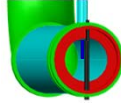


Sustainable Municipal Drinking Water Treatment



continuing

Coagulation and Rapid Mix: A search for a basis for rational design

Aggregation
Intermolecular bonding
Mixing
Energy Dissipation
Shear and Diffusion



The quest to improve water treatment: What are our resources?

- ✓ • Experience operating water treatment plants
- ✓ • Conventional wisdom
 - Predictive performance models for drinking water treatment (Why is this hard?)
- ⊗ • Rapid mix model
- ✓ • Flocculation
- ⊗ • Sand filters
- ✓ • Opportunity! If we can figure out the physics we will be able to create better designs

Gravity separation is awesome, but we need help

- How could we increase the sedimentation rate of small particles?

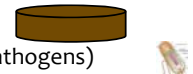
$$V_t = \frac{d^2 g}{18\nu} \frac{\rho_p - \rho_w}{\rho_w}$$

Annotations for the equation:

- d : Increase d (stick particles together)
- g : Increase g (centrifuge)
- $\rho_p - \rho_w$: Increase density difference (dissolved air flotation)
- ν : Decrease viscosity (increase temperature)

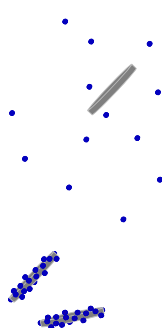
Seeking favorable interactions between particles

- We add a sticky insoluble coagulant that forms nanoparticles
- We design reactor geometry and flow regimes to create interactions between
 - Nanoparticles of coagulant precipitate
 - Dissolved organic molecules
 - Inorganic particles (like clay)
 - Organic particles (including pathogens)



Definitions

- Coagulation: The process of adding a sticky solid phase material (adhesive nanoparticles) that attaches to the particles so they can attach to each other (the topic of these notes)
- Flocculation: The process of producing collisions between particles to create flocs (aggregates) (next set of notes)



Aluminum Sulfate Chemistry Alum $[\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}]$

- A widely used coagulant
 - Typically 10 mg/L to 100 mg/L alum is used (0.9 to 9 mg/L as Al)
 - High concentrations (stock solutions) don't precipitate because the pH is low
 - The alum precipitates when it blends with the water in the water treatment plant
 - The primary reaction produces $\text{Al}(\text{OH})_3$
- $$\text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_3 + 6\text{H}^+ + 3\text{SO}_4^{2-}$$
- ↓ $\text{pH} = -\log[\text{H}^+]$

Acid Neutralizing Capacity (ANC or Alkalinity) Requirement



- ANC is measured as mg/L of CaCO_3
- How much ANC is consumed by alum?

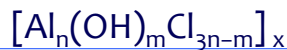
	Alum	Calcium Carbonate
Molecular Formula	$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$	CaCO_3
Molecular mass	600 g/mol	100 g/mol
eq/mol	6	2
Molecular mass/eq	100 g/eq	50 g/eq
Simple guide	1 mg/L Alum consumes	0.5 mg/L Calcium Carbonate ANC

This sets the maximum alum dose that can be used for low alkalinity waters

Polyaluminum Chloride (PACl)

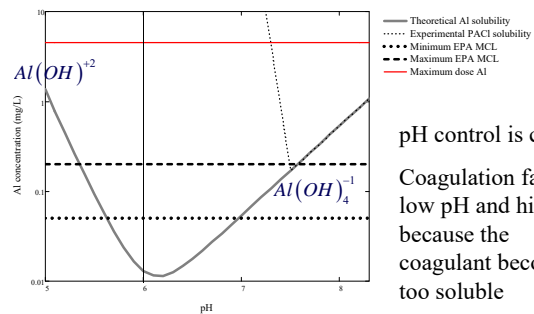
- Slowly titrated with a base (in the chemical plant) to produce a meta-stable and soluble polymeric aluminum (partially neutralized)
- Consumes less alkalinity (ANC)
- Aluminum mass fraction is higher than in alum (no $14.3 \text{ H}_2\text{O}$) so the mass of PACl required is less than for alum (0.4-10 mg/L as Al)

PACl Formula and Basicity



- Basicity: Ratio of hydroxyl equivalents to aluminum equivalents $\text{Basicity} = \left(\frac{m}{3n}\right)$
 - Basicity of 1 would mean that it does not produce any protons when it dissolves in water
 - 0 means it produces 3 protons per Al (like alum)
- The lowest basicity commercial PACls are about 10%
- Most PACls are in the medium to high basicity range (50-70%)
- Highest stable basicity (83%) is aluminum chlorhydrate (ACH) – would be useful for treating water with very low ANC

Aluminum Solubility



pH control is critical!
Coagulation fails at low pH and high pH because the coagulant becomes too soluble

The Conventional Coagulation Hypothesis*

- “The purpose of addition of coagulant chemicals is to neutralize the negative charges on the colloidal particles to prevent those particles from repelling each other.
- Coagulants due to their positive charge attract negatively charged particles in the water.”

<http://www.thewater treatments.com/wastewater-sewage-treatment/coagulation-flocculation-process/>

* This hypothesis has been the explanation of coagulation for close to 100 years.

Surface charge of Particles and Natural Organic Matter (NOM)

- NOM significantly increases the required coagulant dose in some waters
- The coagulant required increases with NOM concentration
- Charge density (conventional explanation)
 - Clay: 0.05 to 0.5 $\mu\text{eq}/\text{mg}$ ($1 \text{ mg/L clay} \approx 1 \text{ NTU}$)
 - Fulvic acid 5 to 15 $\mu\text{eq}/\text{mg C}$
- NOM also has a larger surface area* per unit mass than clay particles and thus provides many attachment sites for coagulant nanoparticles

Electrostatic Charge Neutralization

- Explains phenomena such as the aggregation of sediment suspensions in estuaries
- Explains many particle stability experiments with pure systems of nanoparticles
- **May not explain the particle interactions that occur in flocculation using aluminum and iron based coagulants**

Coagulation: The adhesive nanoparticle hypothesis

- Aluminum coagulants (alum and polyaluminum chloride) produce adhesive nanoparticles of precipitated aluminum hydroxide that attach to surfaces including other nanoparticles
- The attractive attachment force must be stronger than the polar bond between water molecules so the nanoparticles can push water out of the way

[Predictive performance model for hydraulic flocculator design with polyaluminum chloride and aluminum sulfate coagulants](#) Karen A. Swetland, Monroe L. Weber-Shirk*, Leonard W. Lion

Sticky nanoparticles?





- Effective flocculation only occurs when the coagulant is in the solid phase
 - Thus NaOH and $\text{Ca}(\text{OH})_2$ are not effective coagulants because they are soluble at neutral pH
- $\text{Al}(\text{OH})_3$ likes to stick to itself and to other surfaces
- Why is the solid phase $\text{Al}(\text{OH})_3$ and $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ sticky? (Perhaps because it is more polar than water)

On Rapid Mixing...

“In summary, little is known about rapid mix, **much less any sensitivity to scale**. However, the models and data reviewed suggest the need to be on the lookout for certain effects. From what is presently known, it can be speculated that since coagulant precipitation is sensitive to both micro- and macro-mixing, scale-up must consider not only energy dissipation rate, but also the reaction injection point and the contacting method.”

Mixing in Coagulation and Flocculation 1991 page 292

Traditional rapid mix units

- Backmix mechanical reactors 
- In-line blenders 
- Hydraulic Jump 
- In-line static mixers 

Traditional Design

- Conventional design is based on the use of G (velocity gradient) as a design parameter. $G = \sqrt{\frac{\epsilon}{\nu}}$
- We don't know what the design objective is for rapid mix and thus it isn't clear what parameter matters
- “... a high degree of turbulence leads to more efficient chemical use for destabilization by adsorption and charge neutralization, whereas destabilization by precipitation is less sensitive to the mixing conditions.” (Water Quality Engineering – Benjamin and Lawler, 2013)
- In drinking water treatment the coagulant dosages are almost always higher than the solubility limit; perhaps rapid mix isn't important

This is the traditional approach Power, height, and G



$$G = \left(\frac{P}{\Psi \rho V} \right)^{\frac{1}{2}}$$

$$\Psi = Q\theta$$

$$P = G^2 \Psi Q \rho$$

$$P = Q \rho g \Delta h$$

$$\Delta h = \frac{P}{Q \rho g}$$

$$\Delta h = \frac{G^2 \Psi \theta}{g}$$

"velocity gradient" caused by mixing

Reactor volume

Power required

Power required to lift water



$$G^2 \Psi = \varepsilon$$

Equivalent potential energy measured as a height used for mixing

Equivalent potential energy as a function of G

Traditional Design Guidelines: Mixing with a Propeller

Average values

Residence Time (s)	"velocity gradient" (G) (1/s)	Energy dissipation rate (W/kg)	Equivalent height (m)*
0.5	4000	16	0.8
10 - 20	1500	2.25	2.3 - 4.6
20 - 30	950	0.9	1.8 - 2.8
30 - 40	850	0.72	2.2 - 2.9
40 - 130	750	0.56	2.3 - 7.5

No mention of scale effects

$$\Delta h = \frac{G^2 \Psi \theta}{g}$$



from Environmental Engineering: A Design Approach by Sincero and Sincero, 1996, page 267

* A measure of mechanical energy converted to heat

Hydraulic Energy Constraint

- If we use the same amount of mechanical energy in hydraulic water treatment plants as is used in mechanical water treatment plants we will need between 0.8 and 7.5 m of water height change just to power the rapid mix unit!!!!
- Rapid mix is one of the largest energy consumers in mechanical plants
- We need to be more efficient (and hence smarter)

Why might RAPID mixing be necessary?

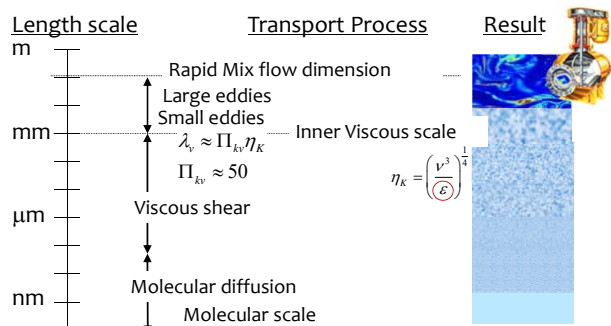
- **Mix** the adhesive nanoparticles uniformly with the raw water (definitely important if the flow is split between treatment trains)
- **IF RAPID** mixing matters then there must be something bad that happens if the mix is SLOW (but maybe it doesn't matter)
 - Self aggregation of nanoparticles into microclusters
 - Non-uniform distribution of nanoparticles between particles

Not clear if this matters or how to control it

Or maybe rapid mix is actually the first stage of flocculation!

- We will prove later that collision potential (and hence particle aggregation) is proportional to $G\theta$
- Rapid mix collision potential can be as great as the collision potential for flocculation
- So this raises the question... Is rapid mix actually the first stage of flocculation?

Rapid Mix: From macro to nano scale (in a few seconds?)



Three steps for mixing

- Large scale eddies to mix at the dimension of the reactor (Macro mixing)
 - Generate large eddies
 - Flow expansion with dimensions similar to the dimension of the reactor, pipe, or channel
 - Critical if the flow splits between treatment trains
- Turbulence to mix down to the scale of the smallest eddies (Micro mixing)
- Fluid shear and diffusion to transport the coagulant nanoparticles to the particles and pathogens

Goals
aren't
clear

Possible constraints

- Fluid must be fully turbulent to get efficient mixing by eddies
 - $Re > 10,000$ (this seems like a good goal)
- Uniform distribution of coagulant between particles (all particles get some glue)
 - Constraint isn't obvious
- Shear/Diffusion of nanoparticles from fluid phase to particle surfaces occurs in a reasonable amount of time (ideally completed before flocculation)
 - Might not be possible

Turbulence – Mixing – Energy Dissipation

- The turbulent eddies cause stretching and thinning of concentration gradients and “shuffle” packets of fluid
- The intensity of the turbulence can be characterized by the rate at which mechanical energy is being lost to thermal energy

$$\varepsilon = \left[\frac{W}{Kg} \right] = \left[\frac{J}{s \cdot Kg} \right] = \left[\frac{N \cdot m}{s \cdot Kg} \right] = \left[\frac{kg \cdot m \cdot m}{s^2 \cdot s \cdot Kg} \right] = \left[\frac{m^2}{s^3} \right]$$

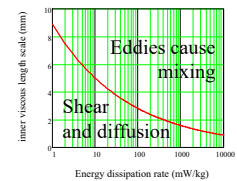
How Far Can Turbulence Mix? (Viscous inner scale)

- Dissipates **energy** from the mean flow through chaotic eddies and through **viscosity** where the kinetic energy is converted to heat
- Turbulence is a great mixer down to about 50x* the Kolmogorov scale

$$\text{Kolmogorov length scale } \eta_K = \left(\frac{\nu^3}{\varepsilon} \right)^{\frac{1}{4}}$$

$$\text{Inner viscous length scale } \lambda_v \approx \Pi_{kv} \eta_K$$

$$\Pi_{kv} \approx 50$$



*http://dimotakis.caltech.edu/pdf/Dimotakis_JFM2000.pdf

Viscosity kills inertia (and eddies)!

ν , viscosity, for water is $10^{-6} \text{ m}^2/\text{s}$

Mixing below the inner viscous length scale is by shear and diffusion

- The viscous shear and molecular diffusion processes are both slow
- There is no practical way to speed diffusion
- A contact chamber might be helpful*
 - Time for dissolved organics to diffuse to coagulant nanoparticles
 - Time for nanoparticles to diffuse to particles and pathogens

* Edge of knowledge

AguaClara design...

- We have speculated that energy dissipation rate mattered
- We had an flawed justification for about 3 W/kg
- We don't currently have a rational basis for design of a rapid mix unit
- The 1 L/s pilot plant offers us the opportunity to do the needed research.

The minimum Reynolds number for efficient mixing is 10,000

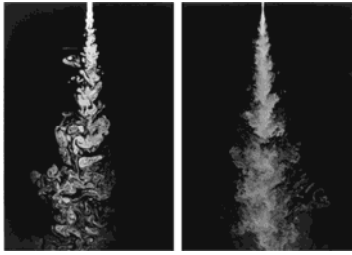


Figure 5. Jet-fluid concentration in the plane of symmetry of a round turbulent jet. (a) $Re \approx 2.5 \times 10^3$ ($0 < z/d_j < 35$). (b) $Re \approx 10^4$ ($0 < z/d_j < 200$). Data from Dimotakis et al. (1983, figures 5 and 9).

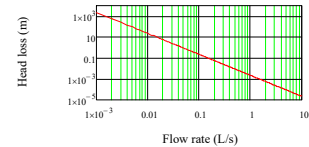
The Reynolds Number requirement may be a challenge for lab scale flows and irrelevant above 0.1 L/s

$$Re_{Mixing} = \frac{V_{Jet} D_{Jet}}{\nu} \quad \text{Definition of } Re \quad V_{Jet} = \frac{Q_{Jet}}{\frac{\pi}{4} D_{Jet}^2} \quad \text{Continuity}$$

$$Re_{Mixing} = \frac{\pi Q_{Jet}}{4 D_{Jet} \nu} \quad \text{Replace } V \text{ with } Q$$

$$D_{Jet} = \frac{\pi Q_{Jet}}{4 \nu Re_{Mixing}} \quad \text{Solve for jet diameter}$$

$$h_{Jet} = \frac{V_{Jet}^2}{2g} \quad \text{Head loss for a flow expansion}$$



Disclaimer

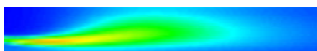
- The following analysis is based on the assumption (without basis) that there may be a goal of achieving a certain energy dissipation rate or velocity gradient.
- Aggregation of large particles may happen faster than deposition of nanoparticles on particles (flocculation may start well before coagulation ends).
- A quiescent contact chamber may be more effective because nanoparticles benefit more (than clay particles) from diffusion.

How do we generate intense turbulence?

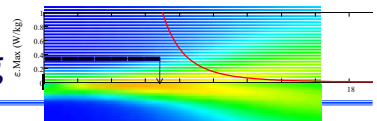
- We need to be converting mechanical energy (kinetic energy) to thermal energy
- We want “concentrated” head loss! (this shouldn’t be too hard to achieve!)
- Therefore use minor loss (related to a change in flow geometry) rather than major loss (from shear at the solid boundaries)
- Almost all minor losses are caused by **expansions (We need a flow expansion)**

Flow Expansion $h_e = \frac{V_{in}^2}{2g} \left(1 - \frac{A_{in}}{A_{out}} \right)^2$

- The control volume analysis gave us the **total** energy loss, but it doesn’t give us the energy dissipation rate.
- The energy dissipation rate varies with location in the expanding jet



Jet Mixing



$$\epsilon_{Centerline} \approx \frac{50 D_{Jet}^3 V_{Jet}^3}{(x - 2 D_{Jet})^4} \quad \text{Minimum } x \text{ for which this relationship is valid is } 7 D_{Jet}$$

$$\epsilon_{Centerline} \approx \frac{50 D_{Jet}^3 V_{Jet}^3}{(7 D_{Jet} - 2 D_{Jet})^4} \quad x \text{ is distance from the jet origin}$$

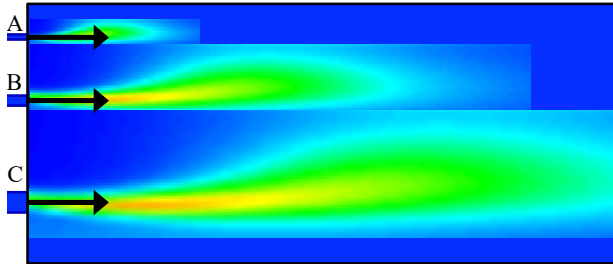
$$\epsilon_{Max} \approx \frac{\left(\frac{50}{(5)^4} \right) V_{Jet}^3 \left(\frac{50}{5^4} \right)^{\frac{1}{3}}}{D_{Jet}} \quad \left(\frac{50}{5^4} \right)^{\frac{1}{3}} \approx 0.431 \quad \Pi_{Jet} = \frac{(\epsilon_{Centerline} - \epsilon_{JetMax})^{\frac{1}{3}}}{V_{Jet}} \approx \frac{(0.482)}{(0.487)} \approx 0.989$$

$$\epsilon_{Max} \approx \frac{(\Pi_{RoundJet} V_{Jet})^3}{D_{Jet}} \quad \Pi_{RoundJet} \approx 0.5$$

The value we will use in our analysis. Further work is required to determine the best value of this parameter for different jet geometries.

Energy Dissipation Rate $\epsilon_{Max} \equiv \frac{(\Pi_{RoundJet} V_{Jet})^3}{D_{Jet}}$ Three orifices, same velocity

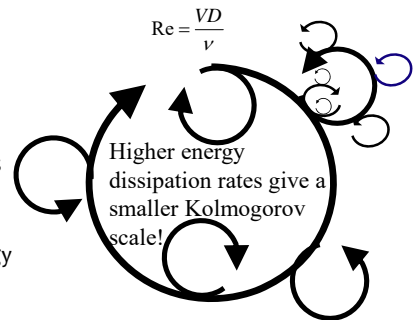
Which jet has the highest energy dissipation rate?



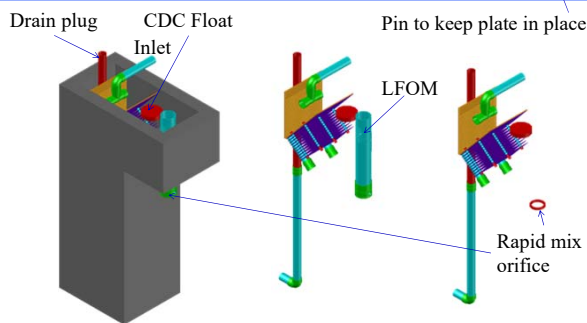
Which jet has the highest shear (or velocity gradient)?

Big eddies create smaller eddies

- Which jet has the largest eddies?
- Which jet will make the smallest eddies first?
- Which jet will dissipate energy the fastest?



Rapid Mix orifice



Orifice Diameter to Obtain Target Mixing

$$\epsilon_{Max} \equiv \frac{(\Pi_{JetRound} V_{Jet})^3}{D_{Jet}} \quad A_{Orifice} \Pi_{vc} = A_{Jet} \quad D_{Orifice} \sqrt{\Pi_{vc}} = D_{Jet}$$

$$\epsilon_{Max} \equiv \frac{\left(\Pi_{JetRound} \frac{4Q}{\pi D_{Jet}^2} \right)^3}{D_{Jet}}$$

Substitute for D_{Jet} and solve for $D_{Orifice}$

$$D_{Orifice} \equiv \left(\frac{4Q \Pi_{JetRound}}{\epsilon_{Max}^{\frac{1}{3}} \pi} \right)^{\frac{3}{7}} \frac{1}{\sqrt{\Pi_{vc}}}$$

The orifice must be smaller than this to achieve the target energy dissipation rate

Rapid Mix Head Loss

$$\epsilon_{Max} \equiv \frac{(\Pi_{JetRound} V_{Jet})^3}{D_{Jet}} \quad D_{Jet} \equiv \left(\frac{4 \Pi_{JetRound} Q}{\pi \epsilon_{Max}^{\frac{1}{3}}} \right)^{\frac{3}{7}}$$

This is one of the scale effects for rapid mix

$$V_{Jet} \equiv \frac{(D_{Jet} \epsilon_{Max})^{\frac{1}{3}}}{\Pi_{JetRound}}$$

$$h_e = \frac{V_{Jet}^2}{2g} \quad h_e = \frac{(D_{Jet} \epsilon_{Max})^{\frac{2}{3}}}{2g \Pi_{JetRound}^2}$$

$$h_e = \frac{\left(\frac{4 \Pi_{JetRound} Q \epsilon_{Max}^{\frac{2}{3}}}{\pi} \right)^{\frac{2}{7}}}{2g \Pi_{JetRound}^2}$$

This assumes discharge into a large tank

Reduce the required head loss through the rapid mix for large plant flows

- Rapid Mix head loss increases with Q
- How could we maintain a high energy dissipation rate while reducing the velocity and the head loss?
- What else is needed?
- Use a plate with multiple orifices in the rapid mix pipe and add macro mixing upstream

$$h_v = \frac{\left(\frac{4 \Pi_{JetRound} Q \epsilon_{Max}^{\frac{2}{3}}}{\pi} \right)^{\frac{2}{7}}}{2g \Pi_{JetRound}^2}$$

$$\epsilon_{Max} \equiv \frac{(\Pi_{JetRound} V_{Jet})^3}{D_{Jet}}$$

Hypothesis: Macomixing minor loss coefficient and length scale

extra

- The eddy velocities are comparable to the mean velocities for a minor loss coefficient of 1
- The minimum distance in the direction of flow (L) for mixing over the dimension perpendicular to the direction of flow (D) would then be equal to D. (L>D)
- This length is the pipe minimum length before the micromixing event (unless the two are combined in a single orifice)

Mechanized Rapid Mix vs. Hydraulic Rapid Mix

- Vampire loads
- A 100 L/s AguaClara plant costs approximately \$1,000,000
- After 25 years the electricity cost for mechanized rapid mix would be \$230,000
- “Another way to give is to not take...”
- The 25 year energy cost for a package plant that uses a total of 400 J/L is 1.5 million USD!
- Or perhaps just turn off the mixer?

$$400 \frac{\text{J}}{\text{L}} \cdot \frac{50 \text{ L}}{10^3 \text{ J}} \cdot 100 \frac{\text{L}}{\text{s}} \cdot 25 \text{ yr} = 1577840 \text{ s}$$

Reflections



- Hydraulic rapid mix should be the default design
- Research is required with our pilot plant to determine if rapid mix makes a difference or if a quiescent contact chamber would be more beneficial
- Rapid mix might be the first stage in flocculation