

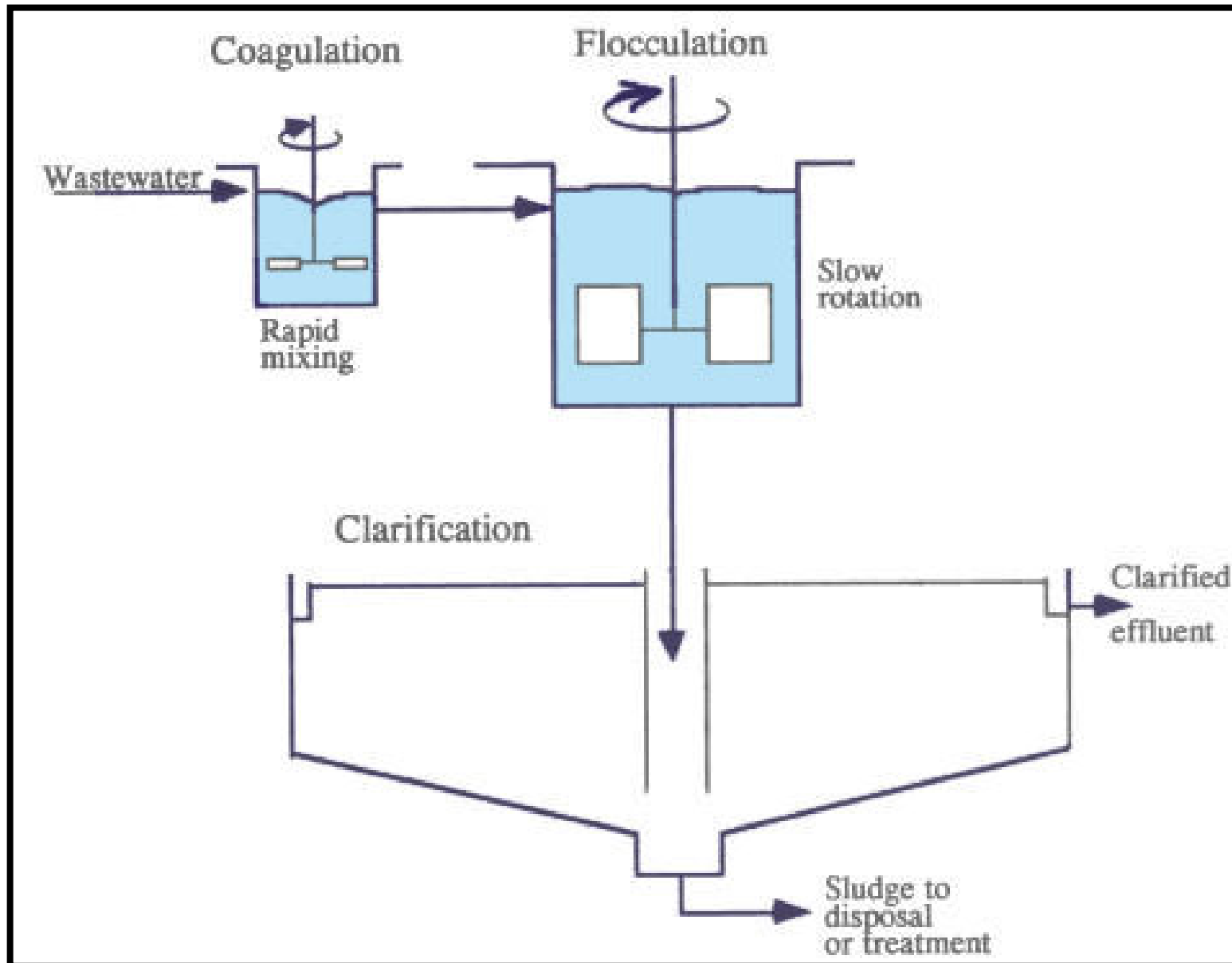
Coagulation and Flocculation at Water Treatment Plants

- Understand conventional treatment to remove turbidity
- Understand turbidity and its primary constituents
- Explain coagulation chemistry
- Understand mechanism of function involved in coagulant aggregation
- Explain flocculation chemistry
- Understand mechanism of function involved in flocculent aggregation
- Understand the role of pH, alkalinity, turbidity, temperature on coagulation and flocculation application

- ❖ Coagulation: adding and rapid mixing of chemicals to remove particles from water. (flash mixing)
- ❖ Flocculation: adding and slow mixing of chemicals and particles to create flocs that settle out of water.
- ❖ Turbidity: suspended, dissolved and colloidal particles in pretreated water that need to be removed to optimize treatment efficiency.
- ❖ Suspended Solids: particles held in suspension by the natural action of flowing waters.
- ❖ Colloidal Solids: fine silt that does not settle out of water but remain in suspension.
- ❖ Dissolved Solids: organic or inorganic molecules that are dissolved into the aqueous phase.

“Ironically, it is easier to clean up dirty water than to make clean water cleaner. The reason is because particles must collide before they can stick together to make larger flocs. More particles means more collisions.”

Water Treatment



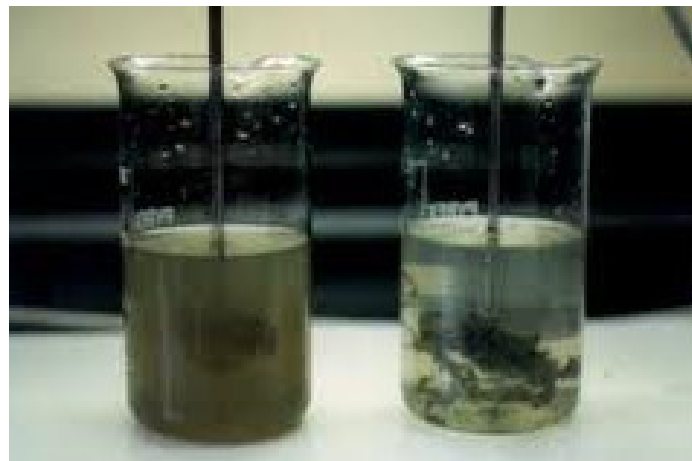
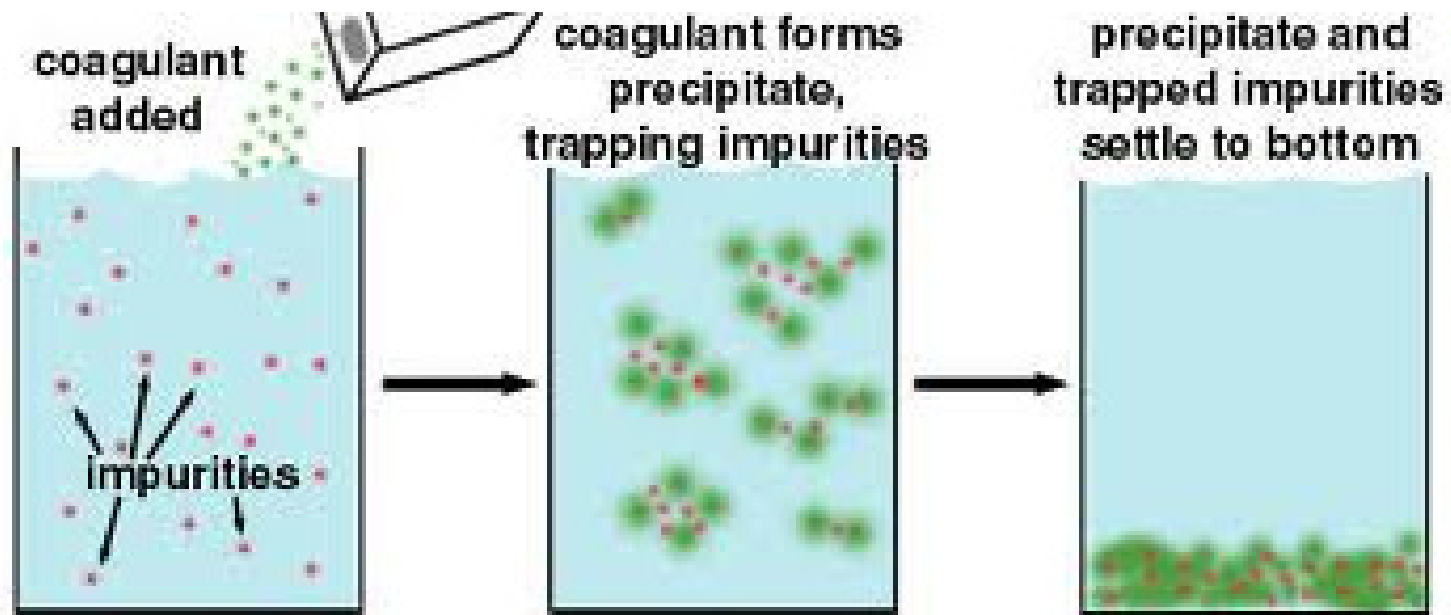
COAGULATION

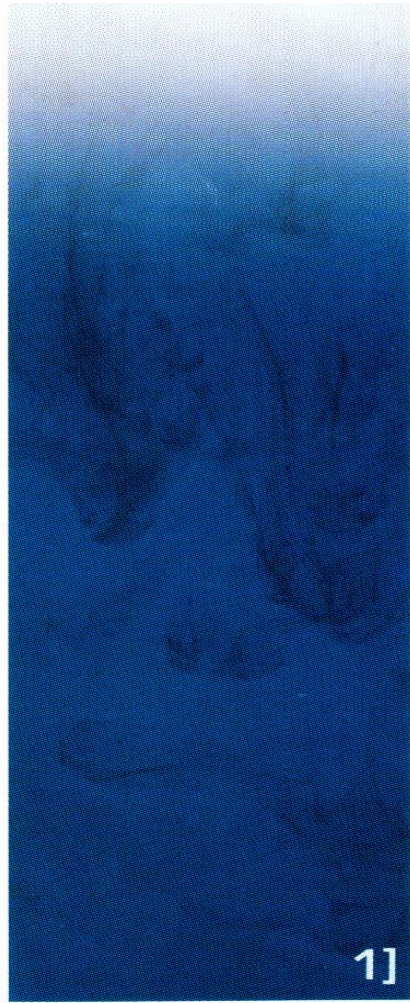
- Definition

Destabilisation of colloid particles by the addition of chemicals (coagulant)

- Applications

Industrial waste containing colloidal and suspended solids (e.g. pulp and paper, textile)





Raw waste



Floc Formation



Settle floc

Flocculation

- is a process of forming aggregate of flocs to form larger settleable particle. The process can be described as follows:
 - Mutual collision of small floc resulting in bigger size.
 - Usually slow speed or gentle mixing is used so as not to break the large flocs due to shear.
 - Polymer or large molecular wt compound is added to enhance floc build up. Most of them are proprietary chemicals.

Conventional Treatment

- Conventional Treatment – common treatment steps used to remove turbidity from the initial source water.

1. Coagulation

Rapid Mixing

2. Flocculation

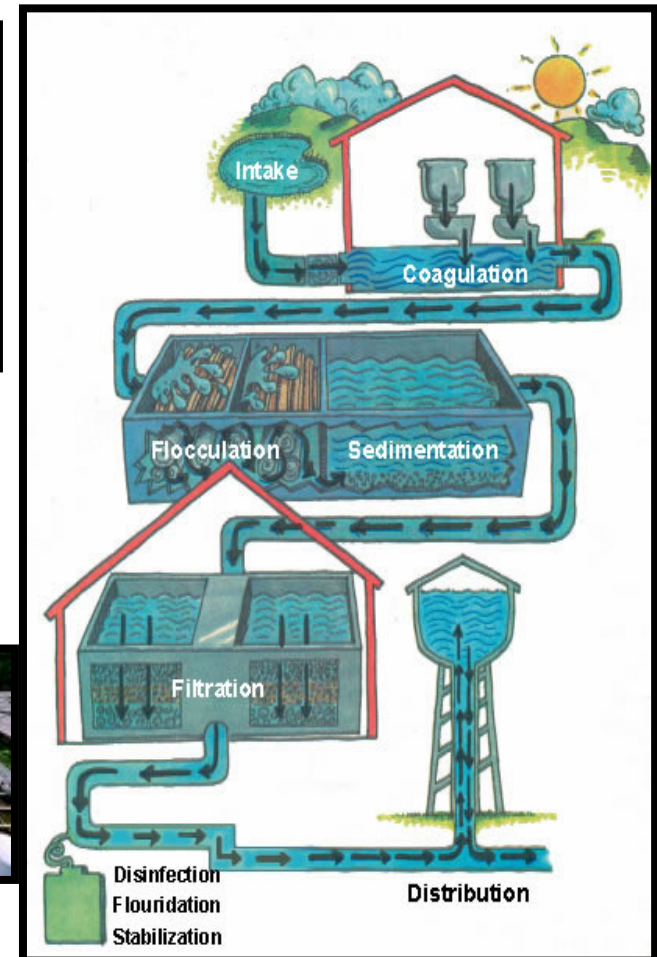
Slow Mixing

3. Sedimentation

4. Filtration

Settling

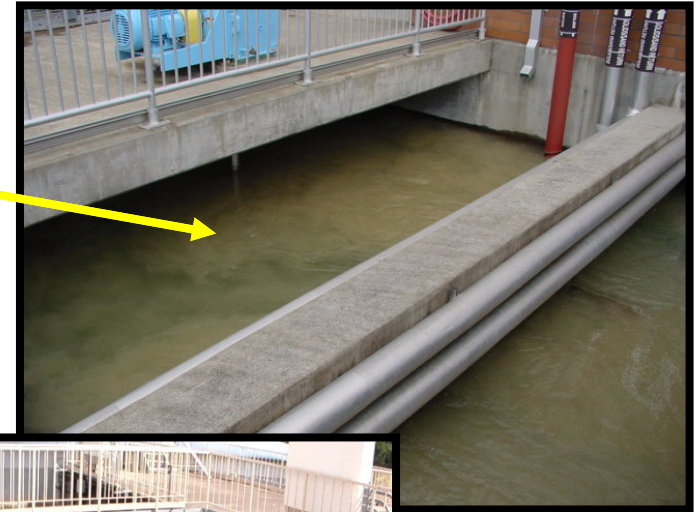
Cleaning



Turbidity

- Turbidity – particles (sand, silt, clay, bacteria, viruses) in the initial source water that need to be removed to improve treatment.

1. Suspended Solids



2. Colloidal Solids (~ 0.1 to $1\ \mu\text{m}$)

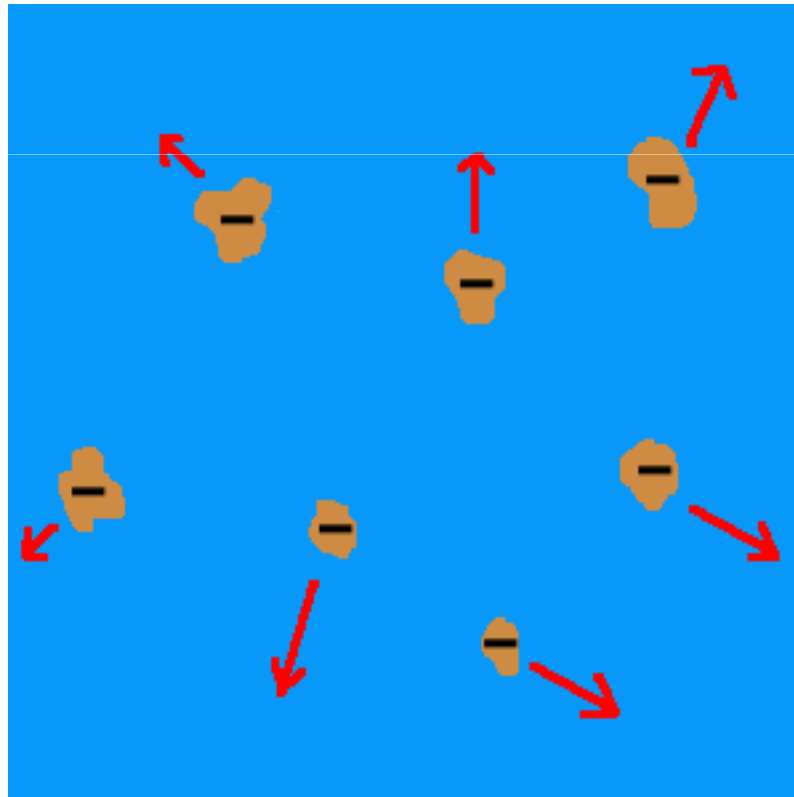


3. Dissolved Solids ($< 0.02\ \mu\text{m}$)



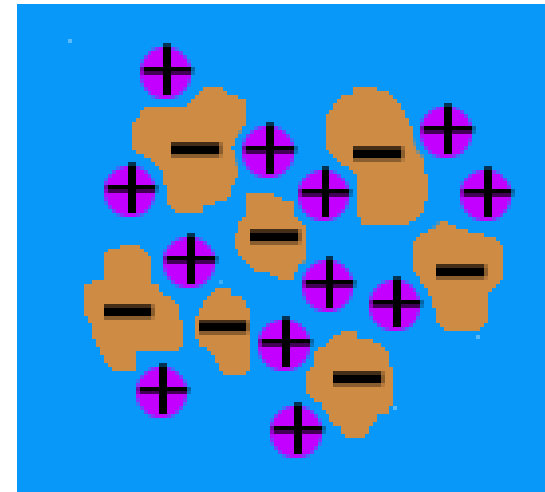
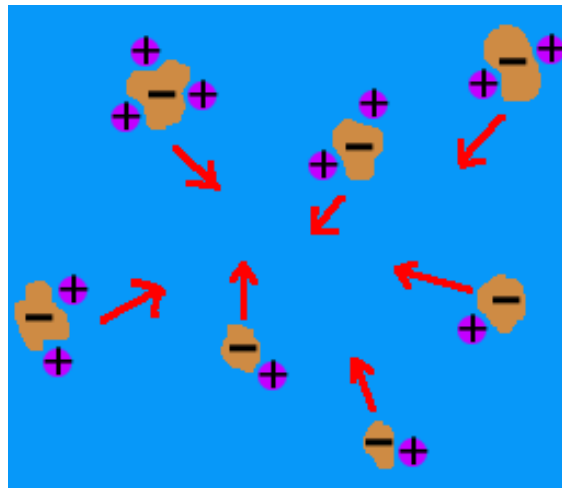
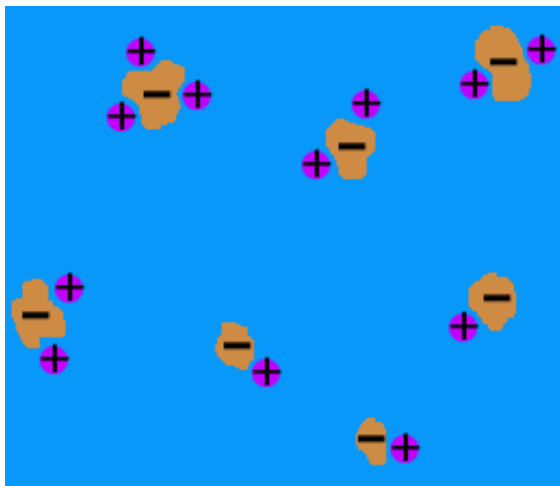
Turbidity

- Turbidity/Colloids– negative charged particles particles (sand, silt, clay, organic matter) in the initial source water that need to be removed to improve treatment.



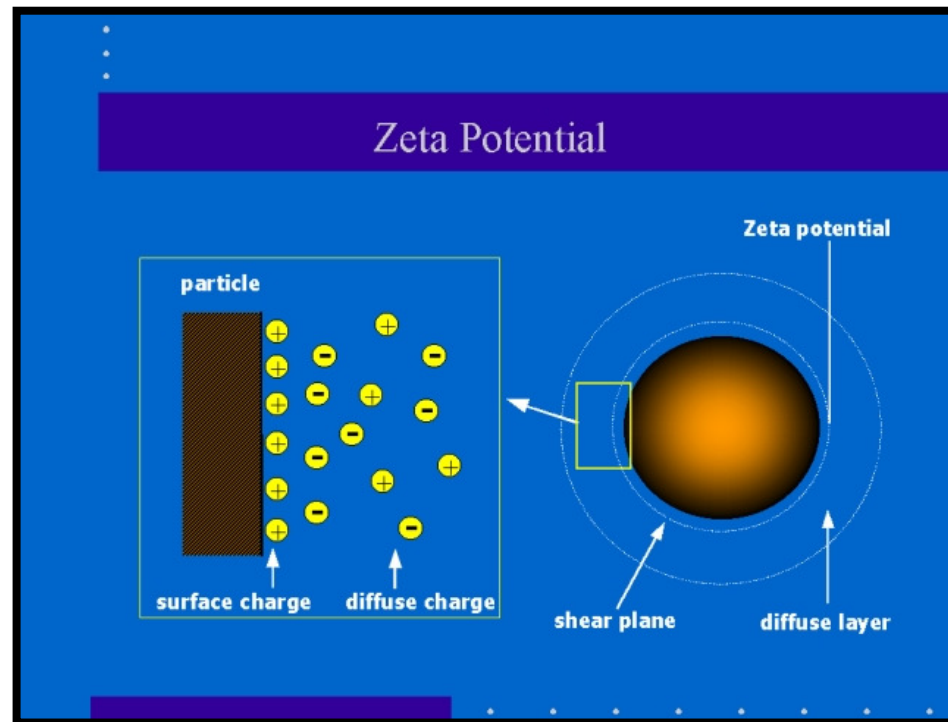
Coagulation

- Coagulants tend to be positively charged.
- Due to their positive charge, they are attracted to the negative particles in the water
- The combination of positive and negative charge results in a neutral or lack of charge
- Van der Waal's forces refer to the tendency of particles in nature to attract each other weakly if they have no charge.



Settling Forces

Zeta Potential refers to the electrostatic potential generated by the accumulation of ions at the surface of the colloidal particle. It can help you understand and control colloidal suspensions



van der Waals Force- van der Waals forces are weak attractive forces that hold non-polar molecules together. They tend to pull molecules together and form flocs.

Settling Forces

Zeta Potential -is the electrical potential that exists at the "shear plane" of a particle, which is some small distance from its surface. Keeps particles apart and in suspension

| | |
|--------------------------------------|--|
| Zeta Potential [mV] | Stability behavior of the colloid |
| from 0 to ± 5, | Rapid coagulation or flocculation |

Water Treatment Coagulants

Particles in water are negative; coagulants usually positively charged.

1. Alum- aluminum sulfate



2. Ferric chloride or ferrous sulfate



3. Polymers

Water Treatment Coagulant Alum

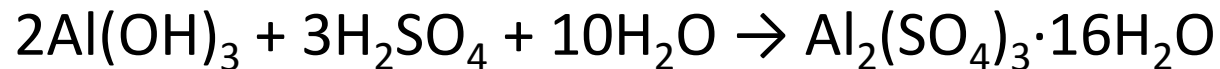
Alum- (aluminum sulfate)- particles suspended in natural, untreated water normally carry a negative electrical charge. These particles are attracted to the positive charges created by aluminum hydroxides. Dosage is generally around 25 mg/L.

1. Trivalent Al^{+3} charge attracts neg – particles
2. Forms flocs of aluminum hydroxide ($\text{Al}(\text{OH})_3$).
3. Impacted by mixing, alkalinity, turbidity and temp.
4. Ideal pH range 5.8-8.5



Alum CHEMISTRY

Alum- (aluminum sulfate)- made by dissolving aluminum hydroxide (bauxite or clay) in sulfuric acid



When ALUM is dissolved in alkaline water, it undergoes hydrolysis (reacts with water) to produce a high surface area gelatinous precipitate of aluminum hydroxide, $\text{Al}(\text{OH})_3$ (gibbsite)($\text{Al}(\text{OH})_3$ sticks the negatives

When ALUM is reacted with water it hydrolyzes to form aluminum hydroxide and dilute sulfuric acid (lowers pH).

Need alkalinity adjustment

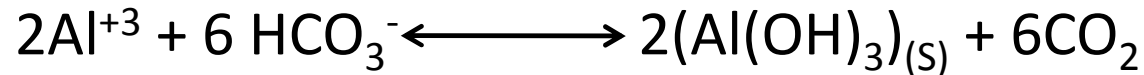
Alum CHEMISTRY

Alum- (aluminum sulfate)-

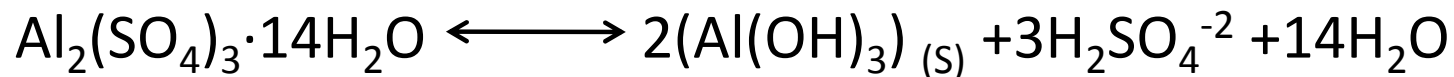


2Al^{+3} + negatively charged colloids \longleftrightarrow neutral surface charge

WHY IS ALKALINITY SO IMPORTANT??



No bicarbonate (low alkalinity, low pH sulfuric acid!):



Optimum pH: 5.5 to 6.5

Operating pH: 5 to 8

Water Treatment Coagulant Iron Salt

Iron salt- (Iron chloride or sulfate)- particles suspended in natural, untreated water normally carry a negative electrical charge. These particles are attracted to the positive charges created by Fe(III) salts.

1. Trivalent Fe^{+3} charge attracts neg – particles
2. Work over a larger pH range than alum
3. Lower costs than alum
4. Better removal of natural organics
5. Corrosive
6. Special handling necessary
7. Leave a residue of Fe in water (taste, stains)



Water Treatment Coagulant Aids

Activated silica (sodium silicate)- helps improve coagulation, decreases volume of coagulant necessary. Typically is sodium silicate.



1. secondary coagulant
2. reduces primary coagulants needed
3. Sodium silicate are alkaline
4. widens pH range for coagulation
5. used at 7-11% of alum
6. Heavier denser floc that settles faster
7. Can be formed on site
8. Corrosion inhibitor (forms a surface coating)

Water Treatment Coagulant Aids

Bentonite (clay)- helps improve coagulation, decreases volume of coagulant necessary.

1. high in color, low turbidity, low mineral content water
2. 10-50 mg/L dosage
3. Heavier denser floc that settles faster



Water Treatment Coagulant Aids

Polyelectrolytes- are water-soluble organic polymers that are used as both primary coagulants and coagulant aids. Act as "bridges" between the already formed particles :

- Anionic—ionize in solution to form negative sites along the polymer molecule.
- Cationic—ionize to form positive sites.
- Non-ionic—very slight ionization.
- effectiveness: particles type, turbidity present, and the turbulence (mixing) available during coagulation.

Water Treatment Coagulant/pH

Alkalinity- Alkalinity is a measure of the buffering capacity of water. These buffering materials are primarily the bases bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}) and occasionally hydroxide (OH^-), borates, silicates, phosphates, ammonium, sulfides, and organic ligands.

Chemicals applied to raise alkalinity

- Lime— CaOH_2 accompanies alum or iron salt
- Sodium bicarbonate- NaHCO_3 - raise alkalinity
- Soda Ash— Na_2CO_3 -raise alkalinity
- Caustic Soda— NaOH -raise alkalinity

Water Treatment WHO Coagulants

| Name | Advantages | Disadvantages |
|--|---|--|
| Aluminum Sulfate (Alum) $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ | Easy to handle and apply; most commonly used; produces less sludge than lime; most effective between pH 6.5 and 7.5 | Adds dissolved solids (salts) to wa-ter; effective over a limited pH range. |
| Sodium Aluminate $\text{Na}_2\text{Al}_2\text{O}_4$ | Effective in hard waters; small dos-ages usually needed | Often used with alum; high cost; ineffective in soft waters |
| Polyaluminum Chloride (PAC) $\text{Al}_{13}(\text{OH})_{20}(\text{SO}_4)_2 \cdot \text{Cl}_{15}$ | In some applications, floc formed is more dense and faster settling than alum | Not commonly used; little full scale data compared to other aluminum derivatives |
| Ferric Sulfate $\text{Fe}_2(\text{SO}_4)_3$ | Effective between pH 4–6 and 8.8–9.2 | Adds dissolved solids (salts) to wa-ter; usually need to add alkalinity |
| Ferric Chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ | Effective between pH 4 and 11 | Adds dissolved solids (salts) to wa-ter; consumes twice as much alka-linity as alum |
| Ferrous Sulfate (Copperas) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | Not as pH sensitive as lime | Adds dissolved solids (salts) to wa-ter; usually need to add alkalinity |
| Lime $\text{Ca}(\text{OH})_2$ | Commonly used; very effective; may not add salts to effluent | Very pH dependent; produces large quantities of sludge; overdose can result in poor effluent quality |

Flocculation

- is a process of forming aggregate of flocs to form larger settleable particle. The process can be described as follows:
 - Mutual collision of small floc resulting in bigger size.
 - Usually slow speed or gentle mixing is used so as not to break the large flocs due to shear.
 - Polymer or large molecular wt compound is added to enhance floc build up. Most of them are proprietary chemicals.

Flocculation mechanism

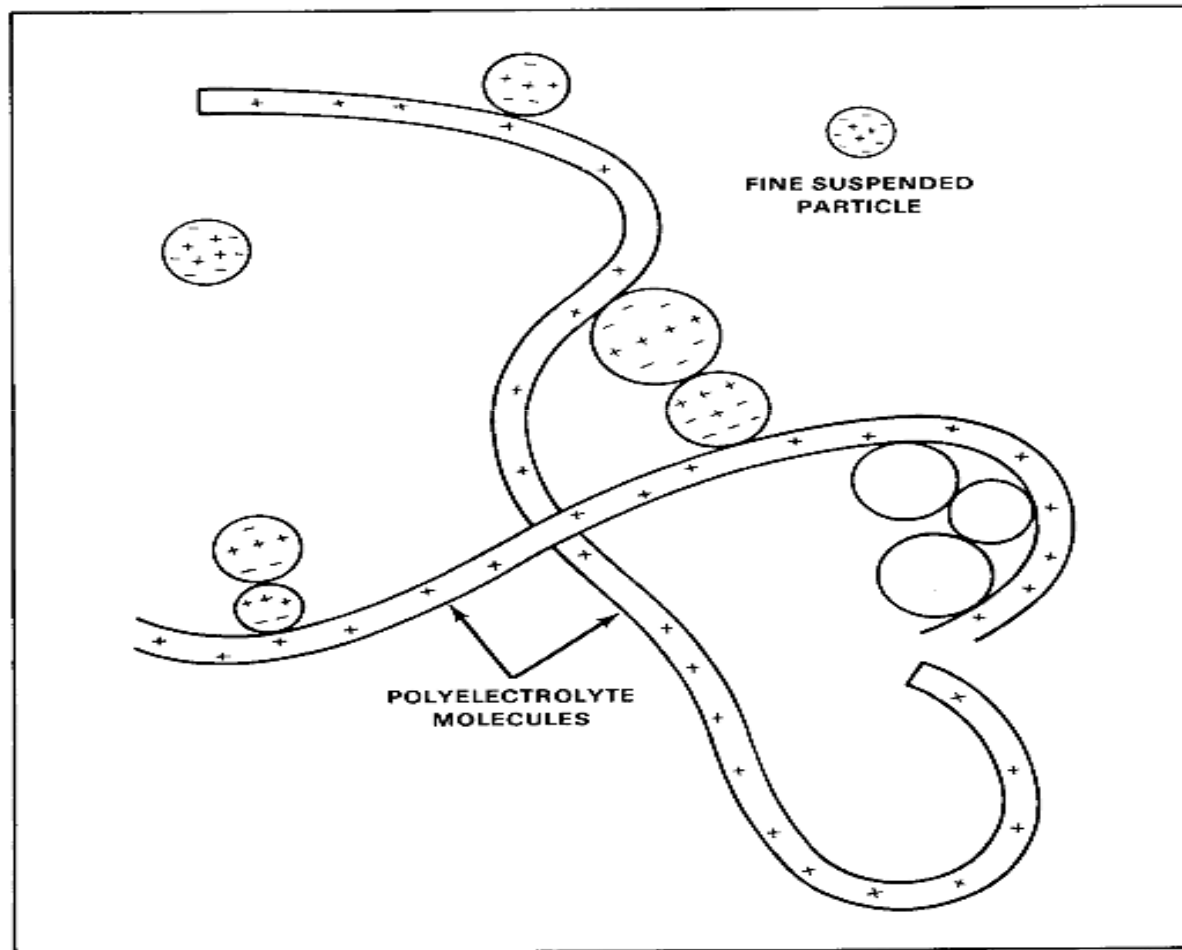


Figure 1-1. Forming a floc particle

Flocculation mechanism

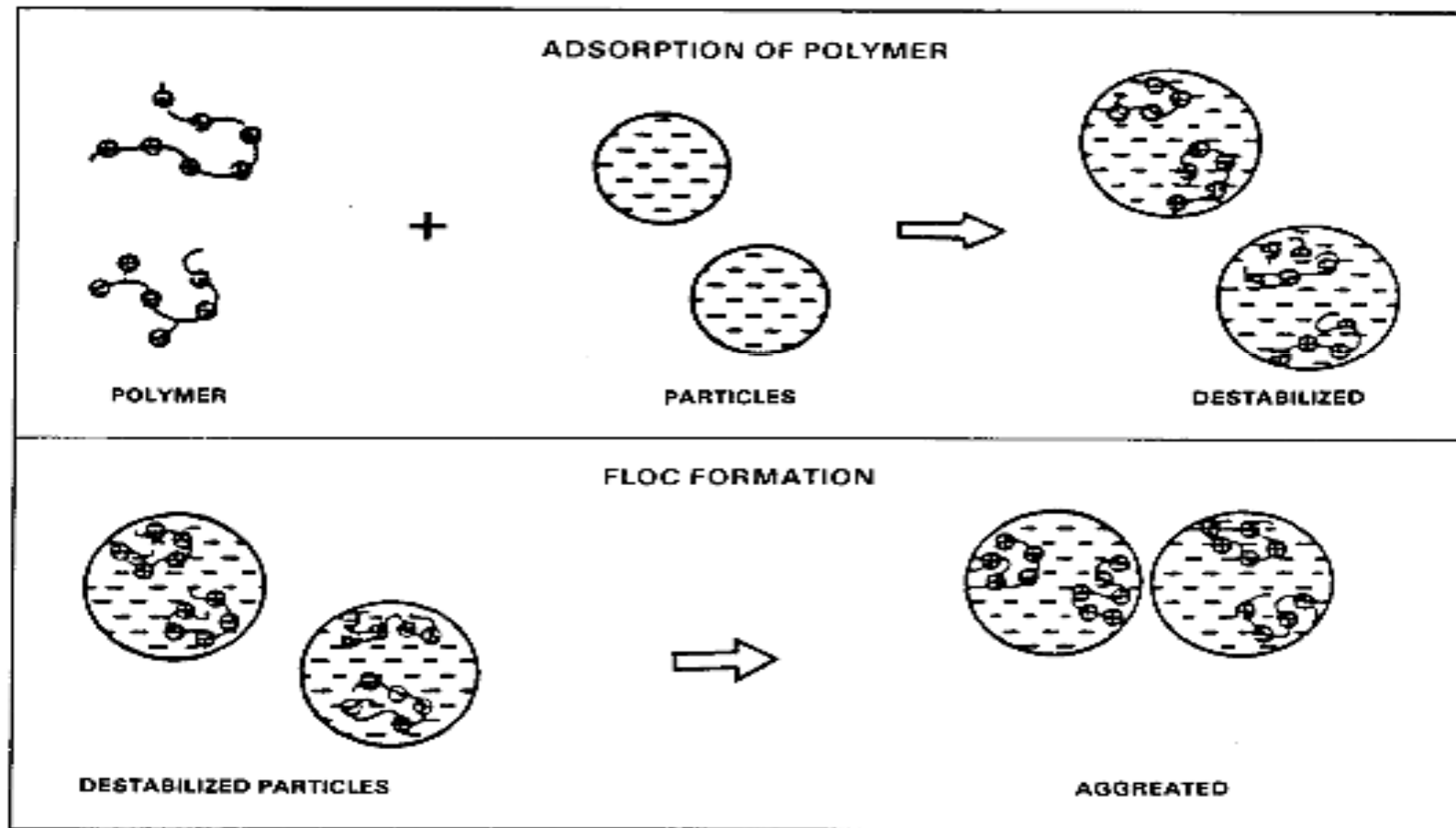


Figure 1-2. Floc formation process

Flocculation mechanism

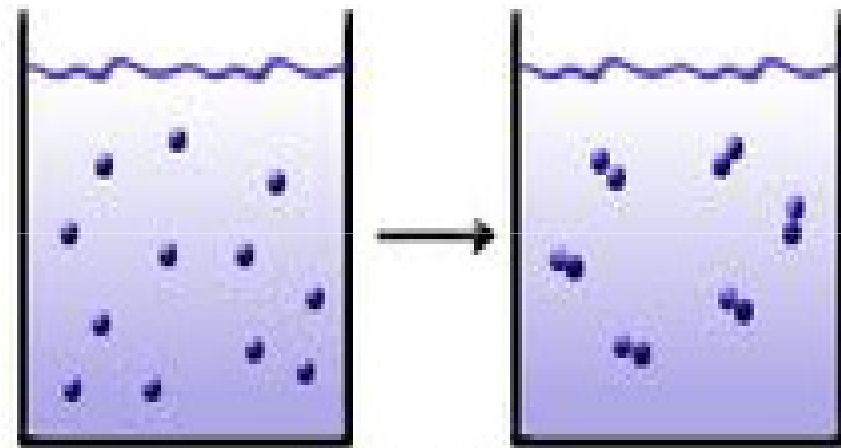
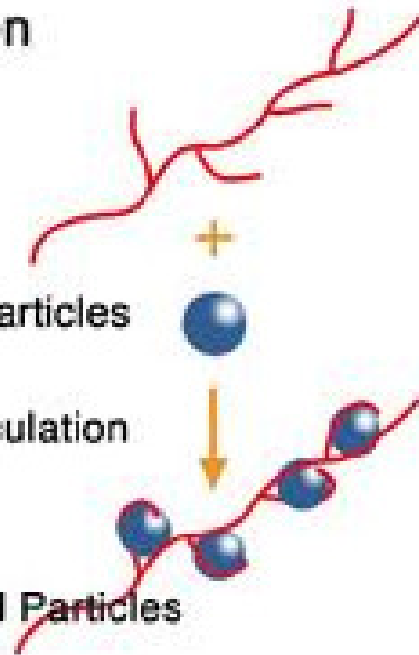
Flocculation

Polymer

Suspended Particles

Flocculation

Agglomerated Particles



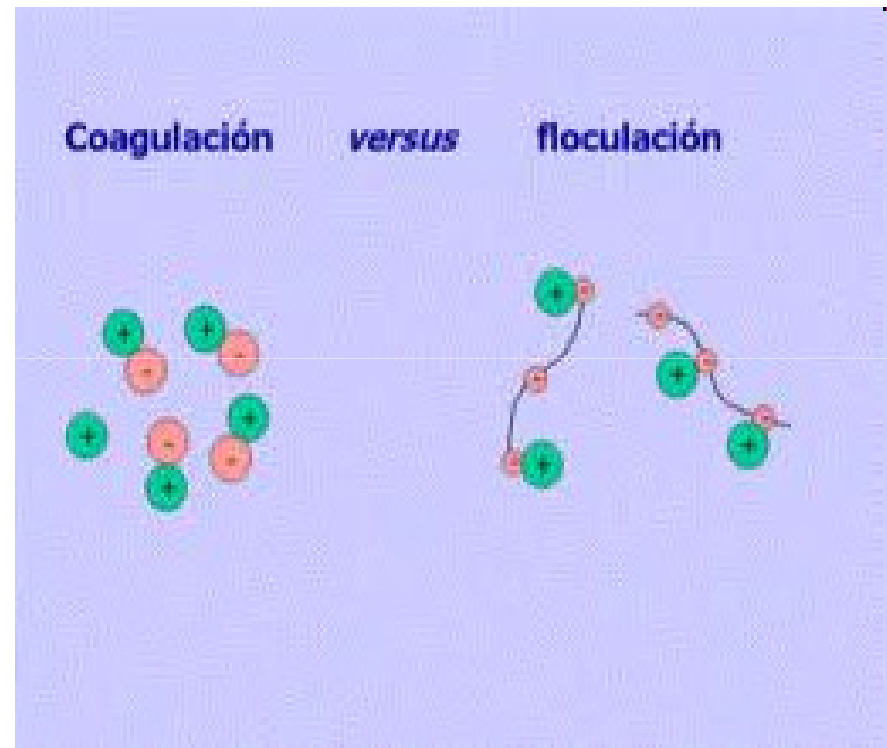
Flocculation

Flocculation

- The benefits of flocculation are:
 - To improve settling of particles in sedimentation tank
 - To increase removal of suspended solids and BOD
 - To improve performance of settling tanks

Differences

- Coagulation: is a chemical technique which is directed towards the destabilisation of the charged colloidal particles.
- Flocculation: is the slow mixing technique which promotes the agglomeration of the stabilised particles.

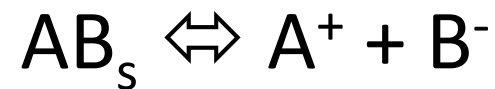


CHEMICAL PRECIPITATION

(Theoretical Background)

- Solubility equilibria

A chemical reaction is said to have reached equilibrium when the rate of forward reaction is equal to the rate of the reverse reaction

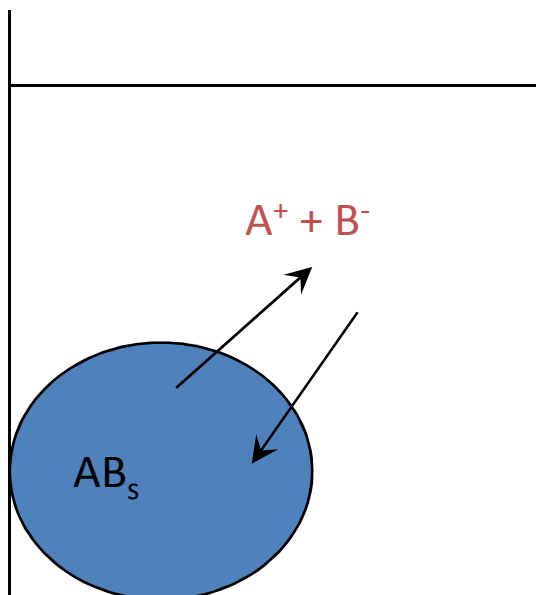


where AB_s : solid; A^+ , B^- - ionic species

CHEMICAL PRECIPITATION

(Theoretical Background)

$$K_{eq} = \frac{(A^+)(B^-)}{(AB_s)}$$



Due to dilute concentration,

$$K_{sp} = [A^+] [B^-]$$

= solubility product constant

where [] refer to molar concentration

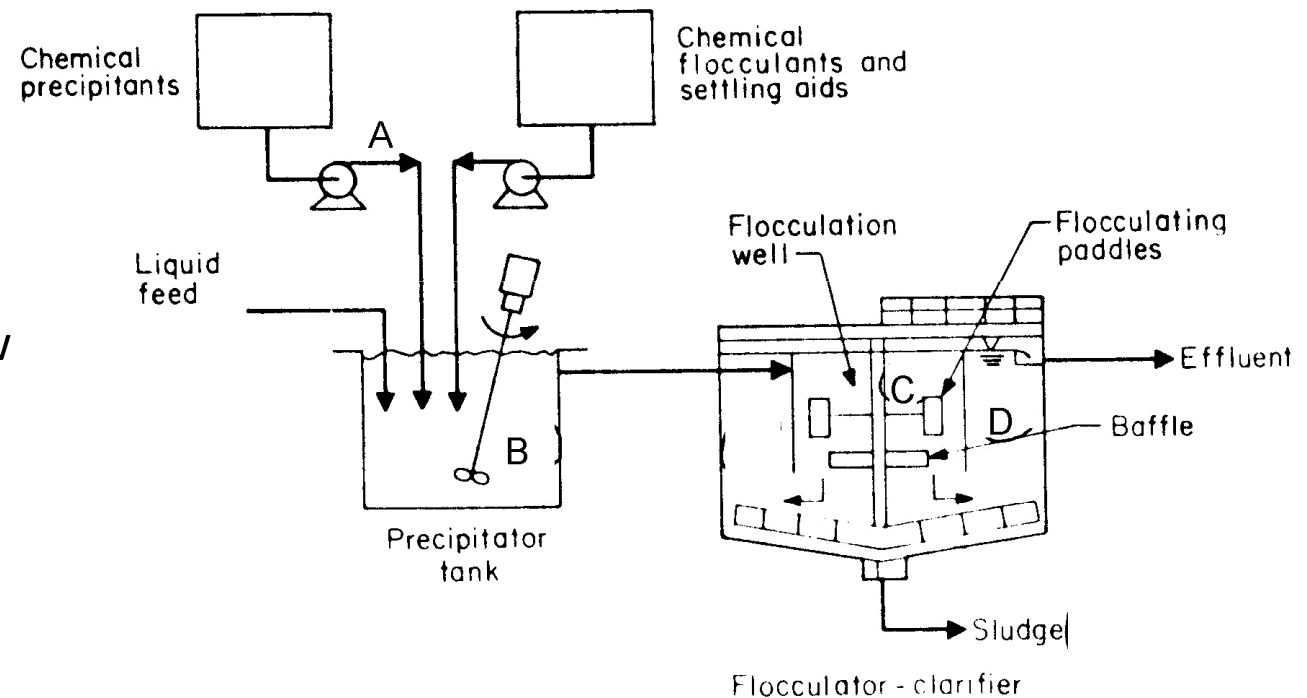
Eg.

| Compound | Solubility (mg/L) | K_{sp} |
|----------|-------------------|--------------------|
| $CaCO_3$ | 18 | 5×10^{-9} |
| $CaCl$ | 745000 | 159×10^6 |

CHEMICAL PRECIPITATION

(Basic Principles)

- A. Add chemical precipitants to waste stream
- B. Mix thoroughly
- C. Allow solid precipitates to form floc by slow mixing
- D. Allow floc to settle in clarifier



CHEMICAL PRECIPITATION

(Types of Precipitation)

Heavy metals removal

- Hydroxide precipitation (OH^-)
- Sulphide precipitation (S^{2-})
- Carbonate precipitation (CO_3^{2-})

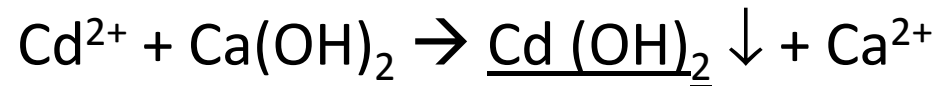
Phosphorus removal

- Phosphate precipitation (PO_4^{2-})

CHEMICAL PRECIPITATION

(Hydroxide Precipitation)

- Add lime (CaO) or sodium hydroxide (NaOH) to waste stream to precipitate heavy metals in the form of metal hydroxides.

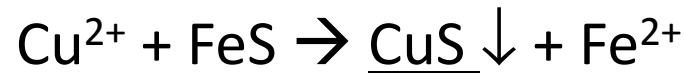


- CaO in the form of slurry (Ca(OH)₂) while NaOH in the form of solution.
- NaOH is easier to handle but is very corrosive.
- Will form floc and settle in clarifier

CHEMICAL PRECIPITATION

(Sulphide Precipitation)

- Use of sulphide in the form of FeS, Na₂S or NaHS
- Better metal removal as sulphide salt has low solubility limit



- Limitation: can produce H₂S (g) at low pH



- At low pH, reaction will proceed to the right. Thus, require pH > 8 for safe sulphide precipitation.

CHEMICAL PRECIPITATION

TABLE 4.10
Summary of trivalent chromium treatment results

| Method | pH | Chromium, mg/l | |
|---------------------------------------|----------|----------------|-----------|
| | | Initial | Final |
| Precipitation | 7–8 | 140 | 1.0 |
| | 7.8–8.2 | 16.0 | 0.06–0.15 |
| | 8.5 | 47–52 | 0.3–1.5 |
| | 8.8 | 650 | 18 |
| | 8.5–10.5 | 26.0 | 0.44–0.86 |
| | 8.8–10.1 | — | 0.6–30 |
| | 12.2 | 650 | 0.3 |
| Precipitation with sand filtration | 8.5 | 7400 | 1.3–4.6 |
| | 8.5 | 7400 | 0.3–1.3 |
| | 9.8–10.0 | 49.4 | 0.17 |
| | 9.8–10.0 | 49.4 | 0.05 |

Sources of Heavy Metals

- Heavy metals → present abundance in nature.
- Enter water cycle through geochemical processes.
- Metals added by human activities:
 - Manufacturing
 - Construction
 - Agriculture
 - Transportation

Effects of Heavy Metals

- Potential adverse effects of soluble metal compounds on human health and on the health of organisms, treatment inhibition, aesthetics of the environment.
- Certain metals in low concentrations are not only harmless , but traces are essential for good nutrition.

Co, Cu, Fe, Se, Zn.

- Some metal salts on the other hand may be toxic.

Evaluation of toxicity:

- Acute
- Chronic
- Synergistic
- Mutagenic / teratogenic

Acute toxic effects show up quickly upon ingestion of, or contact with a metal compound.

Examples for Metal Toxicity

- Soluble copper → gastroenteritis symptoms with nausea
- Chromium → lung tumors, skin sensitizations, inflammation of the kidneys
- Selenium → Poison in high concentrations, carcinogen, cause tooth decay.

Examples for Metal Toxicity

- **Chronic poisoning** → e.g. cadmium and lead accumulate in body tissue
- Certain metals are more toxic in combination with other metals or under specific environmental conditions
- e.g. Cadmium toxicity increases in the presence of Cu / Zn. pH, T, hardness, SS, CO₂ effect the toxicity.
- Lead is more toxic if dissolved oxygen concentration is low.

- **Mutagenic / teratogenic toxicity** → when certain metals combine with organic compounds, these substances may produce changes in genetic makeup or cause abnormal tissue development in embryos (teratogenicity)

Effects of Heavy Metal Content

- Heavy metal content may affect taste, staining and corrosion characteristics
- Taste
 - Cu > 1 mg/L
 - Fe > 9 mg/L
 - Zn > 5 mg/L
- Fe, Mn stain fixtures, discolor laundry, obstruct pipes with bacteria
- Interference with industrial processes.
e.g. Cu may cause adverse color reactions in food industry.

Effects of Heavy Metal Content

- If found in irrigation water → may damage crops.
- Continuous exposure of biological systems (in treatment plants) to such metals → biological system can become acclimated (what would normally be inhibitory or even toxic).
- Heavy metals accumulate in the solids produced.
- Land application !

Recycling / recovery of heavy metals

- Recycling rinse water in metal plating industry may reduce wastewater generation. Closed loop recovery system may be appropriate for wastes that are different or expensive to treat.
- **Recovery systems:** Evaporation, reverse osmosis, electrodialysis, electrolytic recovery, ion exchange

Cost analysis for metal recovery

- Capital & operating cost

vs

Total benefits from

- reductions in raw material losses
- wastewater treatment capacity
- chemicals
- sludge disposal fees

Hydroxide ppt / coagulation

- Conventional method of removing heavy metals. Chemical ppt of the metal as hydroxides followed by coagulation of the metal particles into larger, heavier floc particles which then separate from the water.
- Metal concentrations can be reduced to 0.3 – 1.5 mg/L

Hydroxide ppt / coagulation

- Typically heavy metals are dissolved under acidic conditions and precipitate under alkaline conditions.
- pH increase by NaOH (caustic), Ca(OH)_2 lime addition
- $\text{Cu}^{2+} + 2\text{NaOH} \rightarrow \text{Cu(OH)}_2 + 2 \text{Na}^+$
- $\text{Cu}^{2+} + \text{Ca(OH)}_2 \rightarrow \text{Cu(OH)}_2 + \text{Ca}^{2+}$

Hydroxide ppt / coagulation

- Often the hydroxide precipitates tend to floc together naturally. Sometimes coagulant / flocculent aids may be added to enhance flocculation, improve sedimentation, ultimately reduce heavy metal concentrations.
- Polyelectrolytes may be used
- Treatability tests → to determine optimum pH and chemical dosages

Sedimentation of Metal Floccs

Overflow rate for metal hydroxides:

More often values range between
10 – 33 m³/m²d

Typically should not exceed 40 m³/m²d

For very thick floc 60 m³/m²d

Most hydroxide sludge after settling →

96 – 99 % water

May be dewatered to 65 – 85 % water

Dewatering of Metal Sludge

- Sand drying beds (climate dependent)
- vacuum filters
- filter presses
- Centrifuges

Other Treatment Alternatives for Metal Removal: Adsorption

- Adsorption on
 - activated carbon
 - aluminum oxides
 - silica clays
 - synthetic materials like zeolites and resins.