsorption and mixing times for suspensions at 1% solids by volume flocculated with a 10 million molecular weight polymer.
nder such conditions, which are typical for chemical and mineral processing applications, inevitably leads to poor flocculation due to non-uniform polymer distribution. Because of the effective irreversibility of the adsorption, continued mixing following polymer addition can effect little if any improvement in the distribution. For the most part, continued mixing serves only to promote floc degradation. Because of the inverse relationship between adsorption time and solids concentration, the mixing problem is critical at high solids content but relatively insignificant for highly dilute systems.

Metered Polymer Addition

It has been observed\textsuperscript{8,16,19} that the performance of batch flocculation processes can be significantly improved in terms of both floc size and liquid clarification by metered addition, either incremental or continuous, of the polymer to the particle suspension. In this way, rapid local adsorption is limited to each increment of added polymer and an fairly uniform overall dosage can be maintained. It follows that the effective rates of adsorption and subsequent flocculation are limited by the rate of polymer addition. An important consequence is that, with continuous polymer addition to concentrated suspensions in stirred tanks, the rates of adsorption and floc growth are determined by the rate of addition rather than by shear rate as suggested by Equations 2 and 16. The independence of initial growth on agitation speed (shear rate) is illustrated in Fig. 6 using floc settling rate as a measure of floc size. The slight offset among the curves for different agitation speeds is probably due to variations in the initial floc size in the unstable suspension prior to polymer addition.

A direct correlation of initial growth rate with time normalized with respect to the rate of polymer addition, i.e., the accumulated polymer dosage, for different rates of addition can be seen in Fig. 7. At the lower addition rates, floc growth per unit of polymer dosage is independent of the rate, but falls off at the higher rates, as the rate approaches the instantaneous condition. At a rate of 35.2 mg/L.min., floc growth is complete at a dosage of 5 mg/L, which corresponds to a total addition time of about 8.5 seconds – not much longer than the estimated mixing time of about 5 seconds.

In contrast to its effects on floc growth and settling rate, increased rate of polymer addition has a somewhat detrimental effect on supernatant turbidity.\textsuperscript{6,20} In all cases, turbidity decreases rapidly with time/polymer dosage eventually leveling off at a limiting value. This limiting turbidity appears to be increased at high rates of addition. The author has shown\textsuperscript{20} that polymer adsorption rates in agitated systems favor preferential adsorption on larger particles/flocs partially starving the residual small flocs and primary particles that contribute to turbidity.

Floc Breakage

Agitation of the suspension during polymer addition provides for mixing of the components and promotes the particle-particle collisions necessary...
for floc formation and growth. At the same time, however, it also causes floc breakage. Numerous investigations have demonstrated that growth rates generally decrease with increasing floc size\(^{24-27}\), eventually leading to a limiting maximum size. The limitation is attributed to floc breakage. Analyses of the breakage of solid particles\(^{28, 29}\) and the disruption of emulsion droplets\(^{30}\) have clearly established that breakage rates increase with increasing size. It has been shown that similar analyses can be applied to floc breakage\(^{31-33}\).

As flocs grow in an agitated suspension, breakage rates increase until a dynamic balance between growth and breakage is reached – at the limiting size. Enhanced breakage with increased agitation intensity leads to a reduction in the limiting size, as shown in Fig. 6, while increased rate of polymer addition increases growth rates with a consequent increase in the limiting size, as shown in Fig. 7.

Scale-up

The effects of tank size on batch flocculation have been investigated by Maffei\(^{34}\). His results, shown in Fig. 8, indicate that the initial floc growth rate, as measured by settling rate, is controlled by the rate of polymer addition per unit volume, essentially independent of tank size and agitation conditions. Variations in the limiting floc size are more complex, depending on agitation conditions as well as rate of polymer addition. Maffei’s experiments suggest a correlation with impeller tip speed. Thus, systems operating with the same relative rate of polymer addition and impeller tip speed (providing similar mixing conditions) should show similar behavior. Some examples can be seen in Fig. 9 and show reasonable agreement over a broad range of tank sizes.

### Floc Structure

Aggregation of solid particles by flocculation does not involve coalescence into new solid particles. Rather, these processes yield porous entities (flocs) in which the original primary particles retain their identity. Numerous investigations, including both computer simulations\(^{35-38}\) and experimental measurements\(^{39-43}\) have shown that floc density decreases (porosity increases) as growth proceeds. Computer simulations have suggested that such aggregates have a fractal dimensionality \(D\) of about 1.75\(^{42}\), indicating that the floc size \(d_s\) should vary with the number of included primary particles \(N\) according to:

\[
d_s \propto N^{1/D}
\]

The floc porosity would then vary according to:

\[
1 - \varepsilon \propto d_s^{D-3}
\]

i.e.,

\[
1 - \varepsilon \propto d_s^{-1.25}
\]

The results of experimental measurements generally agree with these relationships indicating fractal dimensions typically in the range of 1.7 to 2.1. There is some evidence that, for flocs produced using polymers under shear, densification of the finest “micro-flocs” can occur, leading to a shift in the size/density relationships to coarser sizes\(^{41, 43}\). The densification effect appears to be largely confined to primary particles in the 1 to 10 \(\mu\)m size range. Other variables, such as polymer type and solids concentration seem to have minimal effects on floc structure.
Continuous Flocculation Processes

While laboratory testing and some industrial operations are carried out in the batch mode, the majority of industrial applications, such as process water treatment, are performed on a continuous basis. Polymer may be added to a continuous stirred tank or directly into a pipe or launder prior to introduction into a separation system such as a thickener.

Stirred Tanks

Suharyono\(^2\) has investigated continuous flocculation in a stirred tank. His results indicate that while general trends in behavior are similar, performance seems to be significantly inferior to that observed in batch tests. Comparisons of batch and continuous test data are shown in Fig. 10. At similar polymer dosage and mixing/residence times, the batch process, with continuous polymer addition, gives much higher settling rates (about double) and much lower supernatant turbidities (less than one third) than those of the continuous system. The higher settling rates obtained in the batch process are attributed to the progressive polymer addition to a system of similar growing flocs, a condition not found in the steady-state continuous process where polymer dosage remains constant with time and the tank always contains a mixture of flocs at various stages of growth including fresh feed slurry. A possible enhancement of the process may be to use two or more tanks in series with polymer addition divided between them. This approach should provide an approximation to the continuous addition seen to be appropriate in the batch process.

The increased turbidity at higher rates of polymer addition observed in batch processes is again evident in the continuous system. The factors responsible for reduced setting rates may contribute to further increase in turbidity for continuous processing. Mixing conditions could also play a role here. Under the agitation conditions used in the tests, the tank was shown to be essentially fully-mixed. This means that, particularly at high flow rates (short residence times), some fraction of the feed slurry could appear in the output stream without being subject to significant flocculation.

It seems reasonable to expect that the scale-up criteria suggested for the batch process – the same rate of polymer addition and impeller tip speed – should also apply to continuous flocculation.

Pipes and In-line Mixers

Flocculation by polymer injection into a pipe is quite common in industrial practice and potentially offers several advantages over addition to a stirred tank. Highly turbulent flow, which can be enhanced through the use of baffles or in-line mixer elements, provides very rapid mixing of feed slurry and polymer solution in the pipe. Fang and Lee\(^3\) have indicated micromixing times of the order of nanoseconds in Kenics mixers at Reynolds numbers greater than about 1000. Sufficiently high turbulence to ensure high polymer-particle and particle-particle collision frequencies can readily be achieved while its role in floc degradation may be less severe than that of the impeller in a stirred tank.

Experimental studies of flocculation in turbulent pipe flow\(^4\) have shown that rapid floc growth to a maximum size took place over a short time (less than 10 seconds, corresponding to 50 – 100 pipe diameters, for the system investigated) and was followed by a continuous decrease in size with continued flow. The initial growth rate and the subsequent reduction in size were found to increase while the maximum
Again, relatively high short-time settling rates were measured with polymers, allowing for the production of small aggregates. Destabilization can be accomplished by polymer bridging, but the process is rather inefficient due to the high polymer concentrations needed to link individual particles. Destabilization, e.g., by pH control, prior to the addition of high molecular weight polymers allows for the production of small aggregates, substantially reducing the number of linkages needed for significant floc growth by bridging.

The basic mechanism involved in the flocculation of fine-particle suspensions by molecular bridging with polymers is the simultaneous attachment of individual polymer molecules to more than one particle. Polymer adsorption rates are generally high – theoretically, in agitated suspensions at solids concentrations greater than about 0.1% by volume, 95% of the polymer can be expected to be adsorbed in a few seconds or less. Furthermore, multiple points of attachment to surfaces render polymer adsorption effectively irreversible. Consequently, mixing of the polymer with the suspension is a critical factor. In order to attain uniform polymer distribution among the particles and to avoid excessive local adsorption at the point of polymer addition, mixing times should be significantly less than adsorption times. Unfortunately, the reverse is typically the case in practice.

For the efficient promotion of floc growth by polymer bridging, it is desirable that growth rates be higher than adsorption rates. In this way, adsorption is mostly limited to the decreasing surface area of the growing flocs. Again, however, adsorption is typically faster than floc growth in practice. In batch processes, metered polymer addition, either incremental or continuous, offers a solution to the mixing problem while also encouraging floc growth. Controlling the rate of addition provides opportunities for optimizing floc growth and supernatant clarification.

Agitation promotes mixing and polymer adsorption and the particle-particle collisions necessary for floc formation and growth. It also causes floc breakage. Breakage rates increase with floc size so that, in batch systems with continuous polymer addition, growth reaches a limiting plateau when growth and breakage rate become equal. Continued agitation in the absence of further polymer addition leads to progressive degradation of the flocs. Increased rate of polymer addition tends to increase the limiting floc size due to increased growth rate while increased agitation intensity reduces the limiting size by increasing the breakage rate.

While laboratory testing and a few industrial processes are carried out in the batch mode, most applications employ continuous operation. These procedures typically involve polymer addition in a stirred tank or direct injection into a flow stream. Comparison of batch and continuous flocculation in a stirred tank reveal similar trends in performance but inferior results – lower settling rates and supernatant clarity – for the continuous systems. The differences are attributed to inability to circumvent mixing problems or to provide progressive polymer addition to growing flocs. A promising modification is the use of incremental polymer addition to two or more tanks in...
Studies of flocculation in pipes with and without inline mixer elements indicate that rapid floc growth occurs following polymer injection. It appears that there may be an optimum flow rate that provides the fully turbulent conditions, probably necessary to ensure adequate mixing, while keeping shear rate low enough to minimize floc breakage. Available experimental data indicate that floc size reaches a maximum after flow over around 100 pipe diameters beyond the injection point which may be reduced to as few as 10 diameters in the presence of static mixer elements. Continued flow leads to progressive floc degradation. Incremental polymer injection along the pipe has been shown to enhance floc growth for a given overall polymer dosage.

**Nomenclature**

- \(d_k\): agglomerate size in class \(k\) [L]
- \(d_p\): polymer molecular size [L]
- \(d_s\): solid particle size [L]
- \(D\): fractal dimension [--]
- \(D_a\): agitator diameter [L]
- \(D_t\): tank diameter [L]
- \(E\): exponential factor defined by Equation 10 [--]
- \(E_{95}\): E value corresponding to \(t_{95}\) [--]
- \(f_{sp}\): particle/polymer molecule collision frequency [L^{-3}T^{-1}]
- \(F_B\): distribution factor for Brownian flocculation [--]
- \(F_S\): distribution factor for shear flocculation [--]
- \(g\): acceleration due to gravity [LT^{-2}]
- \(Gur\): mean shear rate [T^{-1}]
- \(H\): liquid depth in tank [L]
- \(k_B\): Boltzmann’s constant [ML^{-2}T^{-3}K^{-1}]
- \(K_B\): rate constant for Brownian flocculation [L^{3}T^{-3}]
- \(K_S\): rate constant for shear flocculation [T^{-1}]
- \(K_p\): rate constant for particle/polymer molecule collisions [L^{2}T^{-1}]
- \(K_{ij}\): rate constant for i and j particle collisions [L^{2}T^{-1}]
- \(n\): agitator rotational speed [T^{-1}]
- \(n_k\): number concentration of k-size particles [L^{-3}]
- \(n_s\): number concentration of solid particles [L^{-3}]
- \(n_p\): number concentration of polymer molecules [L^{-3}]

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