Chapter 6-1.

Coagulation & Flocculation
I Introduction

Colloidal impurities in surface waters cause the water to appear turbid or may impart color

- Turbidity caused by colloidal clay particles produced by soil erosion
- Color may result from colloidal forms of Fe and Mn from organic compounds by decaying vegetation (Humic substance)

Colloidal particles are difficult to separate from water because the particles will not settle by gravity are so small that they pass through the pores of most common filtration media → colloidal must aggregate and grow in size

However, aggregate is complicated due to 1) small size of particles 2) physical and electrical forces keep the particle separate prevent the collisions

To destroy the stability of colloidal particles,

- Coagulation → process of destabilization
- Flocculation → aggregation & collision of destabilized colloids
II. Colloidal Systems

- Colloidal system: A system in which particles, in a finely divided state (dispersed phase) are dispersed in a continuous medium (dispersing phase).

- A definite surface of separation (interface) exists between colloids and the continuous medium.

- It is quite difficult to distinguish between colloids and solution (at the lower end of scale), and between colloids and suspension (at the upper end).

- Size: 1mm-10um

- Hydrophobic (clay, gold, metal)
  - Hydrophilic (protein, soaps, detergents)
Table 6.1 Types of colloidal dispersions

<table>
<thead>
<tr>
<th>Dispersed Phase</th>
<th>Dispersal Medium</th>
<th>Name</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>Gas</td>
<td>Liquid aerosol</td>
<td>Fog, liquid sprays</td>
</tr>
<tr>
<td>Solid</td>
<td>Gas</td>
<td>Solid aerosol</td>
<td>Smoke, dust</td>
</tr>
<tr>
<td>Gas</td>
<td>Liquid</td>
<td>Foam</td>
<td>Foam on soap solution, fire-extinguisher foam</td>
</tr>
<tr>
<td>Liquid</td>
<td>Liquid</td>
<td>Emulsion</td>
<td>Milk, mayonnaise</td>
</tr>
<tr>
<td>Solid</td>
<td>Liquid</td>
<td>Sol. Colloidal suspension: Paste (high solid concentration)</td>
<td>Au sol, AgI sol:</td>
</tr>
<tr>
<td>Gas</td>
<td>Solid</td>
<td>Solid foam</td>
<td>Expanded polystyrene</td>
</tr>
<tr>
<td>Liquid</td>
<td>Solid</td>
<td>Solid emulsion</td>
<td>Opal, pearl</td>
</tr>
<tr>
<td>Solid</td>
<td>Solid</td>
<td>Solid suspension</td>
<td>Pigmented plastics</td>
</tr>
</tbody>
</table>
II-1. Surface charge on colloidal particles

Charge acquisition by clay and protein particles

(a) Charge acquisition through isomorphous replacement of Al for Si. (after Fair, Geyer, and Okun, 1968.)

(b) Effect of pH on the ionization of a protein particle.

FIGURE 6-2 Charge acquisition by clay and protein particles.
II-1. Surface charge on colloidal particles

Colloidal stability

i) solvation (hydrophilic)
ii) Electrical repulsion forces (hydrophobic)
   * clay particles are of prime importance in water supply

The electric charge can be acquired by the particle in a number of ways
i) Isomorphous Replacement (Lattice Imperfection)
   Ions in the lattice structure are replaced with ions from solution
   (Si with Al) → clay, other soil particles.

ii) Ionisation of structure sites
   - Many colloidal particles acquire and electrical charge through
     the ionization of surface functional groups
   - Proteins, Microorganisms acquire their charge as a result of
     the ionization of carboxyl or amine groups

\[
\begin{align*}
\text{SiOH}_2^+ & \rightleftharpoons \text{SiOH} + \text H^+ \\
\text{SiOH} & \rightleftharpoons \text{SiO}^- + \text H^+
\end{align*}
\]
II-1. Surface charge on colloidal particles

iii) Adsorption of Ions onto the particle surface
- Many colloidal particles acquire a charge as a result of the preferential adsorption of either positive or negative ions on their surface.
  (adsorption ions: peptizing ions)
- They usually adsorbs anions and acquire negative charges.
  (Cations are generally more hydrated their anions and are separated from the colloids by the shield of hydrated water)

- Oil droplets, gas bubbles, other chemically inert substances dispersed in water adsorb anions (hydroxyl ions)

* In natural water \( \rightarrow \) colloids invariably carry a negatively charge
In wastewater \( \rightarrow \) this is often the case

iv) Surface complex formation

\[
\text{SiOH} + \text{Ca}^{2+} \leftrightarrow \text{SiOCa}^{2+} + \text{H}^+ \\
\text{SiOH} + \text{HPO}_4^{2-} \leftrightarrow \text{SiOPO}_3\text{H}^- + \text{OH}^- 
\]
III. Destabilization Mechanisms

<table>
<thead>
<tr>
<th>TABLE 6-2. Surface Characteristics of Particulates Commonly Found in Natural Waters and Wastewaters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero Point of Charge, $\text{pH}_{ZPC}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>INORGANIC (hydrophobic)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Al(OH)$_3$&quot; (amorph)</td>
<td>7.5–8.5</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>&quot;Fe(OH)$_3$&quot; (amorph)</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>2–4.3</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>2–3.5</td>
<td></td>
</tr>
<tr>
<td>Clays</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3.3–4.6</td>
<td></td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Asbestos</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chrysotile</td>
<td>10–12</td>
<td></td>
</tr>
<tr>
<td>Crocidolite</td>
<td>5–6</td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>8–9</td>
<td></td>
</tr>
<tr>
<td>Ca$_3$(PO$_4$)$_2$OH</td>
<td>6–7</td>
<td></td>
</tr>
<tr>
<td>FePO$_4$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>AlPO$_4$</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ORGANIC (hydrophilic)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>3–5</td>
<td></td>
</tr>
<tr>
<td>Bacteria</td>
<td>2–4</td>
<td></td>
</tr>
<tr>
<td>Humic acid</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Oil droplets</td>
<td>2–5</td>
<td></td>
</tr>
</tbody>
</table>

*Source: Parks (1967) and Stumm and Morgan (1981).*
II-2. Steric Stabilization

Illustration of adsorbed polymer configuration with loops, trains, and tails
II-2. Steric Stabilization

Two possible repulsive interaction of adsorbed polymer layers in sterically stabilized colloidal system

\[ \text{Compression} \quad \text{Interpenetration} \]

*Figure 6.5* Two possible repulsive interactions of adsorbed polymer layers in sterically stabilized colloidal systems. (*From Gregory.*)
Although individual hydrophobic colloids have an electrical charge, a colloidal dispersion, like an ionic solution, does not have a net electrical charge. For electroneutrality to exist, the charge on the colloidal particle must be counterbalanced by ions of opposite charge (counter-ion) contained in the dispersing phase.
II.3 The electrical Double layer

A positive colloidal particle with its electro static field.
II.3 The electrical Double layer

A negative colloidal particle with its electrostatic field.
II-3. The electrical Double layer

Electrical Double layer(300nm)

i) Inner layer (Fixed layer or stern layer)(5nm)
   - hydrated cation or nonhydrated anion
   - adsorbed ions attached by electrostatic and/or Van der Waals’ force

ii) Diffuse layer
    - Counter ions are attracted electrostatically to the interfacial region. This attraction gives rise to a concentration gradient, so that random thermal agitation can cause these ions to diffuse away from the surface of the particle toward the bulk of solution where (diffusion and electrostatic attraction) spread the charge in the water over a diffuse layer.

Plane & shear : the shear plane surrounding the particle enclose the volume of water (Bound water) that moves with the particle. The exact location is not known
II-3. The electrical Double layer

Zeta potential (Zp)

- The electrical difference between the shear plane and the bulk solution (Zp=0)
- a qualitative tool to predict the potential for coagulation
- it can be measured (zeta-meter)
- \( Z_p = \frac{4\pi gd}{D} \)
  - g: charge per unit area on the particle for coagulation
  - D: Dielectric constant
  - d: thickness of the zone of influence of the charge on the particle
- high Zp \( \rightarrow \) Strong forces of separation, stable colloid system
  - low Zp \( \rightarrow \) less stable colloidal system
- Zp is a function of pH as well as the concentration of other ions in solution, including the coagulant
  - Zp \( \rightarrow \) 0, coagulation should increase.
III. Destabilization Mechanisms

Some coagulants can achieve colloidal destabilization by more than one mechanism.

A) Double-layer repression: alters the charge distribution within the diffuse layer
the thickness of double layer → the distance from the surface at which the potential falls to 37% (1/e) of its surface value

\[ z = 0.33 \times 10^{-2} \left( \frac{E_d}{I} \right)^{1/2} \]

\[ z = \text{thickness of layer, cm} \]
\[ E_d = \text{ionic strength of the solution, coul/v/cm} \]
\[ I = \text{ionic strength of the solution, mol/L} \]

\[ I = \frac{1}{2} \sum c_i z_i^2 \]
\[ c_i \rightarrow \text{molarity} \]
\[ z_i \rightarrow \text{charge of component I} \]

for water and monovalent electrolytes
\[ z = 10A \text{ (at 0.1 molar)} \]
\[ = 100A \text{ (at 0.001 molar)} \]
III. Destabilization Mechanisms

(1) Increasing Ionic Strength (I) → thickness of double layer (z) decrease
→ the repulsive forces are dissipated over shorter distances → shifting the repulsive curve to the left → a potential energy maximum ($E_m = \text{activation energy}$) is reduced → colloidal particles can approach one another closely enough to allow attractive forces to dominate

(2) Concentration of salts to achieve destabilization by charge dissipation decrease as the cation changes from Na$^+$, to Ca$^{2+}$ to Al$^{3+}$

Schulze – hardy rule (empirical)

Na$^+$, Ca$^{2+}$, Al$^{3+}$ = 1: 10$^{-2}$:10$^{-3}$ (approximately)
A. Double-layer repression

(a) Low electrolyte concentration with normal double-layer thickness. System is stable and agglomeration is imperceptible.

(b) Intermediate electrolyte concentration causes some double-layer compression. Slow agglomeration can occur.

(c) High electrolyte concentration causes severe double-layer compression. Rapid agglomeration can occur.

**FIGURE 7-2** Effect of electrolyte concentration on double layer compression (after Van Olphen, 1977).
III. Destabilization Mechanisms

B) Charge neutralization

(1) attachment of the destabilizing chemical containing counter ions to the colloid within the stern layer so that the effective charge outside of the shear layer is reduced

(2) Change neutralization acts primarily within the mono layer around the colloid

(3) Overdoses of a coagulant can result in charge reversed
B) Charge neutralization

Variations of final zeta potential with pH when treating refinery effluent having negative zeta potential with three levels of coagulant dosage
III. Destabilization Mechanisms

![Graph showing coagulation curves for different coagulants.](image)

Figure 2-2 Schematic coagulation curves for several different coagulants.
III. Destabilization Mechanisms

C) Entrapment (sweep-floc) mechanism

(1) Coagulate added the wastewater → form various hydrous polymers which will precipitate from solution → colloids are trapped within the floc (voluminous and three-dimensional polymers) → The solids remain trapped within the settling floc and appear to be swept from the water

(2) Generates a large amount of wet aluminum or iron sludges → must be de-watered and dispersed

(3) Fig -2C → At most water treatment, coagulation/flocculation takes place in the “sweep floc” range because it is very difficult to vary the coagulant dose to correspond to changing influent conditions as required to operate in the range of complete particle destabilization
III. Destabilization Mechanisms

D) Bridging

- 1960 years, a rapid increase in the use of synthetic organic-polymer as destabilizing agents

- Even though the solid particle in the water are also negatively charged, it is often observed that the most economical treatment is obtained with an anion polymer → such observations can’t be explained by simple electrostatic model, a bridging theory was developed and provides an acceptable qualitative model

- polymer-molecule must contain chemical groups which interact with sites on the surface of colloidal particle
IV. Destabilization Chemicals

D) Bridging
III. Destabilization Mechanisms

Reaction 1 → Some of chemical groups of a polymer adsorb at the particle surface

Reaction 1 → a second particle with some vacant adsorption sites contacts these extended segments (floc formation), polymer serves as a bridge

Reaction 3 → If a second particle is not available, in time the extended segments adsorb on other sites on the original particle → no serves as a bridge

Reaction 4 → overdose, no sites are available for the formation of interparticle bridges → it is not ascribed to charge reversal as $C_{12}H_{25}NH_3^+$

Reaction 5 → By extended agitation, breaking of polymer-surface bonds

Reaction 6 → Restabilization
III. Destabilization Mechanisms

A polymer molecule will become attached to a colloidal particle at one or more sites

Attachment
i) polymer and particle are of opposite charge $\rightarrow$ coulombic attraction of similar charge
ii) ion exchange, hydrogen bonding, Van der Waals forces
TABLE 7-2. Comparison of various coagulants (after Weber. 1972)

<table>
<thead>
<tr>
<th>Type of Water</th>
<th>Alum</th>
<th>Ferric Salts</th>
<th>Polymer</th>
<th>Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>High alkalinity.</td>
<td>Addition of alkalinity and coagulant aid not required.</td>
<td>Addition of alkalinity and coagulant aid usually not required.</td>
<td>Anionic and non-ionic may also be effective. High molecular weight materials are best.</td>
<td></td>
</tr>
<tr>
<td>(Type 1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low turbidity.</td>
<td>Effective for pH 5-7.</td>
<td>Effective for pH 6-7.</td>
<td>Same as above.</td>
<td>Effective and results in increased alkalinity, which makes water easier to stabilize.</td>
</tr>
<tr>
<td>Low alkalinity.</td>
<td>May need to add alkalinity if pH drops during treatment.</td>
<td>May need to add alkalinity if pH drops during treatment.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Type 2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High turbidity.</td>
<td>Effective in relatively large dosages, which promote precipitation of Al(OH)$_3$. Coagulant aid may be needed to weight floc and improve settling.</td>
<td>Effective in relatively large dosages, which promote precipitation of Fe(OH)$_3$. Coagulant aid should be added to weight floc and improve settling.</td>
<td>Cannot work alone due to low turbidity. Coagulant aids such as clay should be added ahead of polymer.</td>
<td>Effective due to precipitation of Mg(OH)$_2$.</td>
</tr>
<tr>
<td>High alkalinity.</td>
<td>(Type 3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low turbidity.</td>
<td>Effective only by sweep-floc formation. But resulting dosage will destroy alkalinity. Must add alkalinity to produce type 3 or clay to produce type 2 water.</td>
<td>Effective only by sweep-floc formation, but resulting dosage will destroy alkalinity. Must add alkalinity to produce type 3 or clay to produce type 2 water.</td>
<td>Will not work alone due to low turbidity. Coagulant aids such as clay should be added ahead of polymer.</td>
<td>Results in increased alkalinity, which makes water easier to stabilize.</td>
</tr>
<tr>
<td>Low alkalinity.</td>
<td>(most difficult to coagulate). (Type 4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Low turbidity < 10 JTU, low alkalinity < 50 mg/l (as CaCO$_3$). High turbidity > 100 JTU, high alkalinity > 250 mg/l (as CaCO$_3$).
IV. Destabilization Chemicals

A) Aluminum and Iron Salts

(i) The composition of various commercial Al and Fe salts

<table>
<thead>
<tr>
<th>Chemical Name, Formula, and Trade Name</th>
<th>Molecular Weight</th>
<th>Common Forms and Commercial Strength</th>
<th>Bulk Density (lbs/ cu ft)</th>
<th>Solubility (g/100 g Water, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum sulfate ( \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} )</td>
<td>594.4</td>
<td>Tan to gray-green: powder ( 17% \text{Al}_2\text{O}_3 ) granules</td>
<td>38–45</td>
<td>65.3 at 10°C</td>
</tr>
<tr>
<td>Alum ( \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} )</td>
<td>594.4</td>
<td>lump ( 60–63 \text{ Al}_2\text{O}_3 ) minimum</td>
<td>62–67</td>
<td>71 at 20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid ( 8.3% \text{Al}_2\text{O}_3 )</td>
<td></td>
<td>78.8 at 30°C</td>
</tr>
<tr>
<td>Ferric Chloride ( \text{FeCl}_3 )</td>
<td>162.2</td>
<td>Anhydrous: green-black powder ( 96–97% \text{FeCl}_3 )</td>
<td>65–70</td>
<td>74.4 at 0°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heptahydrate: yellow-brown lump ( 60% \text{FeCl}_3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid: dark brown solution ( 37–47% \text{FeCl}_3 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferric Sulfate ( \text{Fe}_2(\text{SO}_4)_3 )</td>
<td>399.9</td>
<td>Dihydrate: red-brown granules ( 20.5% \text{Fe} )</td>
<td>70–72</td>
<td>300 at 20°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trihydrate: red-gray granules ( 18.5% \text{Fe} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reagent grade alum is \( \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \). Commercial alum or filter alum differs from reagent grade and has no exact composition. Filter alum is usually written as \( \text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} \).
(ii) Solubility Diagram: effect of complexation on solubility.

“When any of the constituent ions of a solid participate in complex formation following dissolution, there will be an increase in the solubility of the solid.”

Salts of Al(III) or Fe(III) $\rightarrow$ Al(III) or Fe(III)

$$\begin{align*}
\text{OH}_2 & \quad \text{OH}_2 \\
\text{OH}_2 & \quad \text{Me} \\
\text{OH}_2 & \quad \text{OH}_2
\end{align*}$$

$3^+$ hydration

$\text{Al(H}_2\text{O)}_6^{3+}, \text{Fe(H}_2\text{O)}_6^{3+}$

(Aquometal complexes)

$\downarrow$ hydrolytic reactions

(H$_2$O Molecules in the hydration shell are replaced by OH$^-$ ions)

Formation of a variety of soluble species.
- Mononuclear species ($\text{Al(OH)}_2^{+1}, \text{Al(OH)}_2^{2+}$)
- Polynuclear Species ($\text{Al}_8\text{(OH)}_{20}^{4+}$)
IV. Destabilization Chemicals

(a) Hydrolysis scheme for iron (III)
IV. Destabilization Chemicals

Fig. 6-7. Equilibrium concentrations of hydroxo iron(III) complexes in a solution in contact with freshly precipitated Fe(OH)$_3$ at 25°C.
IV. Destabilization Chemicals

Figure 2.4. Solubility of Ferric Hydroxide. (Shaded area is the usual operating region used in water treatment.) Adapted from Journal of American Water Works Association, Volume 60, Number 5 (May 1968), by permission. Copyright 1968, the American Water Works Association.
IV. Destabilization Chemicals

Increasing pH

\[ \text{Al}[\text{H}_2\text{O}]_6^{3+} \rightleftharpoons [\text{Al(H}_2\text{O})_5(\text{OH})]^{2+} \rightleftharpoons [\text{Al(H}_2\text{O})_3(\text{OH})_3]_{(s)} \rightleftharpoons [\text{Al(H}_2\text{O})_2(\text{OH})_4 ]^{-1} \]

\[ \text{Al}_8(\text{OH})_{20}^{4+} \rightleftharpoons \text{AlO(OH)}_{(s)} \rightleftharpoons \text{Al}_2\text{O}_3(s) \]

(Other polynuclear species) (Crystalline phases)

FIGURE 7-5 Hydrolysis scheme for iron (III) and aluminum (III)

(after Rubin and Kovac. 1974).
IV. Destabilization Chemicals

(iii) Acidic nature of Al(III) and Fe(III) salts

\[
\begin{align*}
\text{Al(H}_2\text{O)}_6^{3+} + 3\text{H}_2\text{O} & \Leftrightarrow \text{Al(OH)}_3(\text{s}) + 3\text{H}^+ + 6\text{H}_2\text{O} \\
\text{Fe(H}_2\text{O)}_6^{3+} + 3\text{H}_2\text{O} & \Leftrightarrow \text{Fe(OH)}_3(\text{s}) + 3\text{H}^+ + 6\text{H}_2\text{O}
\end{align*}
\]

H\(^+\) liberated by the addition of alum will react with natural alkalinity in the water as follows.

\[
\text{Al}_2(\text{SO}_4\text{O})_3 \cdot 14\text{H}_2\text{O} + 3\text{Ca(HCO}_3)_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 14\text{H}_2\text{O} + 6\text{CO}_2
\]

| 549.4 | 100 | 155.71 | 33 |

The quantity of alkalinity required to react with 1 mg/L alum is

\[
\begin{align*}
1.0\text{ mg/L} \times \frac{(3\times100)}{594.4} & = 0.5\text{ mg/L (as CaCO}_3) \\
1.0\text{ mg/L} \times \frac{(6\times44)}{594.4} & = 0.44\text{ mg/L CO}_2
\end{align*}
\]
IV. Destabilization Chemicals

If the natural alkalinity is not sufficient to react alum and buffer the pH, it may be necessary to add alkalinity to the water in the form of lime or soda ash (Na₂CO₃).

\[
\text{Al}_2(\text{SO}_4\text{O}_3)\cdot14\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3 + 3\text{CaSO}_4 + 14\text{H}_2\text{O}
\]

\[
\text{Al}_2(\text{SO}_4\text{O}_3)\cdot14\text{H}_2\text{O} + 3\text{Na}_2\text{CO}_3 \rightarrow 2\text{Al(OH)}_3 + 3\text{Na}_2\text{SO}_4 + 3\text{CO}_2 + 11\text{H}_2\text{O}
\]

- Caution: the quantities determined by such calculations are only approximate because equation 1 does not describe what actually occurs during the coagulation process.
IV. Destabilization Chemicals

Figure 2.3. Solubility of Aluminum Hydroxide. (Shaded area is the usual operating region used in water treatment.) Adapted from Journal of American Water Works Association. Volume 60. Number 5 (May 1968). By permission. Copyright 1958. The American Water Works Association.
III. Destabilization Mechanisms

Effect of pH and alum dose on zeta potential of kaolin

FIGURE 6-3. Effect of pH and alum dose on zeta potential of kaolin (after Packham, 1965).
IV. Destabilization Chemicals

Remark

a) Possible combinations of the various hydrolysis products is endless

b) One or more of the hydrolysis product may be responsible for the observed action of Al or Fe

c) Because the hydrolysis reaction follow a stepwise process, the effectiveness of Al and Fe will vary with time. For example, an alum slurry that has been prepared and stored will behave differently from a freshly prepared solution when it is added to a wastewater.

d) The optimum pH range for alum : 4.5 - 8.0

The optimum pH range for Fe$_2$(SO$_4$)$_2$ : 4-12 (advantage over alum)

Because these are relatively insoluble within this pH range, less soluble products will be in effluents
IV. Destabilization Chemicals

e) According to Stumm and O’Melia (1968), Al(III) and Iron(III) accomplish destabilization by two mechanisms

i) Al(III) or Fe(III) salt is added to water in concentrations < the solubility limit of the metal hydroxide

   → hydrolysis products will adsorb onto the particles cause destabilization by charge neutralization

ii) > hydrolysis products will forms kinetic intermediates in the formation of the metal hydroxide precipitate.
IV. Destabilization Chemicals

B) Ferrous sulfate and lime

$$2\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 2\text{Ca(OH)}_2 + 1/2\text{O}_2 \rightarrow 2\text{Fe(OH)}_3 + 2\text{CaSO}_4 + 13\text{H}_2\text{O}$$

- oxidation-reduction reaction requires some dissolved oxygen in the water
- Ferrous sulfate and lime is less expensive than alum

C) Lime and/or Magnesium

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$$
$$\text{Ca(OH)}_2 + \text{Ca(HCO}_3)_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$$
$$\text{Ca(OH)}_2 + \text{Mg(HCO}_3)_2 \rightarrow \text{MgCO}_3 \downarrow + \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$$
$$+ \text{Ca(OH)}_2 + \text{MgCO}_3 \rightarrow \text{Mg(OH)}_2 \downarrow + \text{CaCO}_3 \downarrow$$

$$2\text{Ca(OH)}_2 + \text{Mg(HCO}_3)_2 \rightarrow \text{Mg(OH)}_2 \downarrow + 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$$
IV. Destabilization Chemicals

- Combination of water softening and coagulation
- Colloidal particles become enmeshed in the gelatinous hydroxide precipitate (Mg(OH)₂)
  * lime raise the pH pf wastewater above 9.5
- For waters low in natural Magnesium, it is necessary to provide magnesium through the addition of a suitable salt
- Advantage: recovery of lime and Mg from sludge
  : Simplify sludge disposal problems and improves the overall economics

\[
\text{Mg(OH)₂ + CO₂} \rightarrow \text{Mg(HCO₃)₂} \rightarrow \text{Return to coagulation process}
\]

Remaining sludge \(\rightarrow\) dewatered CaCO₃ \(\rightarrow\) CaO + CO₂
IV. Destabilization Chemicals

Figure 7-7 Flow diagram of turbidity removal plant using magnesium and lime recovery (after Thompson, Singley, and Black, 1972)
IV. Destabilization Chemicals

D) Polymers

- Polymers (Cationic, anionic, nonionic) → polyelectrolytes (contain ionizable groups)
- Used as coagulants or coagulant Aids
- Cationic polymer: 0.5-1.5 mg/L, 10-20 times alum dosage gives same effect
- Polymers are not acidic and do not lower the pH of water as alum: advantage for treating low alkalinity water.
- Reducing the volume of sludge produced
- Providing a sludge that is easier to dewater
## IV. Destabilization Chemicals

### TABLE 6-3. Synthetic Organic Coagulants Used in Water Treatment

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
<th>Molecular Weight Range</th>
<th>Uses</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonionic</td>
<td>Polyacrylamide</td>
<td>$10^3 - 10^7$</td>
<td>Coagulant aid, filter aid</td>
<td>Used to increase floc strength, available as powder or emulsion, used mostly as filter aid</td>
</tr>
<tr>
<td>Anionic</td>
<td>Hydrolyzed polyacrylamide</td>
<td>$10^4 - 10^7$</td>
<td>Coagulant aid, filter aid, sludge conditioning</td>
<td>Produced by controlled hydrolysis of polyacrylamide; range of MW, charge density available, charge depends on pH</td>
</tr>
<tr>
<td>Cationic</td>
<td>Poly(DADMAC) or poly(DMAA) polymers</td>
<td>$10^4 - 10^6$</td>
<td>Primary coagulant, turbidity/color removal, sludge conditioning</td>
<td>Most widely used primary coagulant; may be used in conjunction with inorganic coagulant; chlorine resistant; charge density not pH sensitive; available in liquid form</td>
</tr>
<tr>
<td></td>
<td>Quaternized polyamines</td>
<td>$10^4 - 10^5$</td>
<td>Primary coagulant, color/turbidity removal</td>
<td>Mostly widely used primary coagulant for color removal; properties similar to poly(DADMAC)</td>
</tr>
<tr>
<td>Cationic</td>
<td>Polyamines</td>
<td>$10^4 - 10^7$</td>
<td>Primary coagulant, color coagulant aid (high MW)</td>
<td>Includes several types of polymers; less widely used as primary coagulant, reacts with chlorine; charge density depends on pH</td>
</tr>
</tbody>
</table>
IV. Destabilization Chemicals

- Preventing the carryover of soluble aluminum into the distribution system
- Preventing the carryover of light floc
- Dosage control is more difficult to achieve because of their narrow range of effectiveness. In the absence of precise dosage control, polymers will not yield satisfactory performance
- Their use has been restricted due to high cost and uncertainties regarding chemical impurities associated with polymer synthesis.

* In France, Japan: synthetic organic polymers are currently not permitted in water treatment

* In U.S.A.: over 600 polymers have been approved for use in potable water treatment by U.S. EPA
IV. Destabilization Chemicals

E) Coagulant Aids

- Flocs produced during coagulation should settle rapidly and be resistant to destruction by shearing forces. In many cases, the flocs produced do not possess these characteristics, particularly in the case of water low in turbidity or low mineralized waters that are high color.

- In case of light weight, fragile, slow-settling floc (Al(OH)₃), coagulant aids can be added to the water to improve floc properties and enhance coagulation.

  a) Bentonitic clay

- For waters low in turbidity, their use can reduce the amount of coagulant required to treat a water and can improve the nature of flocs (the increased concentration of colloids provides greater contact opportunity and leads to destabilization by charge neutralization rather than by sweep-floc coagulation.

- It weight the flocs and causes them to settle more rapidly than flocs containing mostly Al(OH)₃.
IV. Destabilization Chemicals

Fig. 7-6(a) represents the results of typical coagulation studies with various concentrations of colloids at a constant pH.

Fig. 7-6(b) is a plot of sections through the curve of Figure 7-6(a) at the points indicated by the vertical lines.
IV. Destabilization Chemicals

Zone 1: Insufficient coagulation dosage → destabilization does not occur

Zone 2: Increasing the coagulation dose results in destabilization

Zone 3: Charge reversal and restabilization occur

Zone 4: A sufficient dosage (removal by sweep-floc coagulation occurs when the solubility of metal hydroxide (Al(OH)$_3$) is exceed

*FIGURE 7.6 Schematic coagulation curves at constant pH. Shaded areas represent regions in which coagulation occurs (after Stumm and O'Melia, 1968).*