Flocculation Models

Overview

- Flocculation definition and regulation
- Mechanical Design
- Hydraulic conventional design
- Fractals
- Collisions
  - Predictive model
- Conclusions
- Surface coverage

What is Flocculation?

- A process that transforms a turbid suspension of tiny particles into a turbid suspension of big particles!
- Requires
  - Sticky particles (splattered with adhesive nanoparticles)
  - Successful collisions between particles
  - Flocs are fractals (“the same from near as from far”)
- The goal of flocculation is to reduce the number of small particles (that haven’t been flocculated)
  - One goal is to understand why some particles are always left behind (turbidity after sedimentation)
  - Another goal is to learn how to design a flocculator

The Challenge of Flocculation

- We would like to know
  - How do particles make contact to aggregate?
  - What determines the time required for two flocs to collide? (flocculation rate)
  - How would you design a flocculator for a target settled water turbidity?
  - How strong are flocs?
- The challenge of the large changes in scale
  - The Al(OH)$_3$ nanoparticles begin at a scale of 10 to 100 nanometers
  - Flocs end at a scale of 100 micrometers
  - Flocculators are meters long

Ten State Standards

- The detention time for floc formation should be at least 30 minutes with consideration to using tapered (i.e., diminishing velocity gradient) flocculation. The flow-through velocity should be not less than 0.5 nor greater than 1.5 feet per minute.
- Agitators shall be driven by variable speed drives with the peripheral speed of paddles ranging from 0.5 to 3.0 feet per second. External, non-submerged motors are preferred.
- Flocculation and sedimentation basins shall be as close together as possible. The velocity of flocculated water through pipes or conduits to settling basins shall be not less than 0.5 nor greater than 1.5 feet per second. Allowances must be made to minimize turbulence at bends and changes in direction.
- Baffling may be used to provide for flocculation in small plants only after consultation with the reviewing authority. The design should be such that the velocities and flows noted above will be maintained.
  - Hydraulic flocculators allowed only by special permission!
### Mechanical Flocculation

- **Particle collisions caused by gentle stirring**
- **Advantage**
  - Energy dissipation rate can be varied independent of flow rate
- **Disadvantage**
  - Potential short circuiting (some fluid moves quickly from inlet to outlet)
  - Moving parts in a wet environment
  - Highly nonuniform energy dissipation rate

### Recommended G and Gθ values:

<table>
<thead>
<tr>
<th>Type</th>
<th>“Velocity gradient” (G) (1/s)</th>
<th>Energy Dissipation Rate (瑁)</th>
<th>Gθ</th>
<th>0° (minute)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low turbidity, color removal</td>
<td>20-70</td>
<td>0.4 – 4.9</td>
<td>50,000-250,000</td>
<td>11 - 210</td>
</tr>
<tr>
<td>High turbidity, solids removal</td>
<td>70-180</td>
<td>4.9 - 32</td>
<td>80,000-190,000</td>
<td>7 - 45</td>
</tr>
</tbody>
</table>

* Calculated based on G and Gθ guidelines + average value assuming viscosity is 1 mm²/s

### Mechanical Design: mixing with paddles

- **Model the mixing unit as a flat plate moving normal to the fluid (infinite fluid)**
- The maximum energy dissipation rate is given by
  \[ \varepsilon_{\text{Max}} = \frac{\Pi_{\text{Mix}} V}{W_{\text{Fluid}}} \]
- Closely spaced plates will have higher \( \varepsilon_{\text{Max}} \)

### Computational Fluid Dynamics Analysis

- Flat plate normal to the flow
- 1 m wide
- Flow was 2-D
- \( V = 1 \text{ m/s} \)
- \( \text{Re} = 100,000 \)
- \( \varepsilon_{\text{Max}} = 0.04 \text{ W/kg} \)
- \( \Pi_{\text{Mix}} = \frac{(\varepsilon_{\text{Max}} W_{\text{Fluid}})^2}{V} \)
- \( \Pi_{\text{Plate}} = 0.34 \)

### What is \( \varepsilon_{\text{Max}} \) for mechanical flocculators?

- The maximum velocity for mixing units given by 10 State Standards is 3 ft/s
- No minimum plate width is specified
- For narrow plates \( \varepsilon_{\text{Max}} \) is comparable to rapid mix!
- Mechanical flocculators may be breaking flocs in the wake of the mixer
- Nonuniformity of the energy dissipation rate is an inefficient use of energy

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Uniformity of mixing requires

- “Flocculation reactors should be designed to have relatively uniform mixing intensities throughout the reactor.”
- “If the mixing intensity varies considerably across the reactor, substantial breakup will occur in the portions of the reactor with the highest intensities, thereby acting against the flocculation desired.”

Benjamin and Lawler. Water Quality Engineering: Physical/Chemical Treatment Processes (page 833)

Mechanical Flocculators Summary

- Waste (a small amount of) electricity
- Require unnecessary mechanical components
- Have a wide distribution of energy dissipation rates (highest in the wake of the paddles) that may break flocs
- Have a wide distribution of particle residence times (completely mixed flow reactors)

Hydraulic Flocculators

- Horizontal baffle
- Vertical baffle
- Pipe flow (w/ orifices)
- Gravel bed
  - A bad idea (cleaning would require a lot of work)

Flocculator Geometry

Why aren’t hydraulic flocculators used more often?

- Simple construction means that there aren’t any items that private companies (vendors) can sell as specialized components
- Consulting firms want to be able to pass the design responsibility off to a vendor
- The presumed operation flexibility of mechanical flocculators (variable speed motor driving a slow mixing unit)
- Poor documentation of design approach for hydraulic flocculators (special permission required to use in the US)
- Using electricity is cool, design innovation is suspect...
- Prior to AguaClara we didn’t have a design algorithm based on the fundamental physics

Schulz and Okun (Hydraulic flocculators)

- Recommend velocity between 0.1 and 0.3 m/s
- Distance between baffles at least 45 cm
- Water must be at least 1 m deep
- Q must be greater than 16,000 m³/day (115 L/s)
- G0 of 20,000 to 150,000

These aren’t universal constants!
We need to understand the real constraints so we can scale the designs correctly
What length scale could make a dimensionless parameter?
AguaClara flocculator design continues to evolve rapidly

- 2005: We used conventional guidelines based on velocity gradient to design the first low flow vertical flocculator.
- 2010: We designed using energy dissipation rate and accounted for the nonuniformity of the energy dissipation rate ($\theta = 15$ minutes).
- 2015: We added obstacles to decrease the distance between expansions to make all of our flocculators have maximum collision efficiency ($\theta = 8$ minutes).
- 2016: We increase the efficiency of removal of small particles ($\theta = 1$ minute).

Edge of Knowledge Alert

- Why would we ever think that the baffled flocculators invented over 100 years ago were the optimal design for flocculation? (room to improve!)
- We have better coagulants now. Might that influence flocculator design?
- We are only now beginning to understand the physics of fractal flocculation.
- We are rapidly improving the design of hydraulic flocculators based on our evolving understanding of the physics of flocculation.

Fractal Flocculation Theory

- Turbulence is caused by expansions.
- Particles and flocs are transported to collide with each other by turbulent eddies and over short distances by viscous shear and Brownian motion.
- Flocs grow in size with each successful collision.
- Collisions between particles of very different sizes are not very succesful.*

*Hypothesis from 2012. Might also be a limit on the sum of the diameters.

Flocculation models based on geometry and stickiness of nanoparticles can predict performance

- The coagulant forms sticky nanoparticles.
- The bond between a coagulant nanoparticle and a clay platelet is strong.
- The bond between two coagulant nanoparticles is weaker.
- Macromolecules of dissolved organic matter (DOM) cover the coagulant nanoparticles (and DOM isn’t sticky).

There is still much to learn about flocculation!

Human hair is 50 mm in diameter

Sizes of a few particles

- Clay: 7000 nm, 7 $\mu$m, 0.007 mm
- Bacteria: 1000 nm, 1 $\mu$m, 0.001 mm
- Nanoparticle of coagulant: 90 nm, 0.09 $\mu$m
- Dissolved organic matter: 50 nm, 0.05 $\mu$m
How much coagulant should we add?

- Our hypothesis:
  - When one clay platelet contacts another clay platelet, they will stick together if and only if there is a coagulant nanoparticle at the point of contact.

Dissolved organic matter (DOM) covers the coagulant nanoparticles

The size changes produced by flocculation are dramatic

- How many sequential collisions are required to make a 1 mm particle starting from 1 μm particles?
- How much larger in volume is the 1 mm diameter particle?
  - 1,000,000,000!

It requires many sequential doubling collisions to make a big floc

- 1 collision 1+1=2
- 2 collisions 2+2=4
- 3 collisions 4+4=8
- 4 collisions 8+8=16
- Number of original particles in the floc $= 2^n$
- What is $n$ to obtain $1,000,000,000 = 2^n$?
- $n=30$

$$\log(1000000000) = n \log(2)$$

This assumes volume is conserved!
Fractals capture the idea that volume isn’t conserved

- What happens to the density of a floc as it grows larger? Floc density approaches the density of water because the floc includes water.

If volume were conserved, what would $D_{\text{Fractal}}$ be? ___

Is floc mass conserved? ___

Fractal Geometry

- Fractal geometry explains the changes in floc density and sedimentation velocity as a function of floc size.
- The fractal dimension of flocs is approximately 2.3 (based on floc measurements).
- Fractal dimension is a function of the size ratio of the colliding flocs.
- Further research to quantify the fractal dimension in flocculation is needed.

Fractal Terminal Velocity Equations

$$V_t = \frac{g d^2}{18 \nu_{\text{floc}}} \left( \rho_{\text{floc}} - \rho_{\text{w}} \right) \left( \frac{d}{d_f} \right)^{2 - D_{\text{fractal}}}$$

- Buoyant density
- Viscous flow terminal velocity
- Algebra!

Collision Model of the Flocculation Process

- The relative velocity between flocs is set by viscous shear because their separation distance is less than the inner viscous scale.
- The time required per collision is a function of the relative velocity between flocs, the average separation distance between flocs, and the floc size.
- In the next slides we will explore how to characterize collision time for flocs.
- We will assume that collisions occur between similar sized flocs. There is some evidence that flocs of very different diameters don't attach when they collide. Or it may be that any collisions with large flocs are unsuccessful.

Buoyant Density of Flocs

$$\rho_{\text{floc}} - \rho_{\text{w}} = \left( \rho_{\text{floc}} - \rho_{\text{w}} \right) \left( \frac{d}{d_f} \right)^{2 - D_{\text{fractal}}}$$

Will these flocs settle faster than the primary particles?

Fractal Terminal Velocity

$$V_t = \frac{g d^2}{18 \nu_{\text{floc}}} \left( \rho_{\text{floc}} - \rho_{\text{w}} \right) \left( \frac{d}{d_f} \right)^{2 - D_{\text{fractal}}}$$

Laminar flow $V_t = \frac{g d^2}{18 \nu_{\text{floc}}} \left( \rho_{\text{floc}} - \rho_{\text{w}} \right)$

Capture velocity for AguaClara plate settlers

Why flocculation is necessary!

Floc Terminal Velocity

$$V_t = \frac{g d^2}{18 \nu_{\text{floc}}} \left( \rho_{\text{floc}} - \rho_{\text{w}} \right) \left( \frac{d}{d_f} \right)^{2 - D_{\text{fractal}}}$$

- shape factor for drag on flocs
- $D_{\text{Fractal}} = 2.3$ and $d_f = 1 \mu m$

The model takes into account the changing density of flocs.
Particle separation length scale ($\Lambda$)

- The average volume of water “occupied” by a particle equals the inverse of number of particles per volume ($n_p$)
  \[ \Lambda = \frac{1}{n_p^3} \]

- The number of flocs decreases as the flocs grow in size
  \[ n_p = n_0 \left( \frac{d_p}{d_f} \right)^{3/2} \]

Comparison of classic and hypothesized collision models

- Classic model: transport and mixing at length scales larger than the diameter of the particle do not influence collisions — therefore slow, long, straight walk toward a collision
  \[ v_i = d_i \Gamma \]

- Hypothesized model: fast random walk clearing volume of fluid equal to volume occupied followed by slow, short, straight walk toward a collision*
  \[ v_i = \Lambda \Gamma \]

Classic Models: Relative velocity scales with diameter

\[ v_i = d_i \Gamma \]

Model assumption differences are about the relative velocities

- Classic particle collision models assume that the average relative velocity of two particles is set by the length scale of the diameter of the particles regardless of their separation distance
- We hypothesize that the majority of the transport time is spent in a long random walk with relative velocities based on the average particle separation distance ($\Lambda$)*

Hypothesis: Relative velocity scales with separation distance

\[ v_i = \Lambda \Gamma \]

Proposed ($\Lambda$) Long Range Transport Hypothesis*

- At all times there exists a differential VOLUME of fluid that will transport any particle with its center located within that differential VOLUME to a collision of the particle and collector between \( \frac{\Lambda}{2 \pi} \) and \( \frac{\Lambda}{2 \pi} + \frac{\lambda}{2} \)
- The time required for that final transport to a collision is \( \frac{\Lambda}{2 \pi} \)
- Long range transport delivers the particle to the differential volume for the final slow transport to the collision
- Next... characterize the time for the long range transport*
**How much water is cleared (filtered) from a floc’s perspective?**

- Volume cleared is proportional to a collision area defined by a circle with diameter = sum of the particle diameters: $V \propto \pi d_p^2$.
- Volume cleared is proportional to time: $V \propto t$.
- Volume cleared is proportional to the relative velocity between flocs: $V \propto \pi d_p^2 v_r t$.

**Collision rates for the two assumptions**

<table>
<thead>
<tr>
<th>$v_r = AG$</th>
<th>$v_r = d_f G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_c = \frac{\Lambda^3}{\pi d_p^2 v_r}$</td>
<td>$t_c = \frac{\Lambda^3}{\pi d_f^2 v_r}$</td>
</tr>
<tr>
<td>$\tau = \frac{\Lambda^3}{\pi d_p^2 v_r}$</td>
<td>$\tau = \frac{\Lambda^3}{\pi d_f^2 v_r}$</td>
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</table>

- $t_c$ is average time per collision.
- $\tau$ is probability of attachment given a collision.
- $\Lambda$ is number of sequential collisions that result in aggregation.
- $\alpha$ is probability of attachment given a collision.

$$dN = \frac{\alpha}{t_c} dt \quad dN = \pi \frac{d^2}{\Lambda} G dt$$

**Integrate**

$$\frac{dn_o}{-kn_o} = \frac{\pi d^3}{\Lambda} G dt$$

$$\frac{\int n_o^2 - n_i^2}{\int n_i^2} = -k \frac{\pi d^3}{\Lambda} G a$$

**Use dimensional analysis to get a relative velocity**

<table>
<thead>
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<tr>
<td>$v_r = f(v, v, \Lambda)$</td>
</tr>
<tr>
<td>$v_r = \frac{\Lambda}{n_f}$</td>
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<tr>
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<table>
<thead>
<tr>
<th>$\Lambda = \frac{1}{n_f^2}$</th>
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<tr>
<td>$N = \frac{1}{n_f}$</td>
</tr>
<tr>
<td>$d_f = \frac{1}{n_f}$</td>
</tr>
<tr>
<td>$v_r = \frac{\Lambda}{n_f^2}$</td>
</tr>
<tr>
<td>$v_r = \frac{d_f}{v}$</td>
</tr>
<tr>
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</tr>
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<td>$v_r = d_f G$</td>
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</tbody>
</table>

**Collision Rate and Particle Removal**

- $v_r = \frac{\Lambda}{n_f^2}$
- $v_r = d_f G$

**pC*: A dimensionless measure of removal efficiency**

- Sloppy parlance...
- What is the target effluent turbidity for a water treatment plant?
- What is pC* for a water treatment plant treating 300 NTU water?
- What is required effluent turbidity?
- How many orders of magnitude reduction?
We can test the collision models with laboratory data

\[ v_r = \Lambda \bar{G} \]

\[ \mu = \frac{1}{3} \log \left( \frac{2}{3} \pi d \Lambda \bar{G} \right) \]

\[ \mu = \frac{1}{3} \log \left( \frac{2}{3} \pi d \Lambda \bar{G} \right) \]

\[ \Lambda = \frac{1}{n_0^2} \]

- Data will converge if we choose the right dimensionless grouping

\[ \mu = \frac{d}{\Lambda \bar{G}} \]

- Plot performance as a function of this dimensionless group

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Relative velocities appear to scale with average separation distance

- These results appear to be different than classic particle collision models
- There might be a confounding assumption that leads to these surprising results
  - Big flocs are useless
  - Small flocs disappear at a rate proportional to the number of their collisions
  - ?

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Floc model for viscous dominated collisions

\[ pC^* = \frac{3}{2} \log \left( \frac{2}{3} \pi d \alpha_G \right) \]

\[ \alpha_G = \frac{1}{2} k \bar{d}_c^2 \]

- A function of fractional surface coverage of particle by coagulant
- Rate constant (model fitting parameter)
- Particle diameter
- Flocculation time
- Velocity gradient
- Initial particle spacing

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Diameter Scaling

\[ v_r = d_r \bar{G} \]

\[ \frac{d_r}{\Lambda \bar{G}} \]

- \( D_{1000} = 7 \mu m \)
- \( D_{1000} = 20 \text{ nm} \)

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Separation Distance Scaling

\[ v_r = \Lambda \bar{G} \]

\[ \frac{d_r}{\Lambda \bar{G}} \]

- \( D_{1000} = 7 \mu m \)
- \( D_{1000} = 20 \text{ nm} \)
Model predictions? \[ \Lambda \sim \frac{1}{N^2} \]

- \[ v_i = \Delta \bar{G} \]
- \[ \frac{3}{2} \left( \frac{n_p^2 - n_i^2}{2} \right) = k \pi d_i \bar{G} \]
- \[ \frac{3}{2} \left( \Lambda_i - \Lambda \right) = -k \pi d_i \bar{G} \]
- \[ G_i = \frac{3}{2} \left( \Lambda_i - \Lambda \right) \]
- Flocculator must be designed for target settled water turbidity
- \[ G_i = \frac{3}{2} \left( \Lambda_i - \Lambda \right) \]

Predictions for required \( G \theta \) also suggest that \( \Lambda \) scaling is correct

- \[ v_i = d_i \bar{G} \]
- \[ v_i = \frac{\Lambda_i}{\bar{G}} \]

Track surface area to assign probabilities to collisions

- \( \Gamma_{\text{CompClay}} \): Fraction of clay surface area coated by coagulant (this includes coagulant that is coated with humic acid)
- \( \Gamma_{\text{HAComp}} \): Fraction of coagulant surface area coated by humic acid
- \( 1 - \Gamma_{\text{CompClay}} \): Fraction of clay surface area that isn’t coated by anything
- \( \Gamma_{\text{CompClay}} (1 - \Gamma_{\text{HAComp}}) \): Fraction of clay surface area that is coated by clean coagulant
- \( \Gamma_{\text{CompClay}} \Gamma_{\text{HAComp}} \): Fraction of clay surface area that is coated by coagulant that is coated by humic acid

The flocculation model is far from complete

- Doesn’t predict decreasing performance at high coagulant dosages
- Likely that coagulant-coagulant bonds are weaker than coagulant-clay bonds and we don’t yet have that effect in the model
- Doesn’t describe floc formation when the dissolved organics concentration is so high that \( \Lambda \) scales are significant
- Doesn’t describe effects of sedimentation tank design

There are 3 possible initial points of contact that can lead to attachment

- \( \omega_{\text{ClayClay}} = \omega_{\text{ClayComp}} + \omega_{\text{CompClay}} + \omega_{\text{CompComp}} \)
- The probability of a clay surface colliding with a PACI surface is equal to twice the probability that the first surface is clay and the second surface is the PACI surface of a PACI-HA nanoaggregates
- \( \omega_{\text{ClayClay}} = 2 \left[ (1 - \Gamma_{\text{ClayComp}}) \Gamma_{\text{ClayClay}} (1 - \Gamma_{\text{ClayClay}}) \right] \)
- The probability of a PACI surface colliding with a PACI surface
- \( \omega_{\text{ClayClay}} = \Gamma_{\text{ClayClay}} \left[ (1 - \Gamma_{\text{ClayComp}}) \right] \)
- The probability of a PACI surface colliding with a HA surface
- \( \omega_{\text{ClayClay}} = 2 \left[ (1 - \Gamma_{\text{ClayComp}}) \Gamma_{\text{ClayClay}} (1 - \Gamma_{\text{ClayClay}}) \right] \)

4 major assumptions of the floc model

- Long range transport velocity to a collision scales with the average separation distance of the particles
- Relative velocities between particles are dominated by viscous shear (not inertia)
- Separation distance is smaller than inner viscous scale
- Collisions with large flocs don’t result in attachment
- Let’s explore this assumption
- Plug flow!
Particle collisions appears to be dominated by viscous shear

\[ \lambda \approx \Pi_s \eta_s \]
\[ \Pi_s = 50 \]
\[ d_{\text{col}} = 4 \mu m \]

Particle separation distances are less than the viscous length scale

Fractal Flocculation Conclusions

- It is difficult to flocculate to a low residual turbidity because the time between effective collisions increases as the number of particles and non-settleable flocs decreases
- Particles can’t attach to full size flocs
  - Perhaps because of high differential velocities at the moment of impact
- We have an unpublished model that predicts settled water turbidity after a flocculator (assuming no flocculation in the sedimentation tank)
- The model is an approximation!

Review

\[ Gt = \frac{3}{2} \frac{\Lambda^2}{k \pi dhi} \]
\[ pC^* = \frac{2}{3} \log \left( \frac{2}{3} \pi k d^2 \frac{Gt}{\Lambda^2} + 1 \right) \]

- Why is it that doubling the residence time in a flocculator doesn’t double pC* for the flocculator?
- Why does increasing initial turbidity decrease the initial time between collisions?
- Which terms in the model are determined by the flocculator design?
- The model assumes plug flow!

What does \( Gt \) mean?

\[ G = \frac{du}{dy} \]
Definition of velocity gradient

\[ \Lambda \int Gdy = \int du \]
Find relative velocity between flocs separated by distance \( \Lambda \)

\[ AG = v_r \]
The relative distance traveled due to fluid deformation is proportional to time

\[ GI = \frac{L_{\text{deformation}}}{\Lambda} \]
A GI of 1 means that the particles have a relative displacement equal to their separation distance

What is the model missing?

- The model doesn’t include any particle aggregation that occurs in the sedimentation tank
- Residence time in the sed tank is long and energy dissipation rate is low
- Flocculation in the sed tank (especially if there is a floc blanket) is very important
- It assumes all nanoparticles interact with clay and not with dissolved organic matter or fluoride or ...

CEE 4540: Sustainable Municipal Drinking Water Treatment
Monroe Weber-Shirk