

Southern Methodist University

School of Engineering and Applied Science

SMU SSH 8321

SMU ME 5315

NTU HW 741-N

Treatment Technology I - Physical and Chemical
Methods

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II. SOLIDS-LIQUID SEPARATION

(A) Coagulation and Flocculation

Coagulation and flocculation are used to remove:

- (1) fine suspended and colloidal solids (i.e., turbidity causing substances) that have natural gravity settling rates that are too slow for effective clarification and/or filtration.

- (2) adsorbable organics that cause color
(e.g., natural humic substances).
- (3) precipitable inorganics
(e.g., metal cations and phosphate anions)
- (4) microorganisms
- (5) stable oil-water emulsions

Applications include:

- (1) industrial and hazardous waste treatment
- (2) municipal wastewater treatment
- (3) municipal water supply treatment
- (4) industrial process water treatment
(e.g., boiler feed water)

Principal disadvantages are:

- (1) High operating costs due to the reagent chemicals required
- (2) Large quantities of sludge are often produced that require further processing and disposal

Definitions -

(1) Coagulation and Flocculation -

Broadly described as a physical/chemical process of blending a coagulant chemical into a liquid and then gently stirring the mixture.

The overall purpose is to improve the removal efficiency of subsequent sedimentation and/or filtration processes.

(2) Colloidal state of matter -

(a) Particle size

true solutions, 10 - 50 Angstroms

colloidal suspensions, 0.001 to 1.0 μ

coarse suspensions, $> 1 \mu$

(b) Physical properties of a solid-in-liquid colloidal suspension (sol)

(i) colloidal particles can not, in general, be removed by filtration

(ii) colloidal particles are not microscopically visible but they reflect light (Tyndal Effect)

- (iii) colloidal particles have a surface electrostatic charge (usually negative)
- (iv) colloidal particles settle extremely slowly, or not at all, under the influence of gravity because they are kept in suspension by Brownian diffusion

- (v) tiny particles often exhibit adsorptive properties due to their very large surface area to volume ratio (A_S/V), for example, consider spherical particles of radius R ,

$$\frac{A_S}{V} = \frac{4\pi R^2}{(4/3)\pi R^3}$$

$$\frac{A_S}{V} = \frac{3}{R}$$

$$\text{Then, } R \rightarrow 0 \Rightarrow \frac{A_S}{V} \rightarrow \infty$$

(3) Rapid Mixing -

Rapid mixing (sometimes called “Flash Mixing” or “Initial Mixing”) is the physical process of rapidly blending or dispersing a chemical additive into a liquid. Rapid mix tanks typically have a hydraulic detention time, T , in the range of 10 seconds to 2 minutes.

(4) Coagulation and Coagulant Chemicals - Destabilization of small, non-settable, non-filterable solid particles is defined as coagulation and is accomplished by blending coagulant chemicals into the waste stream in a rapid mix tank.

Destabilization occurs by the following mechanisms:

- (a) Charge Neutralization - the negative charge of colloidal particles is neutralized by adding multivalent cationic metal salts that reduce the electrostatic repulsion force allowing the particles to collide and adhere by van der Waals attraction forces.

Common metal salt coagulants include:

- (i) alum - $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$
- (ii) ferric chloride - $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
- (iii) ferric sulfate - $\text{Fe}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$
- (iv) other aluminum and ferric iron salts

Al^{3+} and Fe^{3+} ions and hydrolyzed Al and Fe ionic species with various charges are produced by addition of metal salt coagulants.

The highly positive charge of Al^{3+} and Fe^{3+} ions and their hydrolyzed ionic species allow for efficient neutralization of the negative surface charge of colloidal particles at relatively low reagent chemical dosages.

Basically, it takes fewer Al^{3+} and Fe^{3+} ions for charge neutralization than it would if divalent or monovalent cations were used.

For example, the relative concentrations of Na^+ , Ca^{2+} , and Al^{3+} cations required to destabilize a colloid by charge neutralization vary approximately in the ratio 1000 : 10 : 1, respectively.

(b) Enmeshment in a Precipitate (“Sweep Floc”)- Insoluble metal hydroxide or carbonate precipitates are formed by the addition of the common metal salt coagulants or lime. Suspended solids and colloidal matter are adsorbed and/or “swept” out of suspension by the precipitate particles.

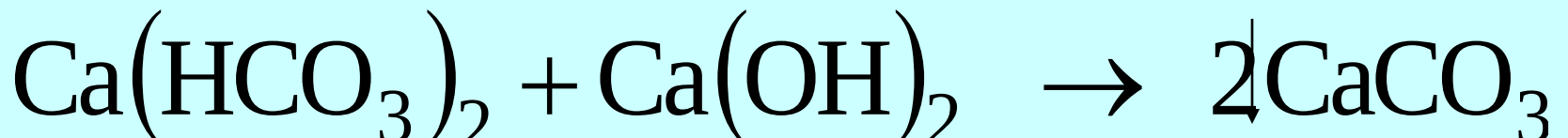
The chemical precipitation reactions are,

(i) alum, [Equations 8.2 and 8.3, p. 174]

(ii) ferric chloride,
[Equations 8.7 and 8.8, p. 176]

(iii) ferric sulfate, [Equation 8.6, p. 176]

(iv) lime,



*Important Points -

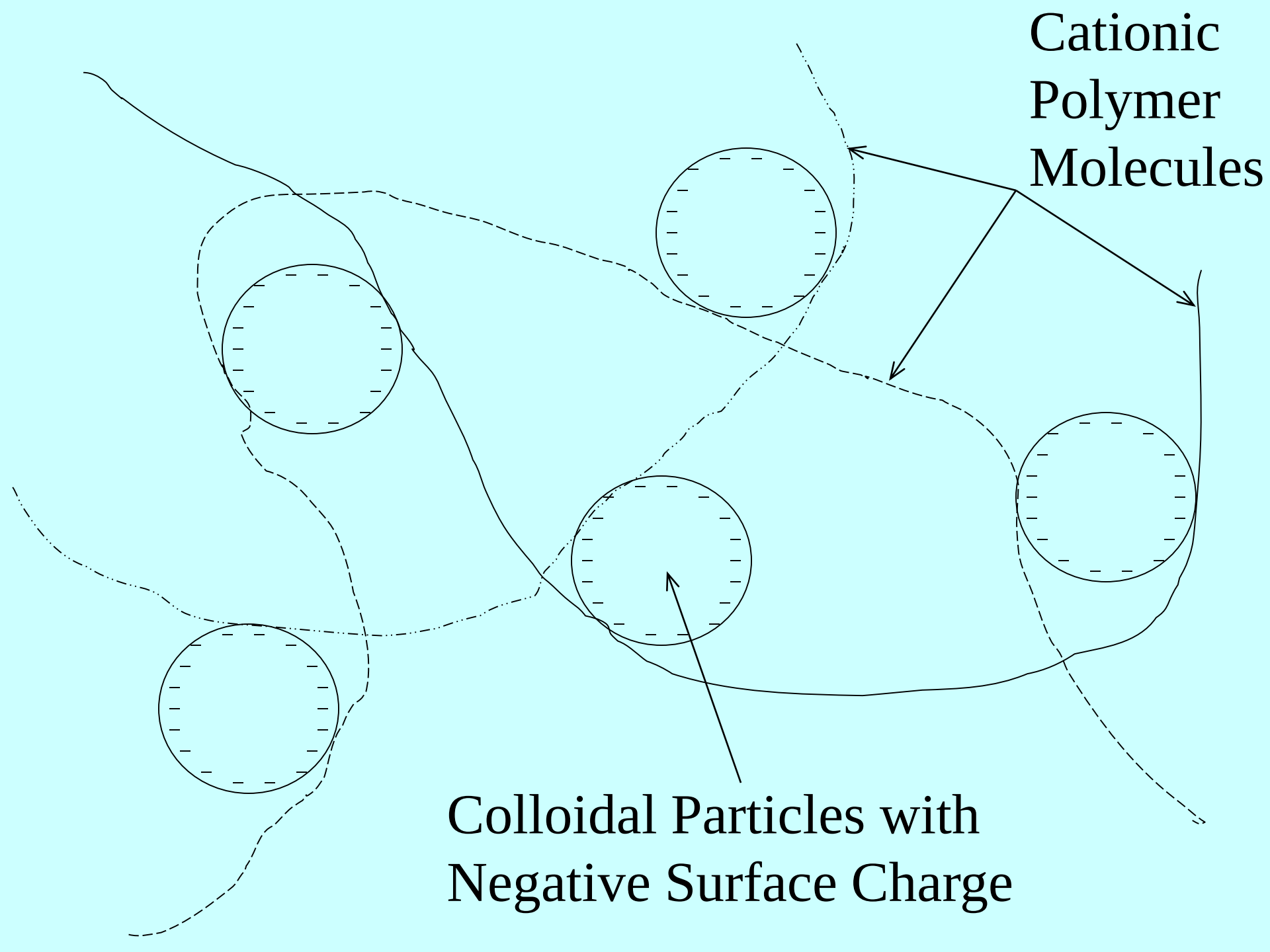
- (i) The pH of minimum solubility for both $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ is in the range of 6 to 9, i.e., in the “normal” pH range. Thus, final pH adjustment is not typically required after coagulation. This is a principal reason for the wide application of these chemicals as coagulants.

(ii) Alum and Fe^{3+} salts are acidic in nature, i.e., alkalinity is consumed by their addition. For example, 0.5 mg/l alkalinity as CaCO_3 is consumed for each 1.0 mg/l $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ added. If there is insufficient alkalinity in the wastewater (as revealed by an excessive drop in pH), then supplemental alkalinity must be added. Lime is usually used as the supplemental source of alkalinity.

- (iii) Precipitation of CaCO_3 requires a $\text{pH} > 10$.
Therefore, use of lime as the coagulant requires pH neutralization with an acid after separation of the solid precipitate from the liquid.

(c) Interparticle bridging - Long-chain cationic organic polymers (also called polyelectrolytes) are added to adsorb to multiple colloidal particles providing a particle bridging effect. Charge neutralization is also an aspect of the effectiveness of cationic polymers as primary coagulants.

Cationic
Polymer
Molecules



Colloidal Particles with
Negative Surface Charge

(5) Flocculation -

Agglomeration of the destabilized colloidal particles into larger settleable and/or filterable particles is called flocculation. Floc particles can be fairly small microflocs (diameter < 0.1 mm) up to large macroflocs (0.1 mm to 3.0 mm diameter).

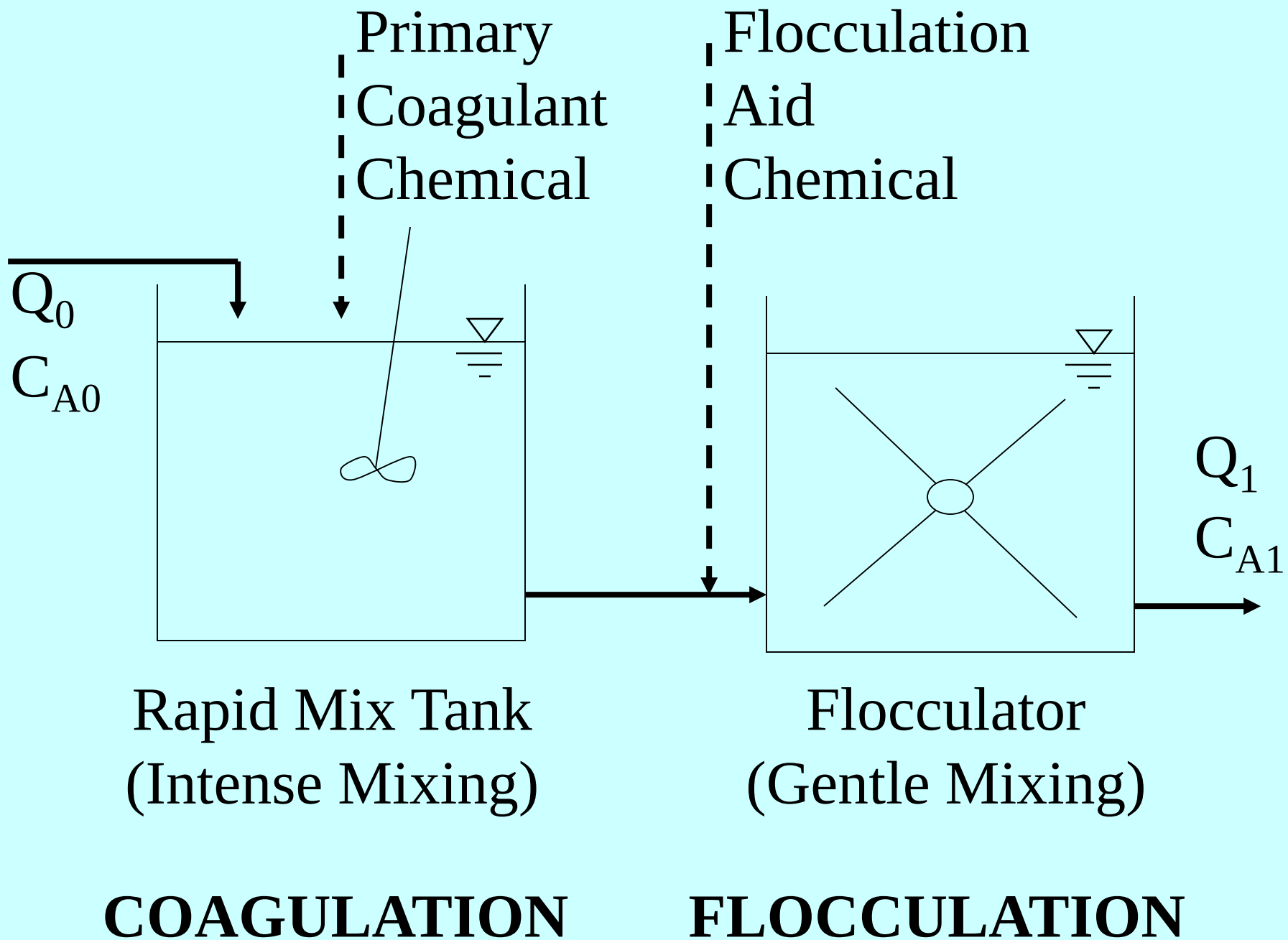
Flocculation typically involves a gentle stirring of the liquid to encourage collision among the destabilized particles. The particles adhere due to van der Waals attraction forces to build floc particles of optimum size, density, and strength for subsequent removal by settling and/or filtration.

(6) Flocculation Chemicals -

“Flocculation Aids” are usually very high molecular weight ($> 10^6$) organic polymers that provide for interparticle bridging during flocculation. These polymers can be cationic or anionic (polyelectrolytes) or non-ionic.

Process Analysis -

A process flow schematic for the coagulation and flocculation process is as follows:



Neglecting the volumetric flow rates of the coagulant and flocculation aid chemical reagents, a steady-state water balance around the entire process yields,

$$Q_1 = Q_0$$

Coagulation and flocculation do not change the chemical nature of any specific chemical, A, in the influent but suspended solids are generated.

Indeed, when chemical precipitation reactions are used to induce sweep floc coagulation, large quantities of suspended solids can be produced. As such, steady-state mass balances on chemical substance A and on TSS around the process yield,

$$C_{A1} = C_{A0}$$

But

$$C_{TSS1} > C_{TSS0}$$

Chemical Selection -

Lab bench scale testing (i.e., “Jar Tests”) or pilot plant testing should be the basis for selection of the specific coagulant and flocculation aid chemicals to be used and to determine their optimum dosages. However, all designs should be flexible enough to allow changes in the types of chemicals and dosages used.

Choosing among the available chemicals is based on:

- Achievable treatment efficiency
- Economics
- Reliability
- Safety

- Chemical storage and feeding requirements
- Sludge production and disposal (e.g., cationic metal salts produce larger sludge volumes than organic polymer primary coagulants)

Often, a combination of a cationic metal salt coagulant and an organic polymer flocculation aid is the most effective and economical option.

The common cationic metal salt coagulants are listed on the previous chemical handout along with properties of the commercially available forms. Most can be purchased in solid form (powder or granules) or as a liquid solution.

Organic polymers can be purchased as liquid solutions, liquid emulsions, or solids depending upon the characteristics of the specific polymer.

Metal salt coagulants and organic polymers used for hazardous waste treatment are often purchased in liquid form for safety and ease of storage and handling (this disagrees with the general discussion in the textbook). When purchased as a solid, most chemicals must be converted to a solution by dissolving in tap water before use. This requires additional steps for preparation and additional tanks plumbing, and equipment.

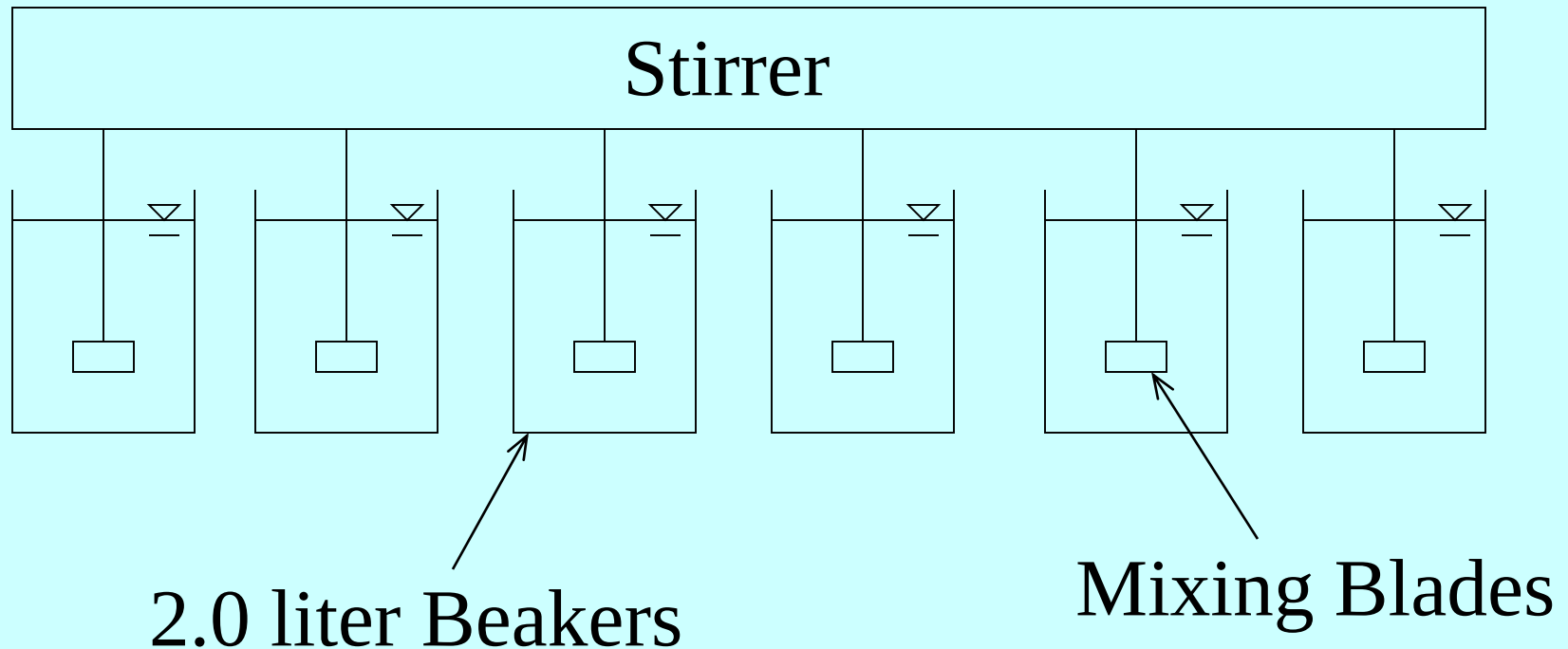
Chemical nature of organic polymers:

- (1) Cationic polymers used as primary coagulants are usually polyamines or quaternary amines with $MW \leq 100,000$
- (2) Cationic, non-ionic, or anionic polymers used as flocculation aids are often polyacrylamides with various functional groups attached, with $MW > 1,000,000$

Chemical Dosages -

During design, “Jar Tests” are commonly conducted in a lab or in the field to select chemicals and dosages. They are also used on a routine ongoing basis at operating treatment plants to establish “current” optimum chemical dosages because dosages tend to vary with time (e.g., dosages vary with temperature and pH).

Jar tests are conducted in a series of 2.0 liter beakers and a “Gang Stirrer” is typically used for mixing,



Manufacturers of chemicals and chemical feed equipment and local chemical suppliers can provide valuable help during testing, design, and operation.

Optimum chemical dosages are typically,

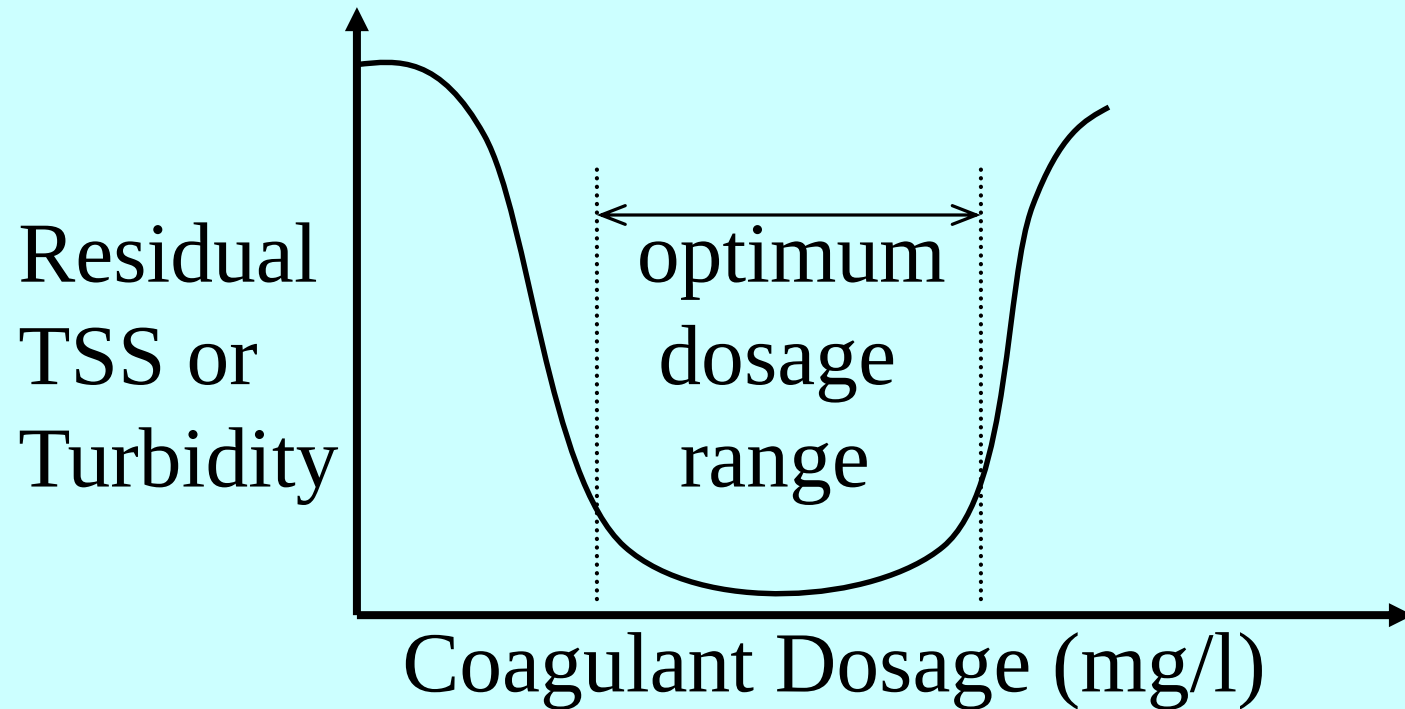
- 1.0 to 10.0 mg/l for cationic polymers used as primary coagulants
- 5 to 200 mg/l alum as $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$
- 5 to 200 mg/l ferric chloride as FeCl_3
- 0.10 to 1.0 mg/l for flocculation aid polymers

The low end of the dosage range for alum and ferric chloride is used for “charge neutralization” and the high end for “sweep floc” coagulation.

Cationic metal salts are usually fed directly from storage tanks at commercial solution strength.

Organic polymers are usually diluted with tap water to produce a 0.25% to 0.50% stock solution in a “stock tank” or “day tank”. They are often further diluted with tap water to 0.05% to 0.10% just upstream of their application point. Low concentrations are used because higher strength polymer solutions tend to have an extremely high viscosity that makes them difficult to pump and difficult to blend efficiently with the waste stream.

Almost all coagulants show an adverse overdosing effect:



Several phenomena account for the adverse overdosing effect including charge reversal of the stable colloid.

Mixing Energy -

The energy input required for rapid mix units and gently mixed flocculation units can be estimated from:

$$P = \mu VC$$

This is a rearranged version of Equation 8.9, p. 181 in the textbook.

where,

P = power input to fluid $\left[\frac{L \cdot F}{T} \right]$

μ = absolute viscosity of the fluid $\left[\frac{F \cdot T}{I^2} \right]$

V = volume of reactor $[L^3]$

G = root-mean-square velocity $\left[\frac{L/T}{I} \right]$ or $\left[\frac{L}{I \cdot T} \right]$
gradient of the fluid particles

Design criteria for rapid mixing and flocculation
with G as the design parameter:

Rapid Mixing,

$$G = 750 \text{ to } 1,500 \text{ sec}^{-1} \text{ with } 900 \text{ sec}^{-1} \text{ typical}$$

Flocculation,

$$G = 20 \text{ to } 200 \text{ sec}^{-1}$$

Example -

Determine the power input (in units of hp) required for a rapid mix tank with a design $G = 800 \text{ sec}^{-1}$, a volume of 100 ft^3 , and a wastewater temperature of 60° F ,

$$\mu = 2.359 \times 10^{-5} \text{ lb}\cdot\text{sec}/\text{ft}^2 \text{ for water at } 60^\circ \text{ F}$$

Rapid Mixing -

Design criteria based on hydraulic detention time, T ; velocity gradient, G ; and the dimensionless product GT :

$T = 10 \text{ sec. to } 2 \text{ min. with } 30 \text{ sec. typical}$

$G = 750 \text{ to } 1,500 \text{ sec}^{-1}$

$GT = 7,500 \text{ to } 200,000$

Flocculation -

Design criteria,

$$T = 15 \text{ to } 60 \text{ min.}$$

$$G = 20 \text{ to } 200 \text{ sec}^{-1}$$

$$GT = 20,000 \text{ to } 750,000$$

$$\text{Paddle tip speed} = 1 \text{ to } 4 \text{ ft/sec}$$