Principles of Coagulation and Flocculation

presented by

Joe Shemanski – Sales Engineer
Coagulation in Water Treatment

- Particle (Turbidity) Removal
  - SWTR
  - Cryptosporidium/Giardia
- Organic Matter Removal
  - Color
  - Precursors for DBP Formation
  - D/DBP Rule
  - Enhanced Coagulation
Properties of Particles

1. Inorganic materials, such as silt or minerals
2. Living or dead organic material
3. Biotic material including algae, viruses and bacteria
Physical Characteristics

**Settleable Solids**
- Large particulate solids
- Separates readily

**Suspended Solids**
- Very small particles
- Requires a long time to settle

**Dissolved Solids**
- Invisible (except for color)
- Will not readily separate
Minerals (Inorganic)

- Metals and oxides of metals
- Clays
- Salts
1. The decomposition of naturally occurring organic materials (plant or animal in the environment (NOM))

2. Industrial, agricultural and domestic activities (PCB’s, pesticides, fuels, etc.)

3. Reactions occurring during the treatment and distribution of drinking water (DBP’s – THM’s HAA’s)
Biotic Material

1. Protozoans – Cryptosporidium (2-5 microns), Giardia lamblia (9-21 microns) and E. histlytica
2. Enteric viruses – viruses affecting the intestine like hepatitis A, Norwalk type (0.004 to 0.1 micron)
3. Algae – green, blue-green (5-100 microns)
4. Bacteria – Salmonella, E. coli, Legionella (1-5 microns)
The Coagulation Process
## Settling Characteristics of Suspended Particles in a Static Environment

<table>
<thead>
<tr>
<th>Diameter of Particle, mm</th>
<th>Order of Size</th>
<th>Total Surface Area*</th>
<th>Time Required to Settle **</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Gravel</td>
<td>0.487 sq. in. (314.2 mm²)</td>
<td>0.3 sec.</td>
</tr>
<tr>
<td>1</td>
<td>Coarse Sand</td>
<td>4.87 sq. in. (31.42 cm²)</td>
<td>3 sec.</td>
</tr>
<tr>
<td>0.1</td>
<td>Fine Sand</td>
<td>48.7 sq. in. (314.2 cm²)</td>
<td>38 sec.</td>
</tr>
<tr>
<td>0.01</td>
<td>Silt</td>
<td>3.38 sq. ft. (0.314 m²)</td>
<td>33 min.</td>
</tr>
<tr>
<td>0.001</td>
<td>Bacteria</td>
<td>33.8 sq. ft. (3.14 m²)</td>
<td>55 hr.</td>
</tr>
<tr>
<td>0.0001</td>
<td>Colloidal Particles</td>
<td>37.5 sq yd. (31.4 m²)</td>
<td>230 days</td>
</tr>
<tr>
<td>0.00001</td>
<td>Colloidal Particles</td>
<td>0.7 acre (0.283 ha)</td>
<td>6.3 yr.</td>
</tr>
<tr>
<td>0.000001</td>
<td>Colloidal Particles</td>
<td>7.0 acres (2.83 ha)</td>
<td>63 years. min.</td>
</tr>
</tbody>
</table>

* Area for particles of indicated size produced from a particle 10 mm in diameter with a specific gravity of 2.65

** Calculations based on a sphere with specific gravity of 2.65 to settle one foot (30.48 cm)
Charge Neutralization

The destabilization of colloidal particles by the introduction of an opposite charge.
Double Layer Theory

Electronegative Particle

Stern Layer

Diffuse Layer

Surface shear
COAGULATION

- Destabilization of colloids by neutralizing the forces that keep them apart
Flocculation

The agglomeration of the destabilized particles by bridging
Organic Polymers
Organic Polyelectrolytes (Polymers)

- long chain synthetic organic compounds with ionic sites that can neutralize the surface charge of suspended colloidal particles
ORGANIC POLYMER DEFINITIONS

- **ORGANIC**
  - Molecule based on one or more carbon atoms

- **MONOMER**
  - Single molecule which can be reacted with itself or other molecules to form long chains

- **POLYMER**
  - Three or more monomer units reacted together. Usually refers to organic molecules, but can be inorganic
## Flocculant Charges

<table>
<thead>
<tr>
<th>Type</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic</td>
<td>+</td>
</tr>
<tr>
<td>Anionic</td>
<td>-</td>
</tr>
<tr>
<td>Non Ionic</td>
<td>+, -</td>
</tr>
</tbody>
</table>
Polymer Chemistry

Key Concepts

Molecular Weight
- Indicates the length of the polymer chain
- Usually based on intrinsic or reduced specific viscosity
- Is often relative or comparative
FLOCCULANTS

- Low to very high molecular weight
- Nonionic, anionic, or cationic
- Bridge destabilized colloids/Increase floc size
- Anionics used as coagulant aids
- Cationics used as coagulant aids and filter aids
- Nonionic used as coagulant aids and filter aids
**Organic Coagulants**

- **Advantages**
  - Less pH dependent
  - Do not alter system pH
  - Minimal contribution to sludge
    - Required in certain applications

- **Disadvantages**
  - Higher cost per pound
  - Proper makeup system may be required
  - Not the best for removing very small colloidal particles
PRODUCT FORMS

- SOLUTION POLYMERS
  - Coagulants
  - Flocculants – also known as mannich
- EMULSION POLYMER
- DRY POLYMERS
- DISPERSION POLYMERS
**Organic Coagulants**

Generally cationic
- Diallyldimethyl ammonium chloride (DADMAC)
- Epichlorohydrin/Dimethylamine (EPI/DMA)
**FLOCCULANTS**

- Emulsion/Latex/Dispersion
  - High MW
  - 25–50% Actives
  - Requires inversion makeup–mixing with water
    - 0.5 to 2.0% concentration
  - Colloidal particles of polymer suspended in water
  - Typically fed at 0.05 to 2.0% solution
Preparing Flocculants

Latex Emulsion Polymers
Neat Polymer
FLOCCULANTS

- Dry
  - High MW
  - Powder or bead form
  - 80–95% Actives
  - Requires activation (dissolution)
  - Dust problems
  - Product is wetted then aged
  - Fed @ 0.1 to 0.5% solution
Organic Polymers in Water Treatment

**Homopolymers (cationic (+) charge)**
- DADMAC
- Epip amines \{ Low Molecular Weight \}

**Copolymers (cationic (+), nonionic (+/-), anionic (-))**
Acrylamide + monomer
- acrylic acid
- methacrylic acid \{ High Molecular Weight \}
- methacrylic acid
FACTORS AFFECTING FLOCCULATION

- Flocculant structure
- Energy input: mixing energy
- Amount of solids
- Nature of solids
- Temperature
- pH
- Presence of oxidants (Chlorine, Permanganate)
**TEMPERATURE/pH**

- **Temperature:**
  - Very hot or cold streams will prevent optimum performance
    - Hot water degrades the polymer
    - Cold water slows the flocculation reaction and can inhibit activation of the polymer

- **pH:**
  - Very high and low pH will degrade polymer
  - Can alter surface charge of particles
Polymer Coagulation
Charge Patch Method
Low Molecular Weight High Charge Cationic
Polymer Coagulation
Destabilization causing particles to attract
Polymer Flocculation
Adsorption and Bridging
High Molecular Weight
Inorganic Coagulants
Metal Salt Coagulants (Inorganic)

- $\text{Al}_2(\text{SO}_4)_3$ (Alum)
- $\text{AlCl}_3$
- Polyaluinum chloride
- $\text{Fe}_2(\text{SO}_4)_3$ (Ferric Sulfate)
- $\text{FeCl}_3$ (Ferric Chloride)

$\text{Al}^{3+}$, $\text{Fe}^{3+}$ (Tri– Valent)
PRECIPITATION

- Making a soluble species insoluble
Hydrolysis and Precipitate Formation

- **COMPLEX** Series of Reactions to form polymeric species of Me$_3^+$
  \[ \text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{Al(OH)}_3(\text{Solid}) + \text{SO}_4^{2-} \]
  \[ \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{Solid}) + \text{SO}_4 \]
  \[ \text{FeCl}_3 + \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{Solid}) + \text{Cl} \]

- Precipitate Formation Dependent on:
  - Solution pH & Alkalinity
  - Me$_3^+$ Concentration (Coagulant Dose)
FACTORS AFFECTING COAGULATION

- Mixing Energy
- Temperature
- pH/Alkalinity
- Particle size
- Presence of oxidants (Chlorine, Permanganate)
- Flow
- Retention time
Simplified Coagulation Process

(Particle Removal)

Particles
(-) charge

Al$_2$SO$_4$

Al(OH)$_3$
(+) charge

solid
Precipitate Sorbs to Particles
(Neutralizes Surface Charge)
Mixing → Floc Formation
Adsorption of Organic Matter to Metal $^{+3}$ Precipitate
# “The Matrix”

TOC removal efficiencies through enhanced coagulation

<table>
<thead>
<tr>
<th>Source Water TOC mg/l</th>
<th>Source Water Alkalinity, mg/l as CaCO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-60</td>
</tr>
<tr>
<td></td>
<td>&gt;60-120</td>
</tr>
<tr>
<td></td>
<td>&gt;120 b</td>
</tr>
<tr>
<td>&gt;2.0-4.0</td>
<td>35.0%</td>
</tr>
<tr>
<td></td>
<td>25.0%</td>
</tr>
<tr>
<td></td>
<td>15.0%</td>
</tr>
<tr>
<td>&gt;4.0-8.0</td>
<td>45.0%</td>
</tr>
<tr>
<td></td>
<td>35.0%</td>
</tr>
<tr>
<td></td>
<td>25.0%</td>
</tr>
<tr>
<td>&gt;8.0</td>
<td>50.0%</td>
</tr>
<tr>
<td></td>
<td>40.0%</td>
</tr>
<tr>
<td></td>
<td>30.0%</td>
</tr>
</tbody>
</table>

**A** Not applicable to water with raw water SUVA ≤ 2.0 L/mg-m

**B** Systems practicing precipitative softening must meet the TOC removal requirements in this column
Enhanced Coagulation

Enhanced coagulation is characterized by coagulant dosages greater than those required for optimum turbidity removal and/or depressing the pH to achieve the removal of organic matter.
Factors Affecting Removing NOM

1. The coagulant dosage
2. The active charge density of coagulant
3. The floc surface area available for adsorption
4. The nature of the bonds between the organics and the metal hydroxide floc (pH dependent)
1. Lower coagulation pH increases the level of organics protonation.

2. The coagulating species are more positively charged at lower pH.

3. Under low pH conditions, it is likely that the mechanisms of charge neutralization and coprecipitation are enhanced.
Polyalumiumchloride (PACl)

- A special basic salt of aluminum chloride designed to give much stronger coagulating flocculating power than ordinary aluminum and iron salts. It is formed in a chemical reactor by neutralizing $\text{AlCl}_3$ with an alkaline agent or driving off Cl under temperature and pressure.

- A poly-nuclear complex of polymerized aquo-aluminum ions – a kind of inorganic polymer with its molecular weight being several hundreds. It is generally formulated as “$\text{Al}_n(\text{OH})_m\text{Cl}_3_{n-m}$”
Why is it Better than Alum?

- Stronger – Larger Floc
  - less sheared floc
  - improved settled water quality
  - improved filtered water quality
  - longer filter runs
- Little or No Alkalinity Consumption
  - no need for pre-lime
  - works well in low alkalinity water
- Typically Eliminates the Need for Coagulant and Filter Aids
- Effective Over a Wide Range of pH
- Not Adversely Affected by Low Water Temperature
- Rapid Floc Formation
  - requires less mixing
  - works well in hydraulically overloaded plants
What are the Differences in PACI?

- Aluminum Oxide ($\text{Al}_2\text{O}_3$) – a measure of the metal content

- Basicity – the percentage of $\text{Cl}^-$ that has been replaced by (OH)

- Addition of anions ($\text{SO}_4^{2-}$) or organic polymers such as DADMAC or DMA Eppi
Coagulation/Flocculation Processes in the Plant
The function of the flash mixer is to disperse the coagulant as quickly as possible so it comes into contact with every particle in the water column.
Vertical Shaft Flash Mixer
Static Mixer
Inline Mechanical Mixer
The function of the flocculators is to agglomerate destabilized particles through controlled collisions.
Vertical Shaft Flocculators
Horizontal shaft flocculators
Operational Observations

- Measure pH coming out of flash mixer
- Measure charge at flash mixer
  - SCD
  - Zeta Meter
- Sample flash mix and put sample under gang stirrer
  - Observe floc formation
  - Measure turbidity
- Floc should build as it progresses through the stages of the flocculators
Design Considerations

- Coagulants need to be dispersed rapidly
- Flocculators should be tapered
- Do not add all chemicals at the same point
- Allow for flexibility by adding additional injection sites
- Flocculant aid polymers can be added at different stages in the flocculators
Review
• Principles of Coagulation (positive and negative charges)
• Differences and Similarities in metal coagulants
• Differences and Similarities in Organic Polymers
• Differences in Polyaluminum Chlorides
Questions & Answers