Chemical Principals
Coagulation to Flocculation

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Wastewater

Before you can use wastewater treatment chemicals you must know the following:

- ✓ How is the Wastewater Generated?
  - Process Water
  - Sanitation / Cleaning Water
- ✓ What are the goals and objectives?
  - Compliance
  - Surcharge Reduction
  - Recycle

Wastewater

Typically, wastewater is generated as part of a washing operation process.

For an example:

- ✓Soils from Textiles
- ✓Grease from cooking pans & ovens
- ✓Lubricating oils from metal-forming
- ✓Coolants from metals extrusion
- ✓Solids from cooling water

Wastewater

What are the wastewater chemical treatment program goals and objectives?

How Clean is Clean?

Wastewater

What are the Program Goals & Objectives?

Compliance

- ✓ Local Discharge Limitations i.e. FOG, BOD/COD
- ✓ Categorical Limitations i.e. Metals

Surcharge Reduction

- ✓ Reduce BOD or TSS

Recycle

- ✓ For reuse back in process or cooling or washing

Wastewater Sources

Examples of Oily Waste Stream

- ✓Lubricating oils from metal extrusion/working.
- ✓Coolants from metals casting.
- ✓Oils and grease from oven cleaning.
- ✓Oils from washing shop towels or bar mops.
- ✓Oils from food plant cleaning.

Wastewater Pollutants

Examples of Insoluble Pollutant Waste Streams

- ✓ Suspended solids from baking operations.
- ✓ Heavy metals from chrome plating processing.
- ✓ Suspended solids from dust control textile processing.
- ✓ Suspended solids from gravel washing.

Wastewater Pollutants

Examples of Soluble Pollutant Waste streams

- ✓ Solvents from inker towel washing.
- ✓ Sugars from baking processes.
- ✓ Salts from leather processing.
- ✓ Molybdenum from oil processing.
- ✓ Starch from paper box plants

Wastewater Treatment Chemicals

Most chemical treatment products *cannot* remove soluble pollutants from wastewater unless the products can be converted to its insoluble form.

Wastewater Emulsions

Most Wastewater Chemical Treatment Products WORK BEST on oily emulsions or colloidal suspensions.

Wastewater Emulsions

To form a stable emulsion a third substance must be present such as a surfactant.

Wastewater Emulsions

What is an emulsion?

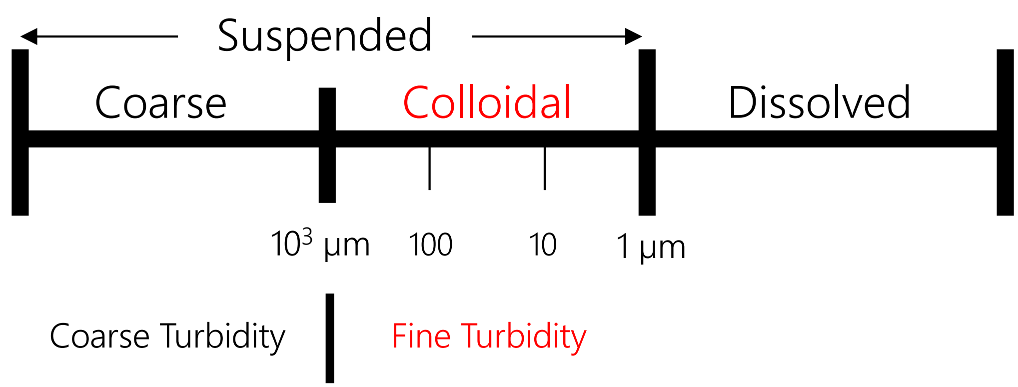
An emulsion is a stable dispersion of one phase into another phase such as oil in water.

Colloidal Suspension

What is a colloidal suspension?

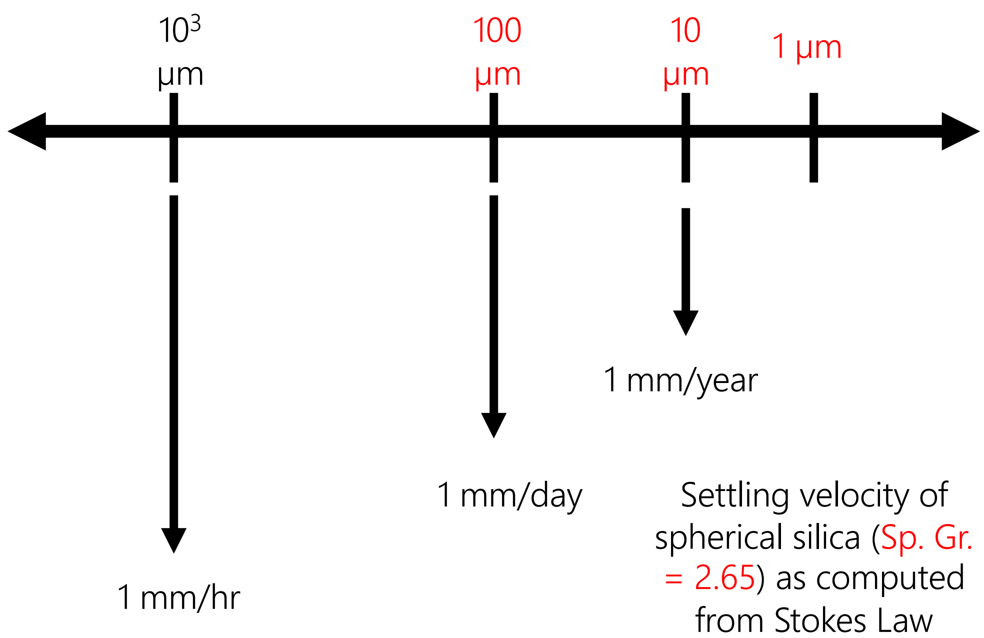
Colloidal Suspension

Particle Size



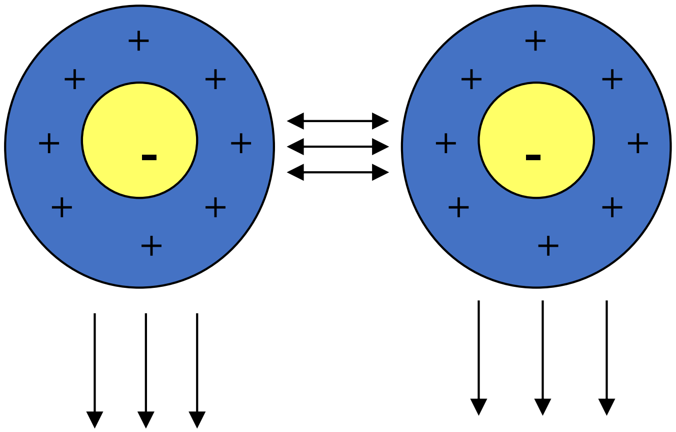
Colloidal Suspension

Colloidal Particle Settling Rate

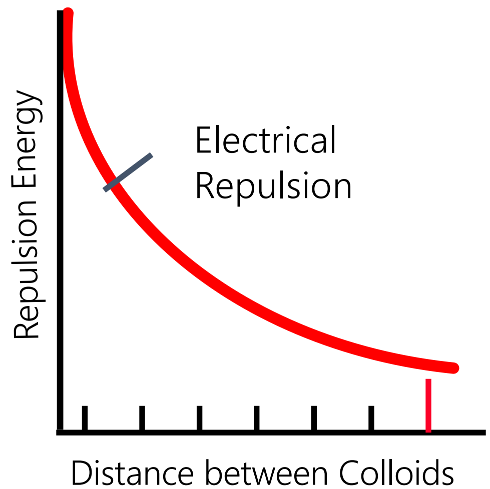


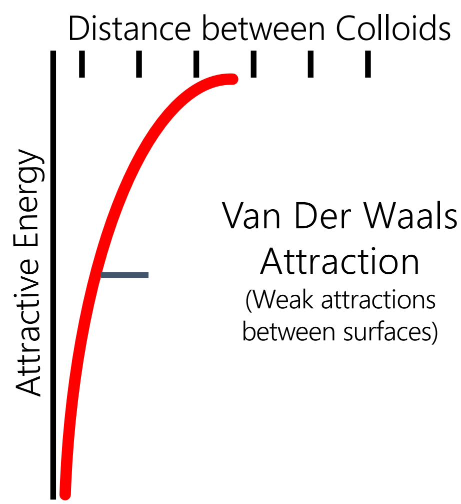
Colloidal Particles

- Most of the particles to be removed have a negative charge.
- Shells of the cationic charges form around the colloidal particles.
- The force of repulsion between the particles is stronger than the force of gravity.
- As a result, the particles stay in suspension.

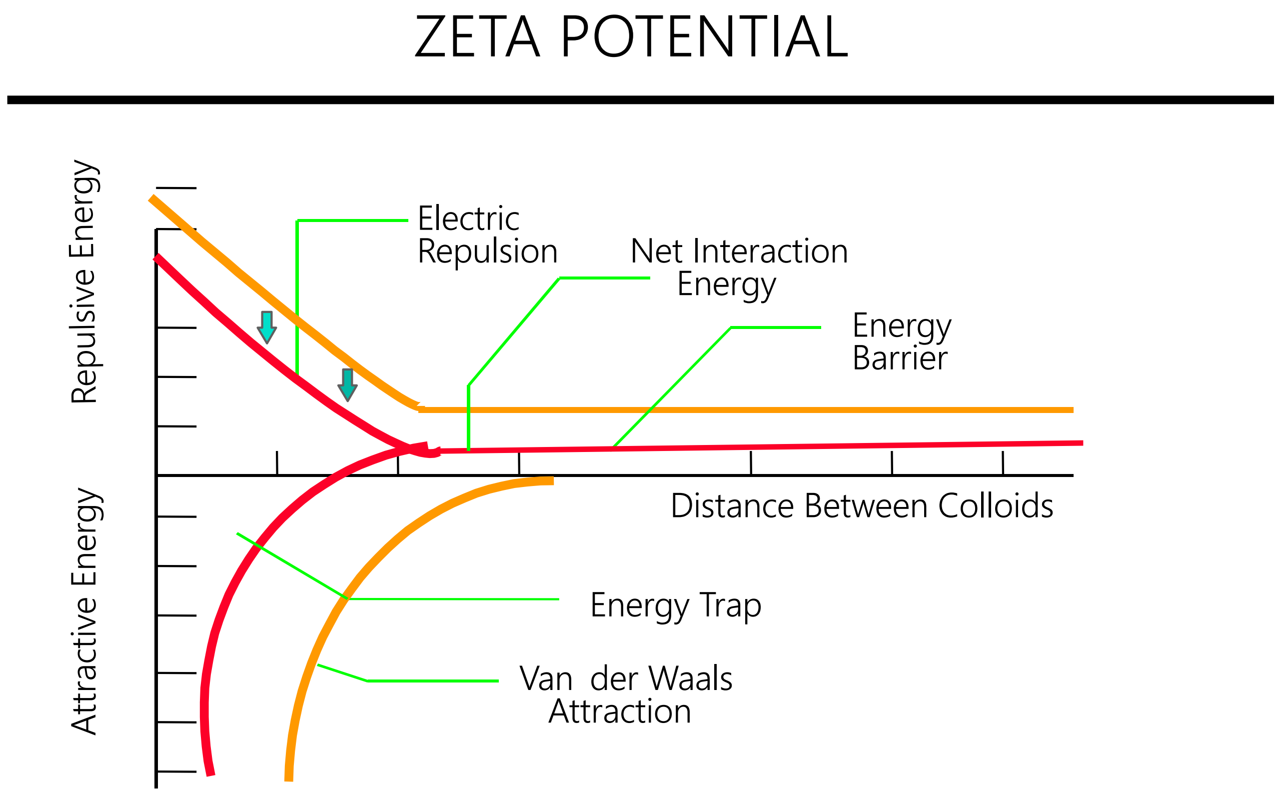


Forming a Stable Emulsion / Colloidal Suspension



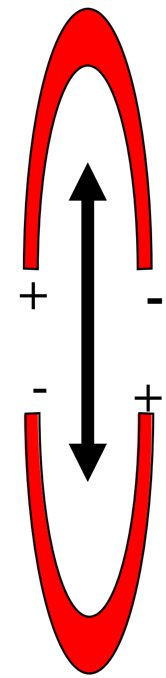


Breaking the Colloidal Suspension



Breaking the Emulsion / Colloidal Suspension

- The primary mechanism is electrostatic.
- Attractions between positive and negative charges.
- Analogous to magnetic attraction.
- Other mechanisms include:
  - Vander Waal's Attraction
  - Hydrogen Bonding

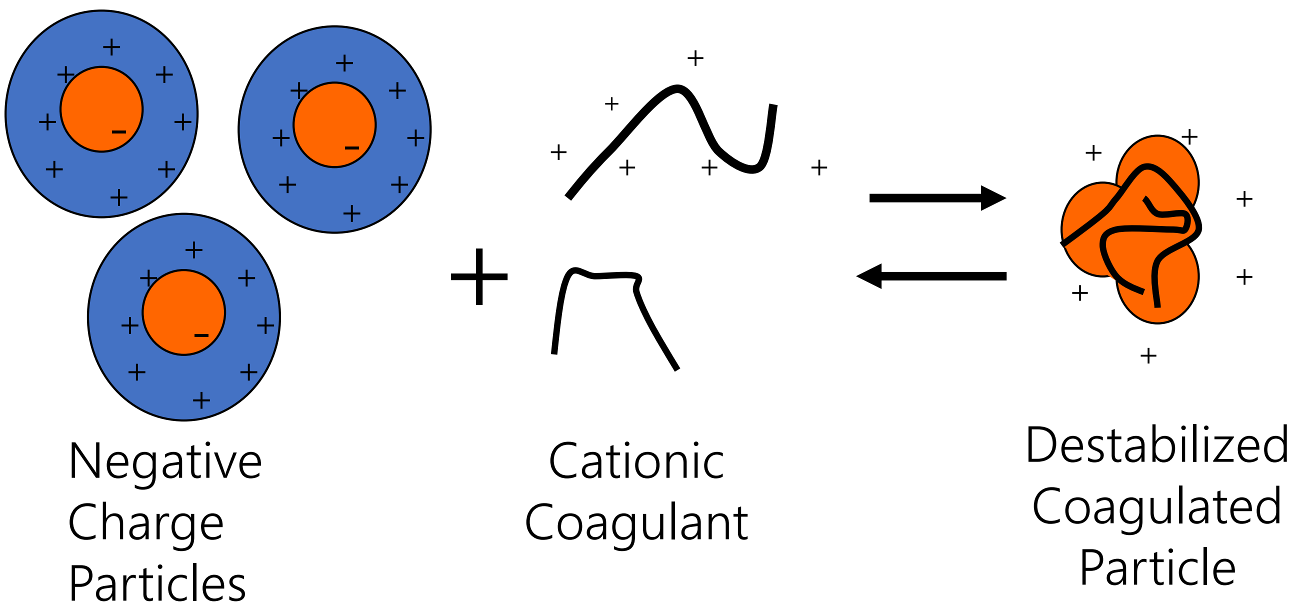


Breaking the Emulsion / Colloidal Suspension

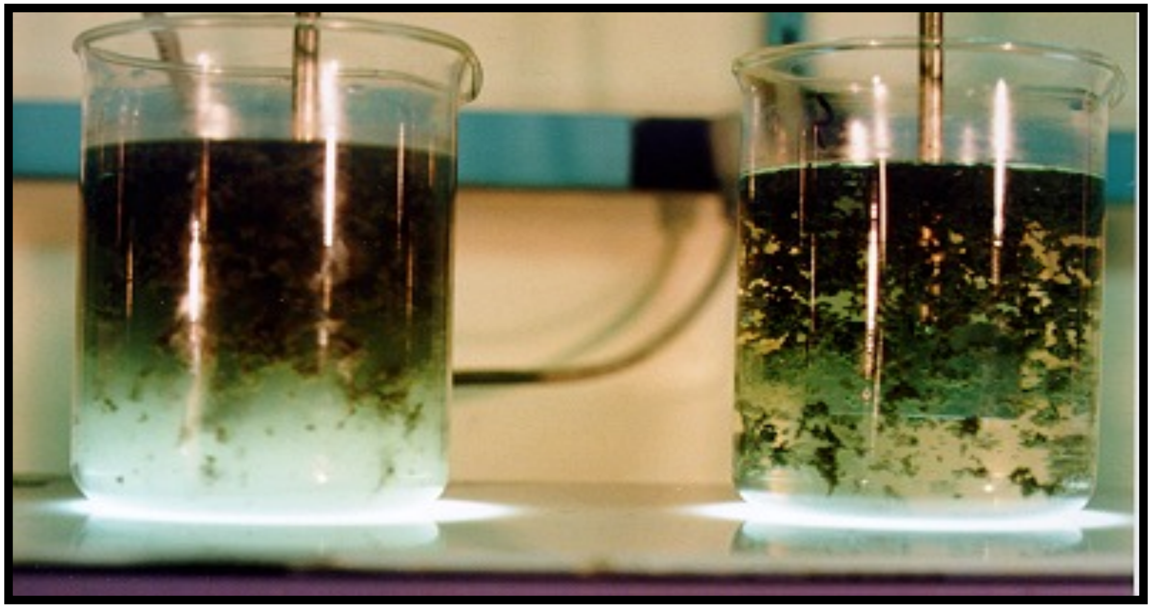
1. Destabilization
2. Microfloc Formation
3. Agglomeration

COAGULATION

Breaking the Emulsion / Colloidal Suspension



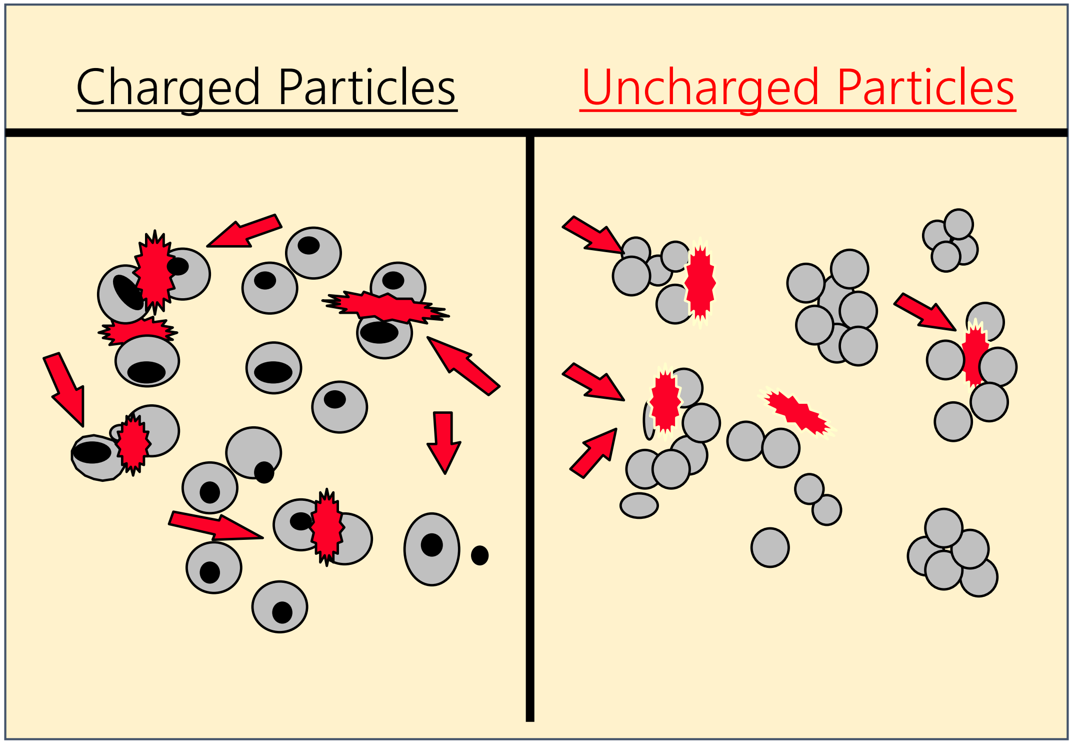
Breaking the Emulsion



Effective Chemical Treatment

Coagulation and Flocculation

Breaking the Emulsion



Coagulation

Coagulation is “the process by which suspended colloidal particles in the wastewater are destabilized or electrically neutralized so that the particles can agglomerate and settle out of the water leaving relatively clean water behind.”

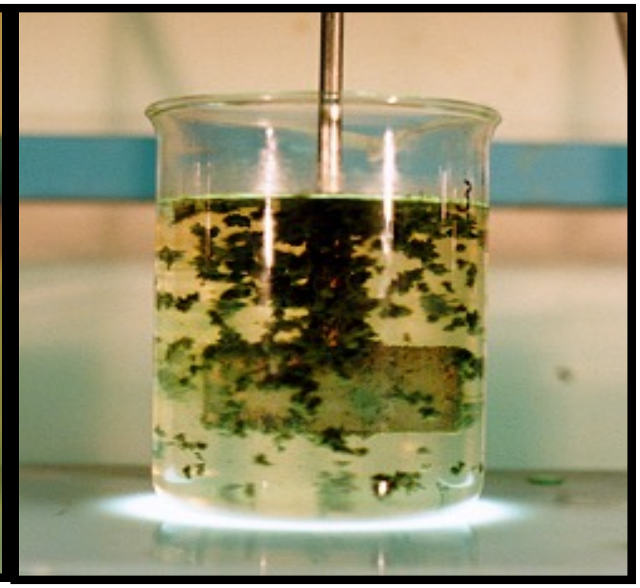
Coagulation

- "Pure Coagulation" involves a single particle.
- Purely electrical in nature.
- Weakly agglomerates.
- Process is completely reversible.

Coagulation

Negative electrical charges keep suspended solids in suspension

Before Coagulant Addition



After Coagulant Addition

Electrical charges neutralized suspended solids now coagulated

Breaking the Emulsion

- ✓ Acid Cracking
- ✓ Inorganic Chemical Coagulants
- ✓ Organic Chemical Coagulants

Breaking the Emulsion

Acid Cracking

- Addition of Sulfuric Acid to the emulsion.
- Converts surfactant carboxyl ion into carboxylic acid.
- Allows oil droplets to agglomerate.
- Salts of Iron and Aluminum can be used in place of acid.

Breaking the Emulsion

Acid Cracking

Advantages

- Waste oil may be sold as a secondary fuel source
- No sludge disposal

Disadvantages

- Dangerous - requires bulk volumes of acid
- Does not remove metals -- Solubilizes Heavy Metals
- Corrosive to Equipment

Breaking the Emulsion

<u>Inorganic Coagulants</u>

Simple, water-soluble inorganic metal salts

form Metal Hydroxide Compounds

- Aluminum sulfate, Aluminum chloride, Aluminum chlorohydrate, Polyaluminum chloride
- Ferric chloride, Ferric Sulfate, Ferrous Sulfate, Ferrous Chloride
- Calcium Chloride

Breaking the Emulsion

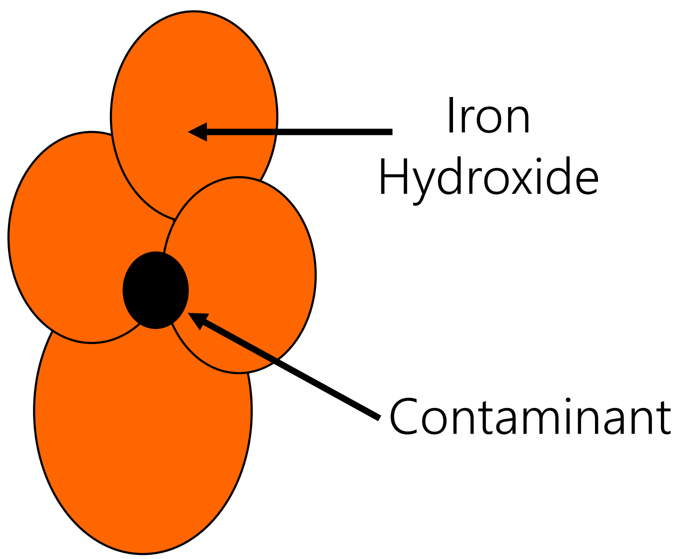
Other Inorganic Coagulants

Simple, water-soluble inorganic metal salts

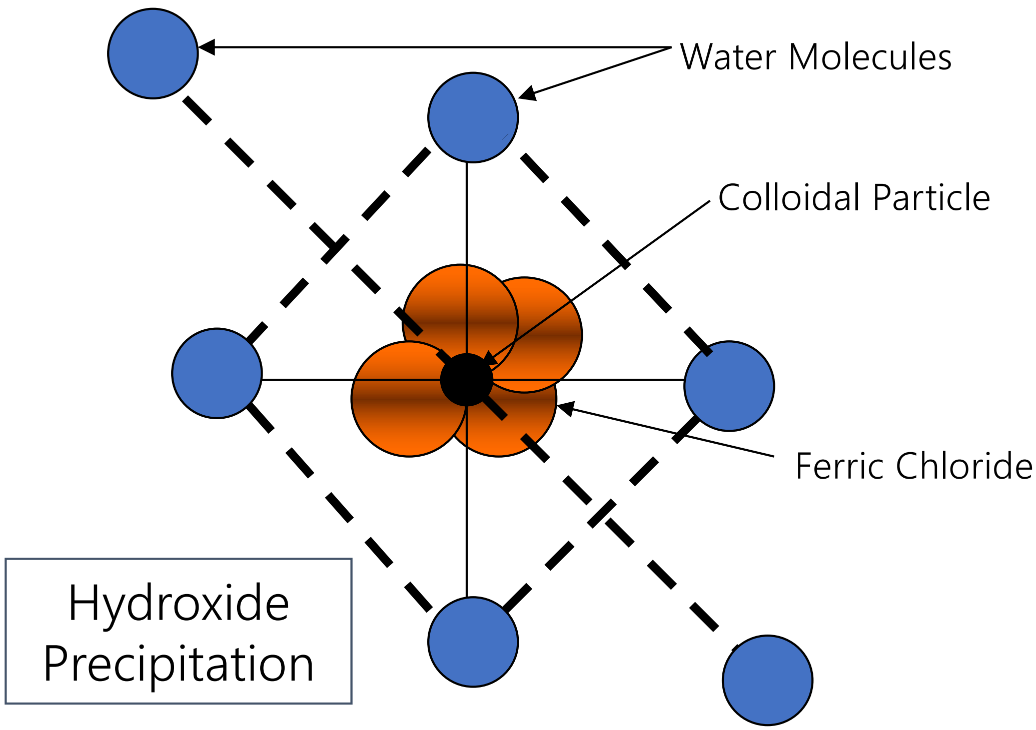
- Bentonite Clay
- Lime Slurry, Calcium hydroxide
- Magnesium Hydroxide

Breaking the Emulsion

Hydroxide Precipitation



Breaking the Emulsion



Breaking the Emulsion

<u>Inorganic Coagulant</u>

<u>Metal Hydroxide Formation</u>

$$\underbrace{Al2(S04)3}_{\text{Alum}} + \underbrace{6H20}_{\text{Water}} \leftrightarrow$$

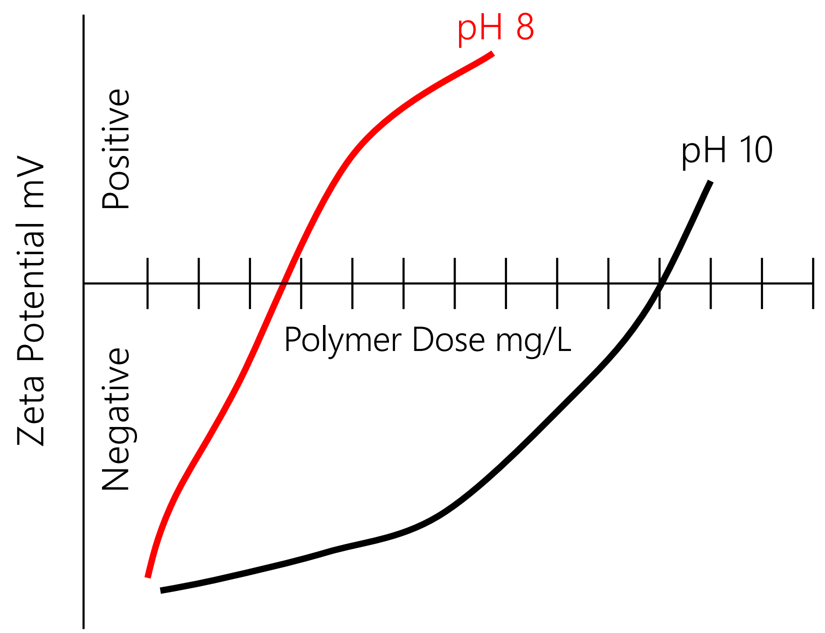
$$\underbrace{2Al(OH)3}_{\text{Aluminum Hydroxide}} + \underbrace{3H2SO4}_{\text{Sulfuric Acid}}$$

$$\underbrace{FeCl3}_{\text{Ferric Chloride}} + \underbrace{3H2O}_{\text{Water}} \leftrightarrow$$

$$\underbrace{Fe(OH)3}_{\text{Iron Hydroxide}} + \underbrace{3HCl}_{\text{Hydrochloric Acid}}$$

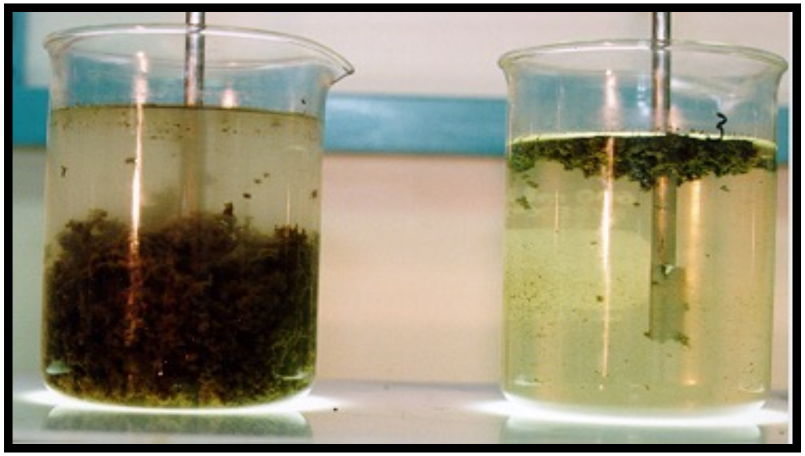
The formation of acid using inorganic coagulants decreases the wastewater pH

Breaking the Emulsion



Breaking the Emulsion

Inorganic Chemical Coagulants



Advantages

- Lower Cost per Pound
- Easy Coagulant Selection

Disadvantages

- pH Sensitive
- Affects Discharge pH
- High Chemical Dosages
- Large Sludge Generation

Breaking the Emulsion

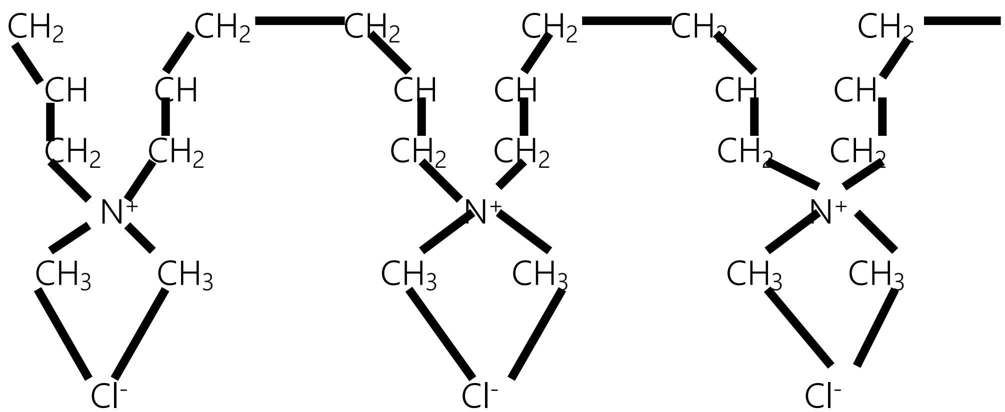
Organic Coagulants

Complex water-soluble organic polyelectrolytes made of natural or synthetic compounds with various charge densities and molecular weights.

Provides charge neutralization and physical bridging of hydrogen-bonding sites.

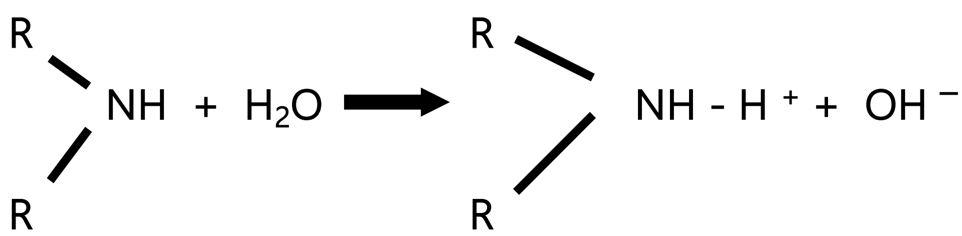
Breaking the Emulsion

<u>Organic Coagulants</u>



Cationic diallyldimethylammonium chloride compound (DADMAC)

Breaking the Emulsion



$$R - COOH \longleftrightarrow R - COO^{-} + H^{+}$$

Organic Coagulant Chemical
Reaction in Water

Breaking the Emulsion

<u>Organic Coagulants</u>

- PolyDADMAC
- Epi-DMA
- Starch-Based
- Mannich (Co-Polymers)

Breaking the Emulsion

Organic Coagulants

Advantages

- Does not affect pH of discharge
- Wide pH Range
- Reduces Sludge Generation
- Low Chemical Dosages

Disadvantages

- Higher Cost Per Pound
- Wide Variety of Coagulant Selection

Breaking the Emulsion

Organic Blended Coagulants

- PolyDADMAC, Epi-DMA, Starch-Based.
- Organics blended with inorganic coagulants, including
  - Aluminum sulfate, Aluminum chloride, Aluminum chlorohydrate, Polyaluminum chloride
  - Ferric chloride, Ferrous chloride, Ferric sulfate
  - Calcium chloride

Breaking the Emulsion

Organic Blended Coagulants

Advantages

Does not affect the pH of discharge as much as all inorganic programs.

Wide pH range.

Reduces sludge generation as all inorganic programs.

Lower chemical dosages than all inorganic programs

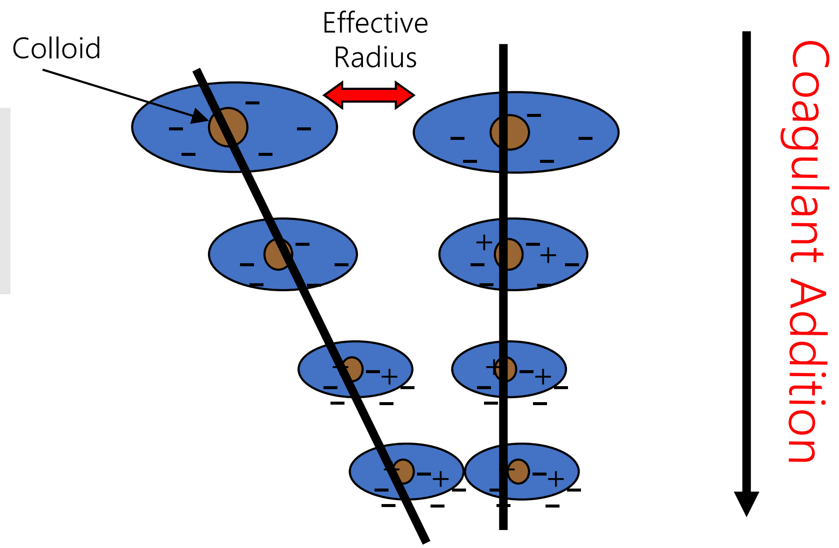
Disadvantages

Higher cost per pound than all inorganic program.

Not a wide variety of coagulant selection.

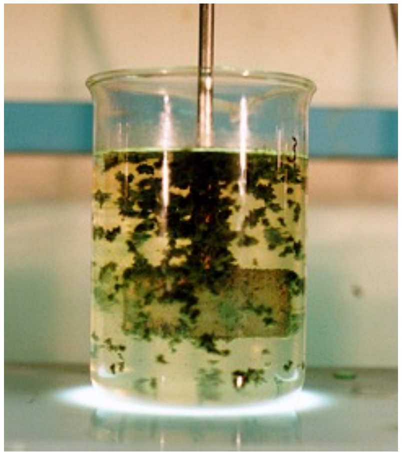
Breaking the Emulsion

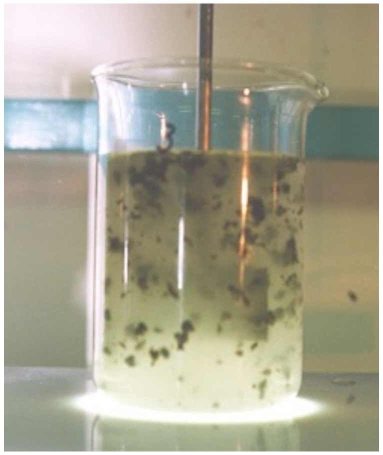
How Much Coagulant?

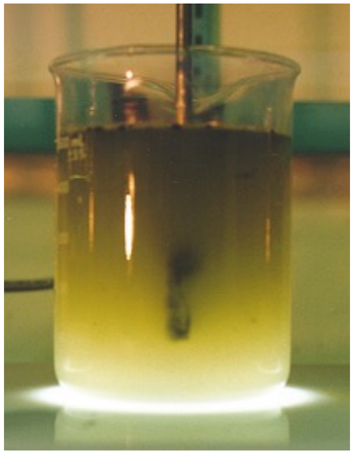


As the coagulant is added the negative electrical charges are neutralized and the effective radius becomes smaller – The colloidal particles come closer together and become larger.

Breaking the Emulsion





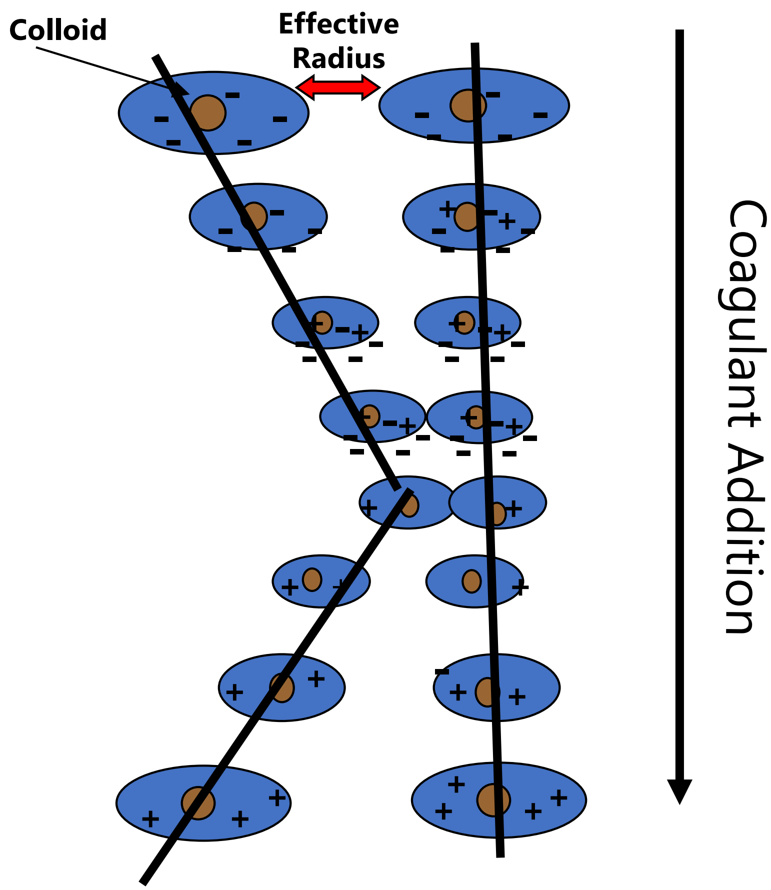


Coagulant Overdose

Breaking the Emulsion

Coagulant Overdose

As additional coagulant is added, more positive charges occur reversing the emulsion charge.



Coagulation

Factors Affecting Coagulation

- pH
- Temperature
- Retention Time
- Mixing Energy
- Dissolved Solids

Flocculation

The agglomeration of the microfloc particles generated during emulsion breaking is accomplished through the use of low to high-charge and molecular weight flocculants.

Flocculation

In the Water Treatment Industry, the terms coagulation and flocculation refer to different mechanisms, although terms are often used interchangeably (and incorrectly).

Flocculation

In flocculation, the polymers act via mechanism of irreversible adsorption of particles along the polymer chain.

The effect of the mechanism depends on the concentrations of polymer and the size of the particle.

Flocculation

Factors Affecting Flocculation

- Size of the particles.
- Nature of the polymer.
- Mixing of the particles with the polymer.
- Solution characteristics.

Flocculation

Factors Affecting Flocculation…

Size of the particles

- Flocculation occurs best on particles smaller than 50 um.
- Particles >100 um do not tend to flocculate because their collision rates are too low.
- It is difficult for polymers to become fixed to large-particle surfaces during collision and rate of breakage of the floc formed is high.

Flocculation

Factors Affecting Flocculation…

Particle Concentration

- Low particle concentrations in solution primarily involves charge neutralization.
- High particle concetraitons in solution involves adsorption and bridging.
- High particle concentration also provides stronger floc structures.

Flocculation

Factors Affecting Flocculation…

<u>Polymer Characteristics</u>

- ✓The <u>longer</u> the polymer chain (greater molecular weight), the greater the possibility of creating bridging and less polymer required for the same result.
- ✓If polymer chain is <u>too short</u>, its efficiency is less.

Flocculants

Characteristics

- Charge Type
- Chemical Backbone
- Molecular Weight
- Charge Density
- Percent Active Solids
- Physical Form

Flocculants

<u>Charge Type</u>

- Anionic – Negative Charge
- Cationic – Positive Charge
- Nonionic – Neutral Charge

Flocculants

Backbone Chemistry

✓Acrylamides

✓Resin-Amines

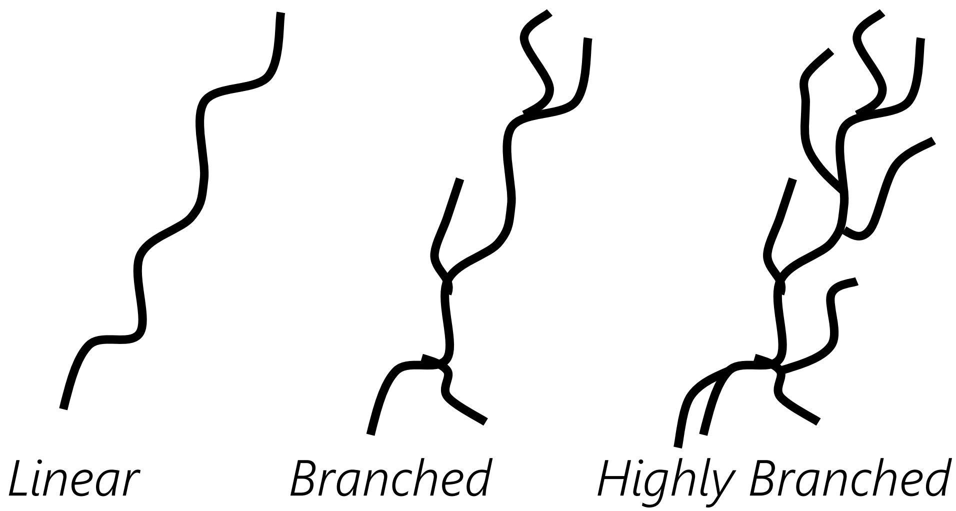
Backbone Structure

✓Linear

✓Branched

Flocculants

Polymer Molecular Structure



Flocculants

Physical Forms

There are four main forms

- Dry polymers
- Emulsion polymers
- Liquid formulas
- Mannich polymers

Each form has its own:

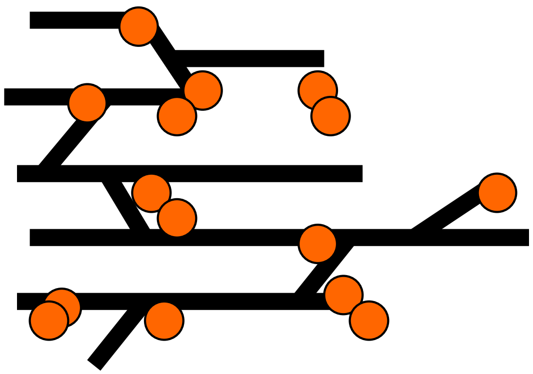
- Characteristics
- Storage and Handling requirements
- Solution preparation requirements

Flocculants

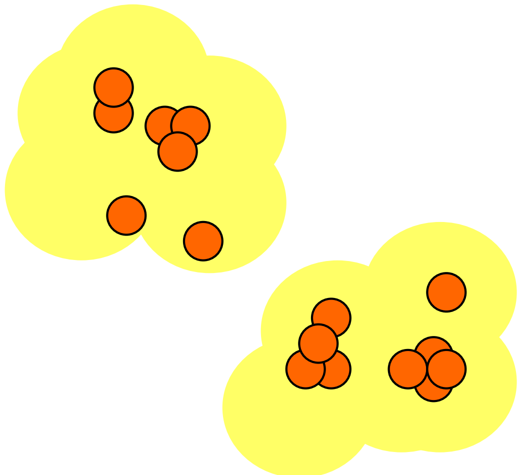
<u>Flocculation</u>

- Multiple Particles
- Physical in Nature – “Bridging” and/or Sweeping
- Strong Flocs Formed
- Shear Degrades Floc – Not Reversible

Flocculation

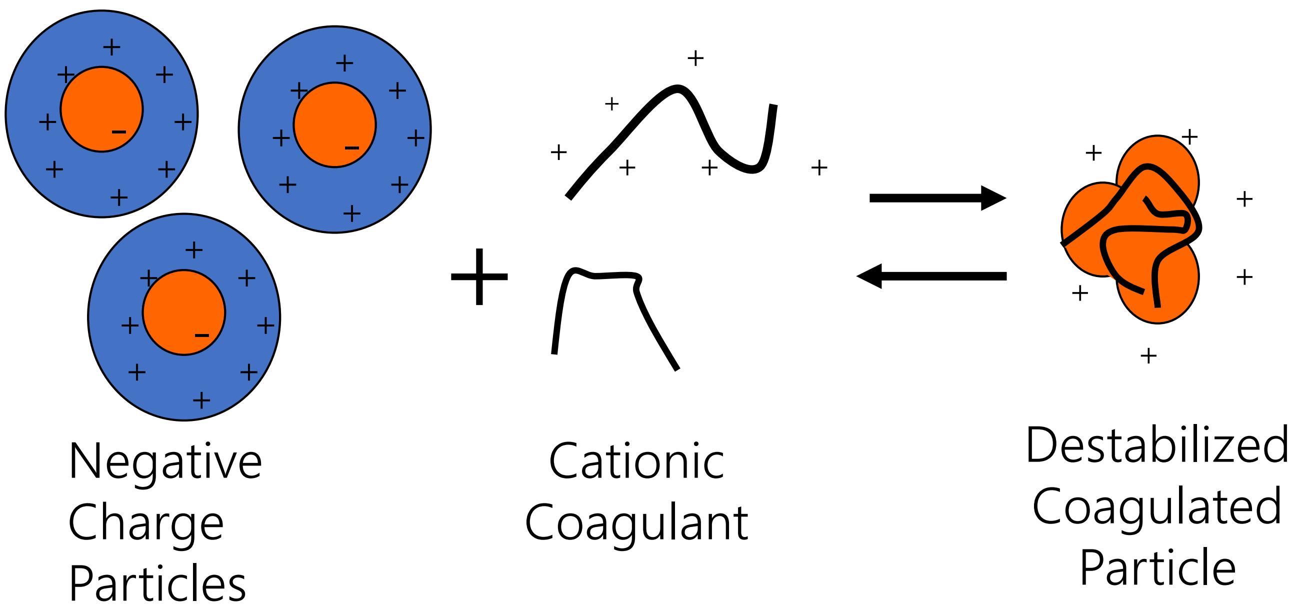


Bridging

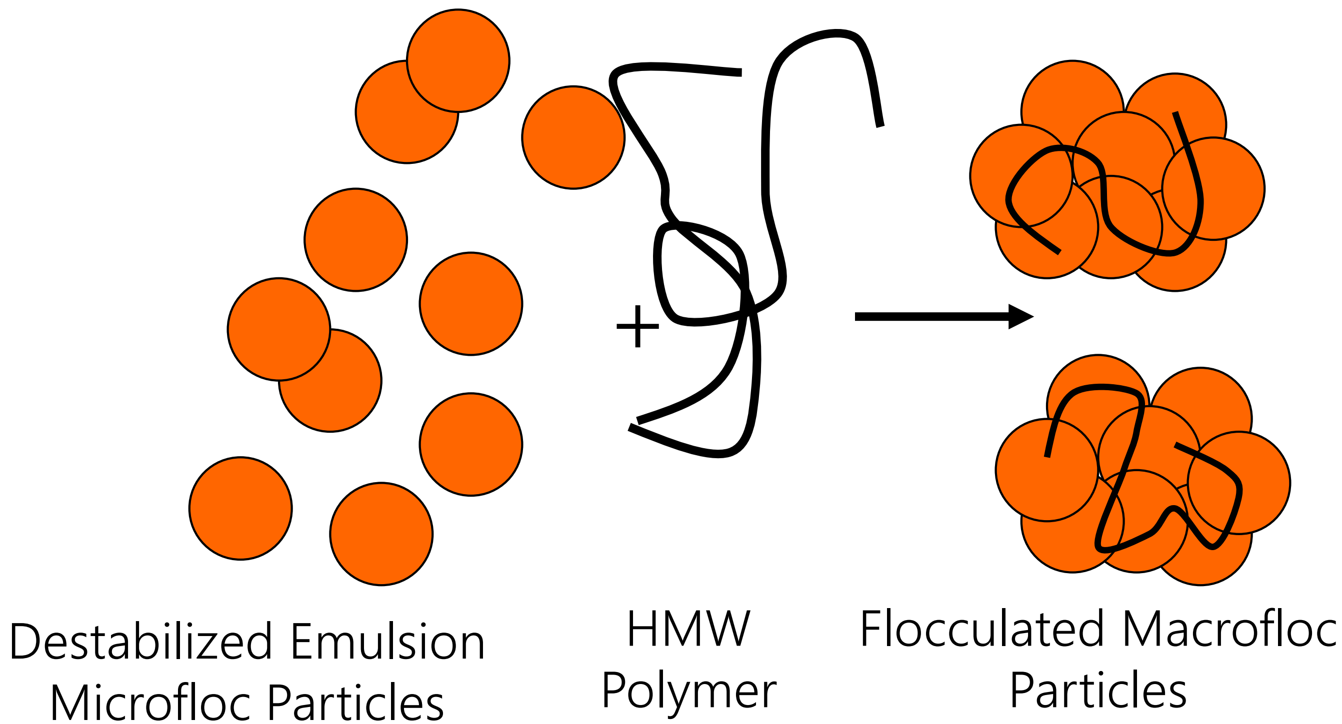


Sweep Floc

Breaking the Emulsion / Colloidal Suspension

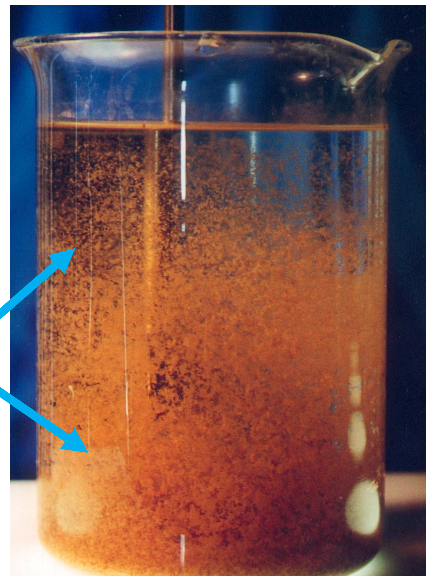


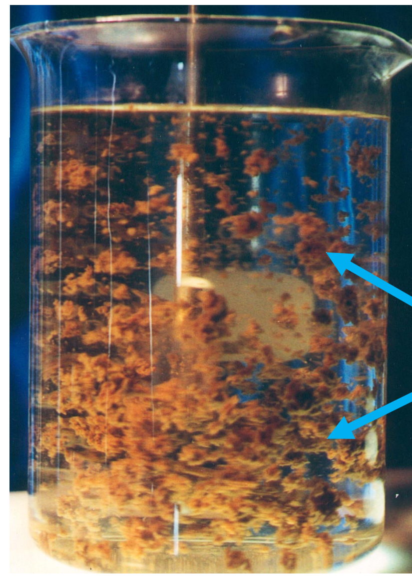
Flocculation



Flocculation

Small microfloc particles





Agglomeration into macrofloc particles

Before Flocculant Addition

After Flocculant Addition