The scientific basis of flocculator design

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Abstract A new guideline for the design of flocculators is proposed. This guideline is to design continuous
flow flocculators on the basis of the characteristic reaction time for the loss of one micrometre particles in the
suspension. The most commonly used guideline at the present time is that of Camp, but later proposals by
Ives and O’Melia expanded the Camp guideline and incorporated more complete knowledge of flocculation.
The suggestion here continues that process, by accounting explicitly for the heterodisperse nature of typical
suspensions and the multiple collision mechanisms for particles in determining a characteristic reaction time.
While the historical guidelines have served the water treatment industry well for reasonably similar size
distributions in waters destabilized by precipitating metal hydroxides, the proposed guideline should be more
robust in considering other suspensions. In particular, the new guideline can account explicitly for the effects
of nanoparticles on flocculation.

Keywords Characteristic reaction time; design guideline; flocculation

Introduction

Guidelines for the design of flocculation reactors have gradually improved as the scientific
understanding of flocculation has increased. Past guidelines have considered all particles
in the suspension to be the same size, because the complexity of accounting for the particle
size distribution was either too difficult or apparently unnecessary to account for. Further,
until recently, it was thought that the interparticle collisions in flocculation facilities were
brought about almost entirely by fluid motion, and hence the current guidelines for design
reflect this collision mechanism only. The current interest in much smaller particles
(nanoparticles) and recent work on the effects of short-range forces on the collisions
between particles make it clear that Brownian motion is also important in successful floc-
culation. In this paper, we propose a new guideline for design of flocculators based on cur-
rent understanding of flocculation and classic chemical engineering design principles for
continuous flow reactors.

The flocculation reaction

The fundamental description of flocculation was given by Smoluchowski (1917), and is a
population balance model that describes the change in concentration of particles of any size
as follows:

Rate of change with time of
the number concentration
of particles of size \( k \) = Rate of increase in the number
concentration of particles of
size \( k \) by flocculation of smaller
particles (the sum of whose
volumes is size \( k \))

Rate of decrease in the number
concentration of particles of size
\( k \) by flocculation of size \( k \) particles
with any size particles

1 Ives organized a NATO Advanced Study Institute with the title “The Scientific Basis of Flocculation” in
1977, and subsequently published the proceedings under the same title. (Sijthoff & Noordhoff
Translating this word equation into symbols yields:

\[
\frac{1}{2} \alpha_{\text{emp}} \sum_{i \text{ and } j} \text{ such that } V_{p_i} + V_{p_j} = V_{p_k} \] 

\[
(\alpha_{ij} \beta_{ij}) n_i n_j - \alpha_{\text{emp}} n_k \sum_{i \text{ and } j}\] 

\[
(\alpha_{ik} \beta_{ik}) n_i \] 

\[
(\alpha_{ij} \beta_{ij}) = Br \alpha_{ij} Br \beta_{ij} + Sh \alpha_{ij} Sh \beta_{ij} + DS \alpha_{ij} DS \beta_{ij} \] 

where \( T \) and the subscripts \( i, j, \) and \( k \) refer to discrete particle sizes; the superscripts \( Br, Sh, \) and \( DS \) refer to the collision mechanisms of Brownian motion, fluid shear, and differential sedimentation, respectively; \( \beta_{ij} \) is the collision frequency function calculated based on long-range transport for each mechanism; \( \alpha_{ij} \) is a collision efficiency factor that accounts for short-range forces that influence collisions, including hydrodynamic considerations and van der Waals attraction; \( \alpha_{\text{emp}} \) is an empirical dimensionless correction factor used to match experimental data with model predictions; and the specification under the summation reflects that particle volume \( (V) \) is conserved in floc formation.

In this description, the particle size distribution is discretized into a chosen number of particle classes, and one equation (like Eq. (1a)) is written for each size class. Overall, flocculation creates a small number of large particles from a large number of small particles. The size distribution shifts to larger particles, so that the particles in the suspension are more susceptible to removal by subsequent processes such as sedimentation (or flotation) and filtration. Hence, for small particles, the second (negative) term on the right hand side of the equation is larger than the first (positive) term, whereas for large particles the opposite is true.

For many years, the influence of short-range forces on the collision frequency was ignored (the equivalent of \( \alpha_{ij} \) being one for all three mechanisms). Han and Lawler (1992), following the work of several others, showed the impact of including the short-range forces in predicting interparticle collisions. Collisions between particles of widely disparate sizes are predicted to occur with far less frequency by fluid shear and differential sedimentation when the short-range phenomena are accounted for. This change suggests that the fluid mixing rate, commonly accounted for by the velocity gradient \( (G) \), is less important in bringing about particle collisions than previous investigators believed, and Brownian motion is more important. In previous writings, the authors have used the terms rectilinear model to describe the situation in which only the long-range forces were considered, and curvilinear model to describe the situation in which the effects of the short-range forces were included. Here, we adopt the more descriptive terms short-range and long-range force models.

To predict how particle size distributions change in batch flocculation, the mass balance (or really, here, a number balance) would lead to the equation \( \frac{dn_k}{dt} = r_k \) and the resulting combination with Eq. (1) would be integrated over time. However, in this paper, our interest is only in the original rate of flocculation because of the definition of a characteristic reaction time.

**Characteristic reaction times**

The concept of characteristic reaction times is familiar from the degradation of radioactive materials, where the idea of half-times is commonly understood. For chemical reactions, one definition of the characteristic reaction time is the time that would be required for the concentration of the reactive substance to reach its ultimate value \( (c(\infty)) \) in a batch reactor if the reaction rate stayed at its initial value continuously. Using this definition, the characteristic reaction time for constituents with a negative reaction rate (for which \( c(\infty) = 0 \)) can be found as:
where \( c(0) \) is the initial concentration of the reactant of interest. For irreversible first and second order reactions, expressions for the reaction rate and characteristic reaction times are shown in Table 1. The detention times (\( \tau \)) required in ideal continuous flow reactors to accomplish a desired fractional removal efficiency (\( \eta \)) of a constituent with a negative reaction rate can be expressed as some number of characteristic reaction times. Expressions for the required detention times for both plug flow (PFR) and continuous flow stirred tank (CFSTR) reactors for first and second order reactions are also shown in Table 1. To illustrate these expressions, the required detention times to achieve 95% removal (\( \eta = 0.95 \)) for the two types of ideal reactors and the two different reaction orders are also shown in Table 1. Recall that one way to categorize non-ideal flow is as some number (\( N \)) of equal-sized CFSTR’s in series, with \( N = 1 \) being a CFSTR and \( N = \infty \) being a PFR (and \( N = 20 \) being quite close to a PFR). So, for example, to achieve 95% removal for a first order reaction would take somewhere between 3 and 19 times \( t_{\text{char}} \) for non-ideal reactors, depending on the value of \( N \).

These concepts of the characteristic reaction time can be applied to the flocculation reaction and to the design of flocculators, but the process is somewhat more complicated because (i) each discrete particle size has its own reaction rate expression (like Eq. (1)), (ii) not all particle sizes have negative reaction rates, and (iii) the reaction rate for any size depends on the concentration of all other size particles. Nevertheless, once a choice of a size is made, it is straightforward (with a computer program) to calculate a characteristic reaction time for that size by substituting the rate expression (Eq. (1)) into the definition of the characteristic reaction time (Eq. (2)).

In this research, we choose the size of 1 µm on which to base the characteristic reaction time for flocculation. This size is chosen as the standard size to use because (i) for almost all suspensions of interest in environmental engineering, the rate of flocculation will be negative for this size, (ii) its flocculation is influenced by all three collision mechanisms, and (iii) it is (approximately) the most difficult size to remove in subsequent deep bed filtration. Hence, in this paper, the characteristic reaction time for flocculation is taken as:

\[
t_{\text{char}} = \frac{n_{\mu m}}{-r_{\mu m}, t=0}
\]  

(3)

where is the number concentration of 1 µm particles (i.e., in a small increment of diameter surrounding one micrometer) in the suspension. The choice of the size increment in modeling does not affect this calculation, since it changes the numerator and denominator identically.

### Table 1

<table>
<thead>
<tr>
<th>Reaction order</th>
<th>Rate expression</th>
<th>( t_{\text{char}} )</th>
<th>( \tau_{\text{pfr}} )</th>
<th>( \tau_{\text{cfstr}} )</th>
<th>( \tau_{\text{pfr}} ) (( \eta = 0.95 ))</th>
<th>( \tau_{\text{cfstr}} ) (( \eta = 0.95 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( r = -k_1 c )</td>
<td>( \frac{1}{k_1} )</td>
<td>( t_{\text{char}} \left( -\ln(1-\eta) \right) )</td>
<td>( t_{\text{char}} \left( \frac{\eta}{1-\eta} \right) )</td>
<td>3 ( t_{\text{char}} )</td>
<td>19 ( t_{\text{char}} )</td>
</tr>
<tr>
<td>2</td>
<td>( r = -k_2 c^2 )</td>
<td>( \frac{1}{k_2 c(0)} )</td>
<td>( t_{\text{char}} \left( \frac{\eta}{1-\eta} \right) )</td>
<td>( t_{\text{char}} \left( \frac{\eta}{(1-\eta)^2} \right) )</td>
<td>19 ( t_{\text{char}} )</td>
<td>380 ( t_{\text{char}} )</td>
</tr>
</tbody>
</table>
Previous design guidelines

In the long-range force model, collisions by fluid shear dominate the total collision frequency function, and so traditionally the other mechanisms have been ignored in considering the design of flocculation facilities. The collision frequency function for fluid shear is:

\[ \beta_{ij} = \frac{1}{6} G (d_i + d_j)^3 \]  

(4)

where \( G \) is the mean velocity gradient and \( d \) is the particle diameter. Further, the ability to measure and account for the size distribution in modeling has been limited until recently, so that earlier investigators considered all particles in a suspension to be the same size. If, in Eq. (1), \( T_{tot}(\alpha_{ij} \beta_{ij}) = Sh \beta_{ij} \), all particles are taken to be equal in size (i.e., \( d_i = d_j = d_k \)), and Eq. (4) is substituted into the resulting monodisperse flocculation equation, the rate of flocculation becomes:

\[ r_k = -\frac{2}{3} \alpha_{emp} d_k^3 G n_0^2 = -\frac{4}{\pi} \alpha_{emp} \phi G n_0 \]  

(5)

where \( n_o \) is the initial particle concentration and \( \phi \) is the volumetric particle concentration (i.e., the volume of particles per unit volume of suspension, found as \( \phi = \pi d_k^3 n_0 / 6 \)). Substituting Eq. (5) into Eq. (3), the traditional view of flocculation in monodisperse terms with fluid shear being the dominant mechanism yields the following expression for the characteristic reaction time:

\[ t_{char} = \frac{\pi}{4} \frac{1}{\alpha_{emp} \phi G} \]  

(6)

Camp (1955) suggested that continuous flow flocculation facilities be built with the dimensionless product \( G \tau \) in the range of 23,000 to 210,000; he studied 20 plants operating successfully in the United States, all of which fell into this range. In essence, he took the characteristic reaction time to be \( G^{-1} \), so that his guideline (in our terms) was that plants should be built with detention times between 23,000 and 210,000 times the characteristic reaction time. These values are far higher than any of the multipliers shown in Table 1 because not all of the factors that enter into the characteristic reaction time shown in Eq. (6) were included in his guideline.

Ives (1968, 1978) recognized that sludge blanket clarifiers (with far higher values of \( \phi \) than water treatment flocculators) achieved a high degree of flocculation with much lower \( G \tau \) values than Camp’s guideline. He proposed that all successful flocculators have a nearly constant value of \( \phi G \tau \). In our terms, he took the characteristic reaction time to be \( (\phi G)^{-1} \). Using values from Ives (1978), we can surmise that his guideline was that values of \( \tau \) be in the range of 40 to 400 \( t_{char} \).

Finally, O’Melia (1972) recognized that the destabilization of particles (expressed in our equations by \( \alpha_{emp} \)) was essential to successful flocculation and proposed that various types of flocculators should have similar values of \( \alpha_{emp} \phi G \tau \). This guideline translates to considering \( t_{char} \) to be \( (\alpha_{emp} \phi G)^{-1} \). All of these previous investigators essentially used the concept of the characteristic reaction time in their guidelines for flocculation design, with each in succession accounting for an increasing portion of the (then) known influences on flocculation kinetics. Our proposal continues this progression by accounting for the other mechanisms of flocculation than fluid shear and by accounting for the heterodispersity of flocculating suspensions.
Results

To illustrate the approach proposed herein, we chose a base case for flocculation conditions, and made several variations from that base case; for each condition, we calculated the characteristic reaction time for the one micrometer size for both the long-range and short-range force models of flocculation. The base case conditions include a $G$ value of $32 \text{ s}^{-1}$, temperature of $25^\circ \text{C}$, particle density of $1.4 \text{ g/cm}^3$, and $\alpha_{em} = 1$. For the size distribution, we used a relatively narrow polydisperse suspension that closely mimics the distribution of Min-u-sil 5 which we have used in previous laboratory studies. Real suspensions in water treatment plants have broader distributions, and such distributions would make the kinds of changes illustrated below more dramatic. In this work, the particle size distribution function is described according to a three parameter model as follows:

$$\frac{\Delta n}{\Delta d_p} = A d_p^{-\beta (\log d_p - 2 \log d_{p,max})}$$

(7)

This function has three parameters ($A$, $\beta$, and $d_{p,max}$) that allow the distribution to be changed in various ways. Increases in $A$ shift the curve upwards, increasing the particle number concentration for all sizes. $d_{p,max}$ is the size where the highest value of the particle size distribution occurs; changes in this parameter shift the curve horizontally. Increases in $\beta$ increase the curvature and therefore make the distribution narrower. $A$ is the value of $\Delta n/\Delta d_p$ at $d_p = 1 \text{ µm}$; for the base case, the value of $A$ was $5.03 \times 10^5 \text{ cm}^{-3} \text{ µm}^{-1}$ and the size increment ($\Delta d_p$) at $1 \text{ µm}$ was $0.069 \text{ µm}$, reflecting the value of $\Delta \log d_p = 0.03$ used throughout the size range ($-1.0 \leq \log d_p \leq 2.0$). $d_{p,max}$ was chosen as $1 \text{ µm}$ for the base case. Finally, the base case value of $\beta$ was 2, which leads to substantial curvature and therefore a relatively narrow distribution. This suspension has a value of $\phi$ of $50 \text{ ppmv}$ (or $5 \times 10^{-5}$) and, with the density of $1.4 \text{ g/cm}^3$, a suspended solids concentration of 70 mg/L.

All results are presented in Table 2 in terms of the characteristic reaction time for the long-range and short-range force models. For all cases, $t_{char}$ is much greater for the short-range model than for the long-range model, because the predicted collision frequencies are much less in the short-range model (i.e., $\alpha_{ij}$ for all mechanisms is less than one). For the base case, the ratio of the characteristic times for the short-range to long-range models is nearly 16. Note that, as more phenomena known to impact the kinetics of the reaction are included, the longer the characteristic time and the smaller the multiplier required for designing a continuous flow reactor. In the base case, for example, Camp’s $t_{char}$ is $0.03 \text{ s} (G^{-1})$ and $t_{char}$ for both Ives and O’Melia (with $\alpha_{em} = 1$) is 10.4 min.

Cases B, C, and D were run under all the same conditions as the base case, but only one mechanism of interparticle collisions was operative in each case. This procedure allows one to see the relative importance of each collision mechanism, with shorter characteristic times reflecting the more dominant mechanism; the relationship between the times for each mechanism and the overall characteristic time is as follows:

$$\frac{1}{t_{char}} = \frac{1}{t_{char,Br}} + \frac{1}{t_{char,Sh}} + \frac{1}{t_{char,DS}}$$

(8)

For the base case, it is clear that fluid shear is the dominant collision mechanism in both models, making this case very close in concept to the historical emphasis on this mechanism in the environmental engineering literature. Note the difference between the two models with respect to the other mechanisms, however; for the long-range model, differential sedimentation is the second most important mechanism, whereas Brownian motion takes over this role in the short-range model. For a broader distribution than the one chosen here, these effects could be more dramatic.
In Case E, the concentration of particles in every size was tripled, and the effect is to reduce the characteristic reaction time for both models (and for the guidelines of Ives and O’Melia) to a third of the base case value. In Eq. (3), the numerator is tripled but the denominator is multiplied by 3². This result is consistent with the second order effects shown in Table 1.

For Cases F and G, the value of \( dp_{\text{max}} \) was shifted to 5 and 0.25 µm, respectively, and the values of A were adjusted to maintain the same particle volume concentration as in the base case. The Camp, Ives, and O’Melia characteristic reaction times for these cases would all be the same as for the base case, but accounting for the heterodispersity and different collision mechanisms by either the long-range or short-range models show some differences from the base case. For the larger particles (Case F), the long-range model shows an increase of \( t_{\text{char}} \) of only 5%, but the short-range model increases \( t_{\text{char}} \) by a factor of 23. This huge difference in the behavior of the two models stems from the fact that the hydrodynamic corrections built into the short-range model suggest that collisions between large and small (here 1 µm, the basis of \( t_{\text{char}} \)) particles happen only rarely, because the fluid motion around the big particle pushes small ones out of its way. With the volume concentration for Case G (smaller particles) held the same as the base case, the number concentration increased substantially and hence caused a decrease in \( t_{\text{char}} \). Of course, the opposite is true for Case F (larger particles).

When the same shift in sizes (to larger and smaller relative to the base case for Cases G and H, respectively) is done such that the particle number stays the same as the base case, both models show a decrease in \( t_{\text{char}} \) for Case H and an increase for Case I. For the increase in \( dp_{\text{max}} \) to 5 µm (Case H), the particle volume is increased approximately 100-fold, causing the large change in \( t_{\text{char}} \). The changes are mitigated in the short-range model in comparison to the long-range model because of the great reduction in collisions between particles of widely different sizes in the short-range model and the relatively greater importance of Brownian motion in causing collisions.

In a final set of changes of the size distribution, we broadened the distribution by decreasing the curvature throughout the distribution (Case J) and increased the number concentration of the small particles only by reducing the curvature below \( dp_{\text{max}} \) (Case K). In Case J, the total number concentration was the same as in the base case, so that (as in Case H), the characteristic reaction time decreased very dramatically in the long-range force model and significantly in the short-range model. Case K showed essentially no

<table>
<thead>
<tr>
<th>Case</th>
<th>Description</th>
<th>( t_{\text{char}} ) (minutes)</th>
<th>Long-range model</th>
<th>Short-range model</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Base case</td>
<td>16.3</td>
<td>258</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Brownian motion only</td>
<td>956</td>
<td>1,496</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Fluid shear only</td>
<td>22.3</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>Differential sedimentation only</td>
<td>64.5</td>
<td>2,030</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>Triple the number concentration</td>
<td>5.4</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Larger particles, same volume</td>
<td>17.1</td>
<td>5,950</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Smaller particles, same volume</td>
<td>10.5</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>Larger particles, same number</td>
<td>0.08</td>
<td>40.8</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Smaller particles, same number</td>
<td>660</td>
<td>2,120</td>
<td></td>
</tr>
<tr>
<td>J</td>
<td>Less curvature, broader distribution</td>
<td>0.13</td>
<td>77.7</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>Less curvature, more small particles</td>
<td>16.3</td>
<td>259</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>Double shear of Case G</td>
<td>5.54</td>
<td>20.7</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Temperature = 3°C</td>
<td>23.6</td>
<td>410</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>Half ( \alpha )</td>
<td>32.6</td>
<td>516</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Loss term only</td>
<td>16.2</td>
<td>244</td>
<td></td>
</tr>
</tbody>
</table>
difference from the base case because the loss of 1 µm particles is caused much more by flocculation with larger particles than that with smaller particles.

Case L shows one of the important differences between the long-range and short-range models. For the distributions of Case G and Case L (shifted to smaller sizes from the base case), Brownian motion is a significant influence in the short-range model but only a small influence in the long-range model. As a result, doubling the shear rate nearly halves \( t_{\text{char}} \) for the long-range model, but the reduction is not nearly so great for the short-range model. The \( t_{\text{char}} \) values associated with all of the earlier guidelines would be exactly halved by this change, so that these results demonstrate the value of accounting explicitly for the other mechanisms.

It is well known that the rate of flocculation is affected by temperature, and this effect is shown in Case M. For this case, the higher viscosity directly reduces the collision rate by Brownian motion and differential sedimentation. We assumed that the power input to the flocculators remained the same as in the base case, and that assumption means that the \( G \) value was also reduced. As a result, \( t_{\text{char}} \) increased by nearly 50% for the long-range model, and slightly more for the short-range model.

The effect of poor particle destabilization (value of \( \alpha_{\text{emp}} < 1 \)) is clear from Eqs (1) and (3) – the characteristic time is inversely proportional to \( \alpha_{\text{emp}} \), as it would be for the O’Melia guideline. This result is shown in Table 2 through Case N.

In making these calculations, we used a previously developed computer program designed to show how the particle size distribution changes in batch flocculation. In such modeling, the first term on the right hand side of Eq. (1a) is difficult to calculate because the size range is broken into equal logarithmic increments of diameter. The size associated with a forming floc falls between two of the standard discrete sizes, and a fraction of that floc is assigned to each of the two sizes surrounding the true size (Lawler et al., 1980). The second term on the right hand side of Eq. (1) is unaffected by this procedure, and hence can be calculated reasonably easily on a spreadsheet (especially for the long-range model). For almost any realistic size distribution in water plants, the second (loss) term far outweighs the first (gain) term for 1 µm particles, the basis of the calculation of \( t_{\text{char}} \). Hence, for virtually all cases, one could calculate \( t_{\text{char}} \) based on the loss term only. As shown in Case O, the change in \( t_{\text{char}} \) from the base case is minor with this simplification.

Conclusions

A new guideline for the design of flocculators is proposed in this paper. This proposal is to calculate a characteristic reaction time \( (t_{\text{char}}) \) for the loss of one micrometer particles based on the most recent scientific understanding of flocculation and provide a detention time in continuous flow reactors that is some (reasonably small) multiplier of the characteristic reaction time. The previous design guidelines presented by Camp, Ives, and O’Melia can also be expressed using this concept of characteristic reaction times. However, because their guidelines were based on monodisperse suspensions and considered only collisions brought about by fluid shear, large multipliers are needed to correlate the characteristic times to practical applications.

Suspensions of interest in environmental engineering are heterodisperse, and the relative importance of each collision mechanism (Brownian motion, fluid shear, or differential sedimentation) is highly dependent on the particle size distribution. The results in this paper suggest that the calculation of \( t_{\text{char}} \) using the reaction rate expression that includes all collision mechanisms leads to a more robust criterion for designing flocculation reactors. In the future, making experimental measurements of the actual particle size distributions of the suspension to be flocculated and then calculating the proposed characteristic reaction time should provide a sound basis for designing continuous flow flocculation basins. The multiplier for the characteristic reaction time needed for design reflects the flow pattern
and the desired removal efficiency. Further development is needed to determine this multiplier before this concept can be used directly in design.

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