

ENVE 301

Environmental Engineering Unit Operations

Lecture 8

Coagulation, Flocculation

SPRING 2014

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Coagulation / Flocculation

- Portion of dispersed solids are nonsettleable.
- Dispersed solids in general have a particle size ranging from 0.1 millimicron (10^{-7} mm) to 100 microns (10^{-1} mm).
- Colloidal particles → 1 millimicron (10^{-6} mm) to one micron (10^{-3} mm)

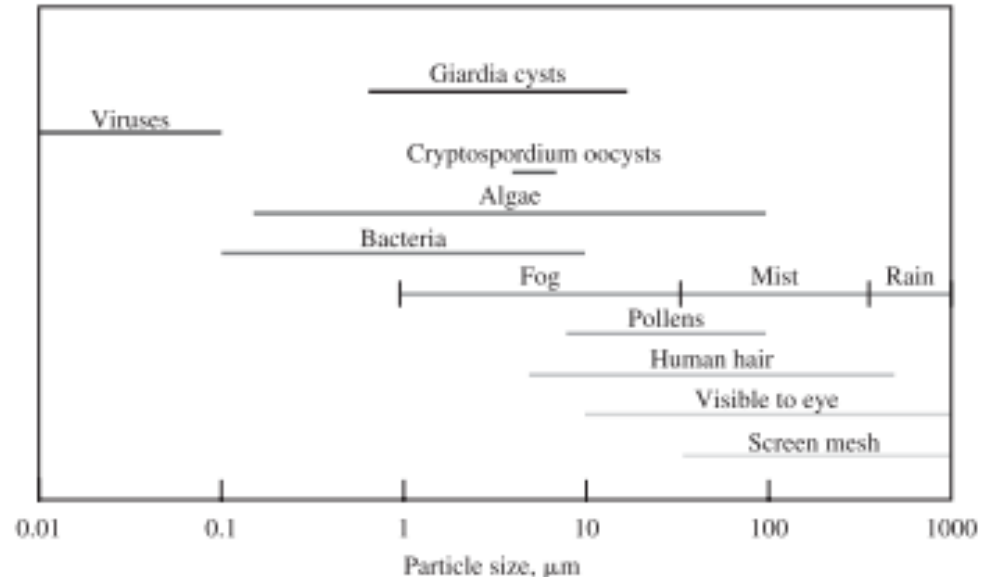
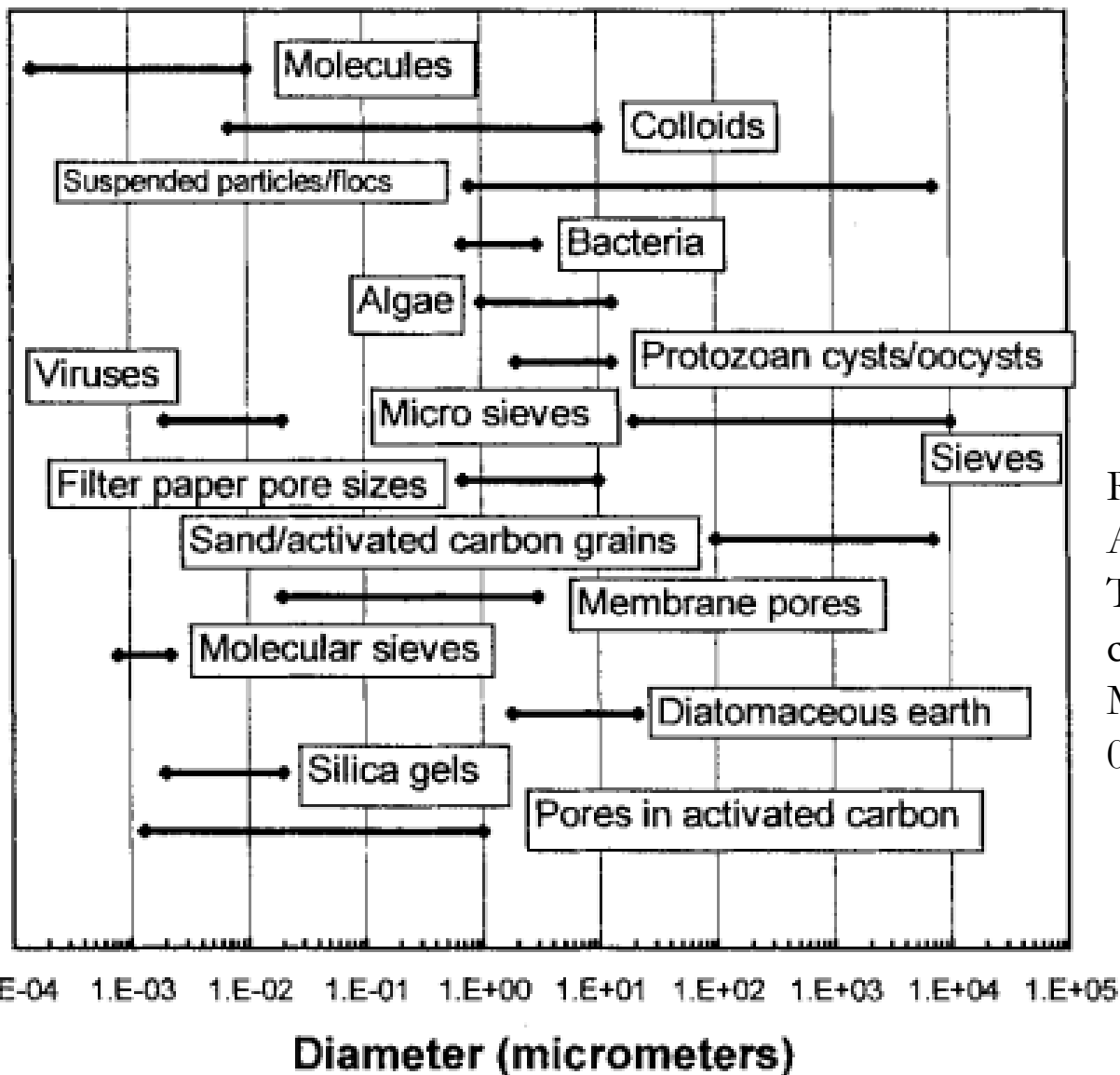


FIGURE 6-1
Particulates in water and miscellaneous other reference sizes.



Ref: American Water Works Association. Water Quality and Treatment: A handbook of community water supplies. 5th ed. McGraw Hill, 1999 ISBN: 0-0070016593

FIGURE 6.1 Size spectrum of waterborne particles and filter pores (from Stumm and Morgan, 1981).

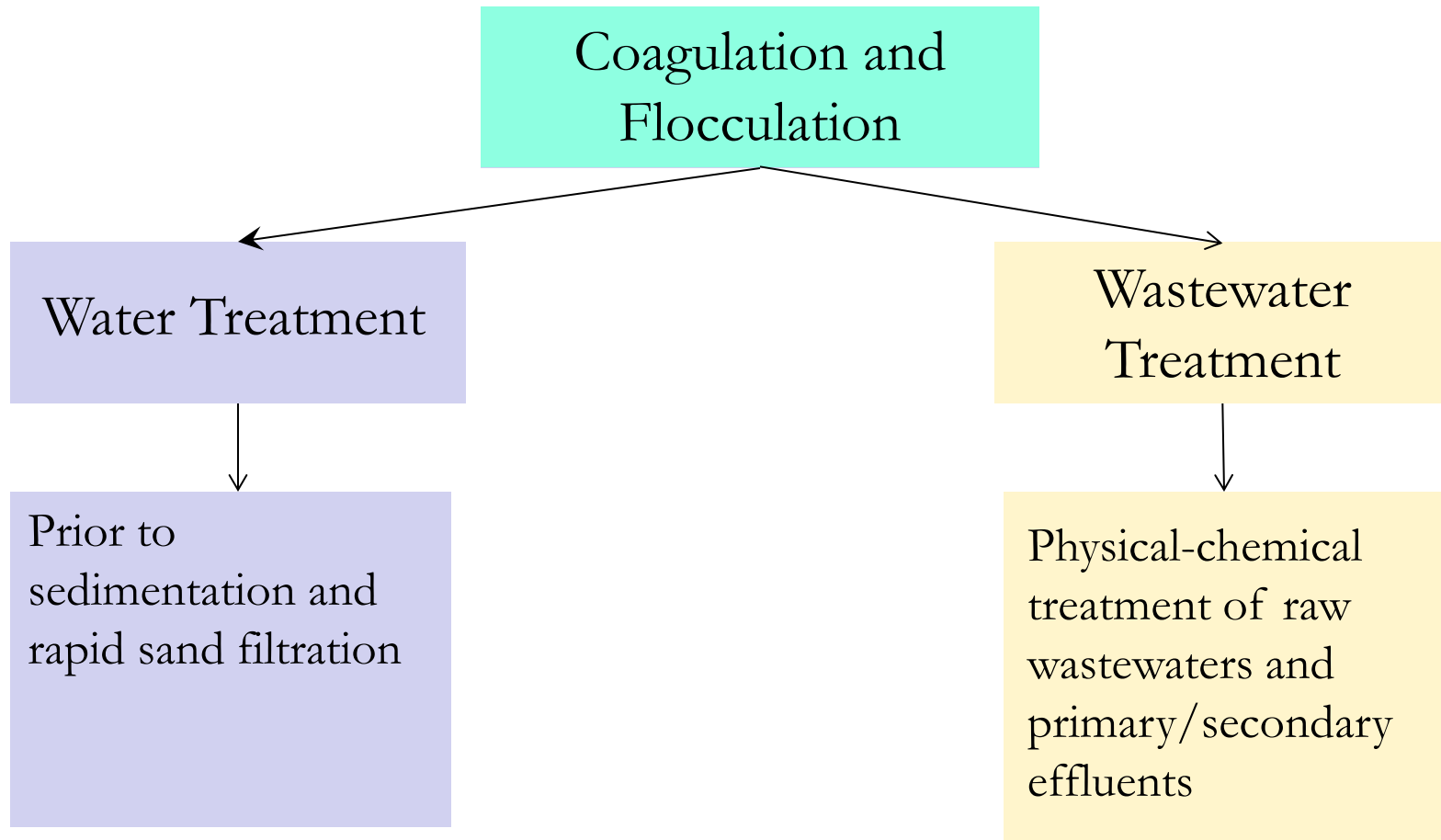
Coagulation / Flocculation

- It is difficult to separate colloids from water, colloids
 - do not settle by gravity
 - are too small, they pass through the pores of most common filtration media
- Natural organic matters, disinfection byproducts, bacteria, cysts of protozoa, clay, silt, mineral oxides may be classified as colloidal particles.

Coagulation / Flocculation

- Coagulation and Flocculation are essential parts of conventional water treatment systems that are designed to;
 - Remove infectious agents
 - Remove toxic compounds that have adsorbed onto the surface of particles
 - Remove precursors to the formation of disinfection byproducts

Coagulation & Flocculation



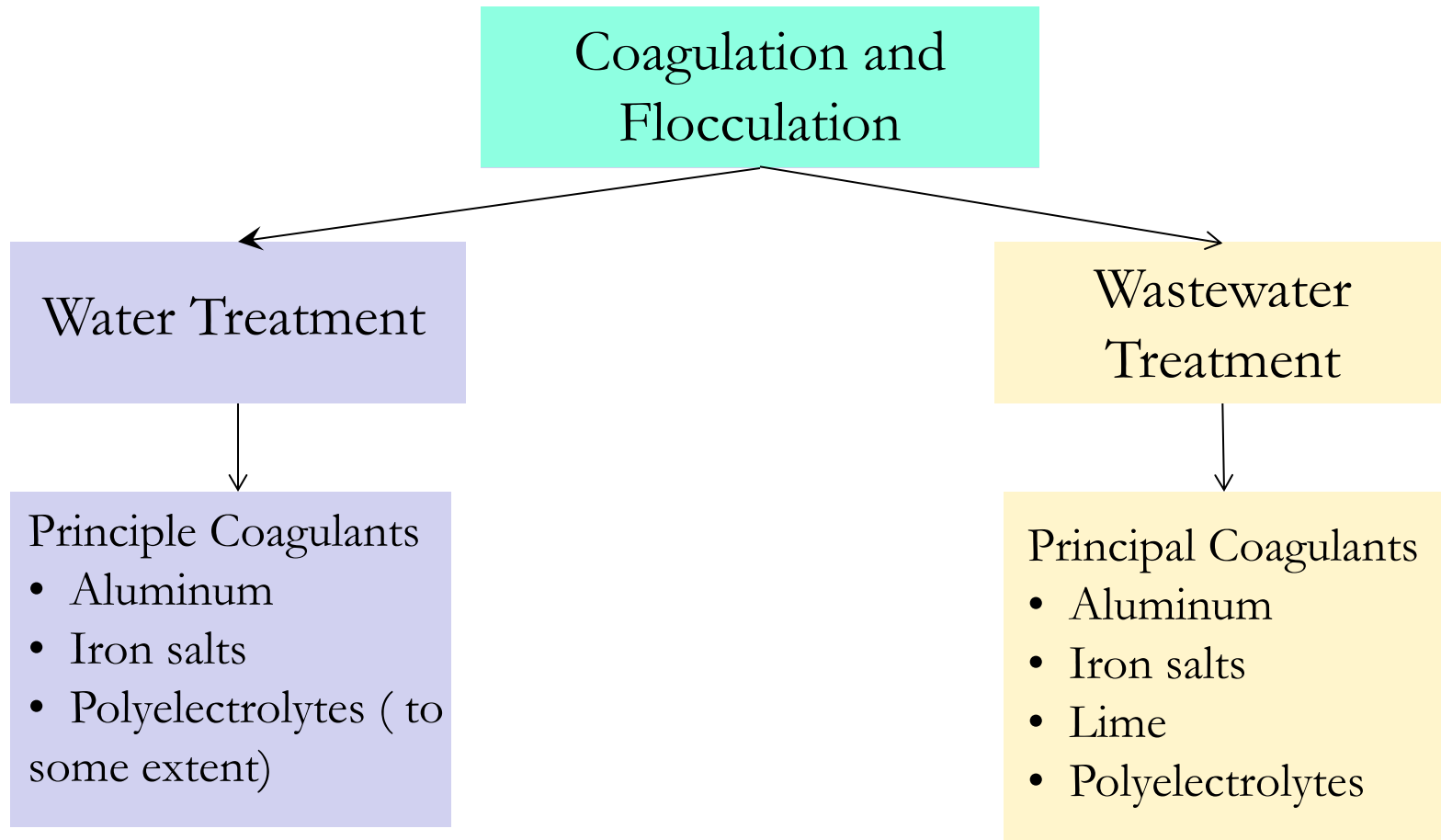
Coagulation / Flocculation

- Coagulation and flocculation consist of adding a floc-forming chemical reagent to a water or wastewater.
 - to enmesh or combine with non-settleable colloidal solids and slow-settling suspended solids to produce a rapid-settling floc.
- Floc is then removed by sedimentation

Coagulation & Flocculation

- Coagulation is the addition and rapid mixing of a coagulant to achieve,
 - destabilization of the colloidal and fine suspended solids
 - initial aggregation of the destabilized particles
- Flocculation is the slow stirring or gentle agitation to
 - aggregate the destabilized particles
 - form a rapid settling floc

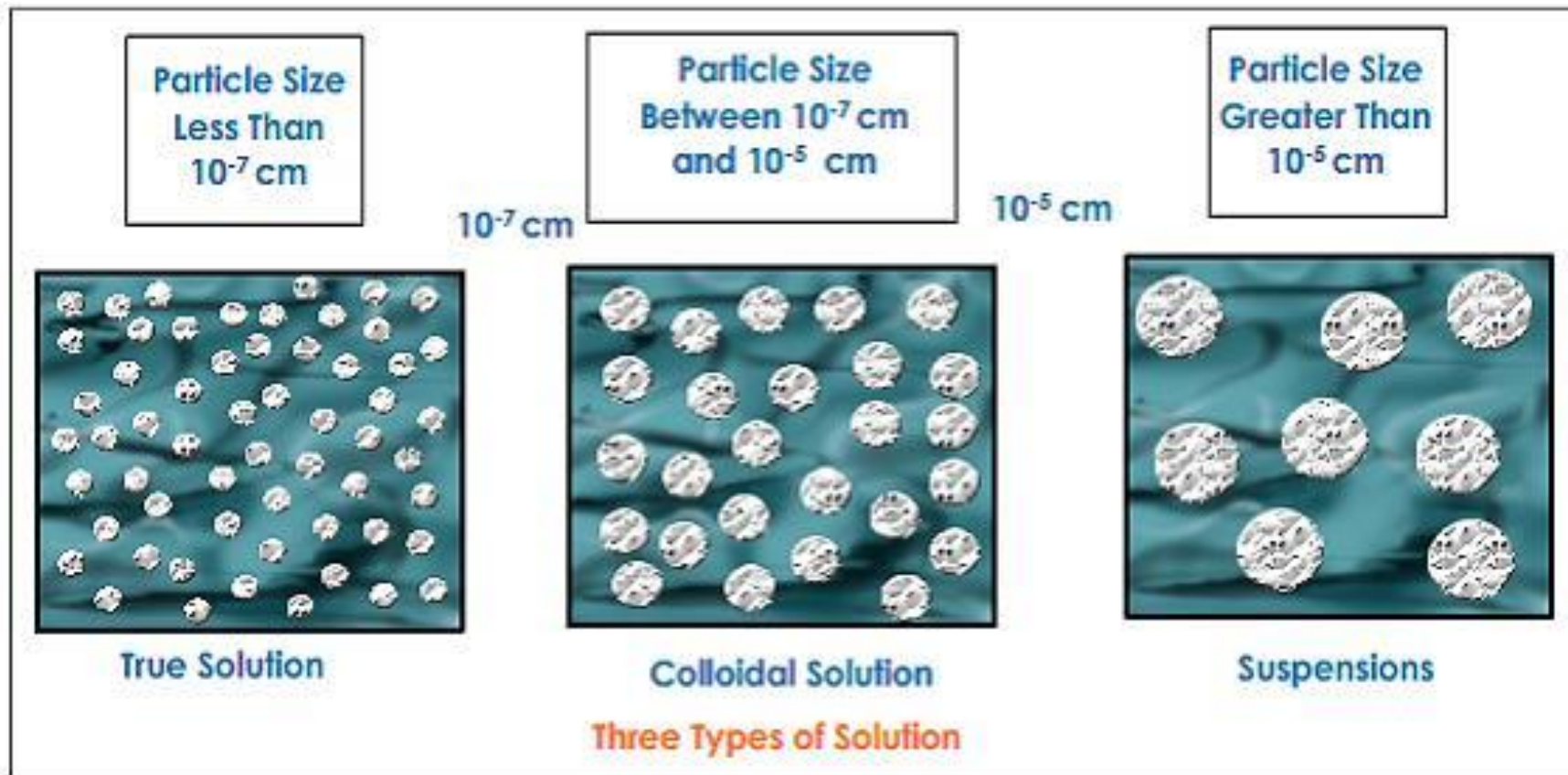
Coagulation & Flocculation



Colloidal Characteristics

- Colloidal dispersions are classified according to;
 - Dispersed phase
 - Disperse medium
- In both water and wastewater treatment;
 - Solids dispersed in liquids (sols) **are of particular interest**
 - Organic matter in suspension → microorganisms
 - Inorganic matter in suspension → clay
 - Liquids dispersed in liquids (emulsions)
 - Oil dispersed in water

Colloidal Characteristics



Ref:<http://chemistry.tutorvista.com/physical-chemistry/classification-of-colloides.html>

Colloidal Characteristics

- Solid particles in colloidal dispersion will not settle by gravity
- Colloids have an extremely large surface area per unit volume of the particles. Therefore, colloids tend to
 - Absorb water molecules and ions from the surrounding water
 - Develop or have an electrostatic charge relative to the surrounding water

Colloidal Characteristics

- Colloidal solids in water may be;
 - Hydrophilic
 - Hydrophobic

Colloidal Characteristics

Hydrophilic Colloids

- **Hydrophilic** colloids have an affinity to water due to the existence of water-soluble groups on the colloidal surface. Some principal groups are;
 - Amino
 - Carboxyl
 - Sulfonic
 - Hydroxyl
 - Usually organic colloids, such as proteins and their degradation products are hydrophilic.
- Water soluble , promote hydration and cause water layer or film to collect and surround the hydrophilic colloid

Colloidal Characteristics

Hydrophobic Colloids

- **Hydrophobic** colloids have little or no affinity for water, therefore, they do not have any significant water film or water of hydration.
- Usually inorganic colloids such as clays are hydrophobic.

Colloidal Characteristics

Electrostatic forces

- Colloidal particles have electrostatic forces. Electrostatic forces maintain the dispersion of the colloid.
- Ionization of surface groups and adsorption of ions from the surrounding solution cause electrical charge on the surface of a colloid.
- Also colloidal minerals such as clays, have an electrostatic charge due to ion deficit within the mineral lattice.

<http://dl.clackamas.cc.or.us/ch105-03/similar.htm>



Colloidal Characteristics

Electrostatic forces

- Hydrophilic colloids (proteins, microorganisms) have charges due to ionization of groups such as amino and carboxyl groups located on the colloidal surface
 - Amino group $\rightarrow -\text{NH}_2$
 - Carboxyl group $\rightarrow -\text{COOH}$
- If pH at isoelectric point $\rightarrow -\text{NH}_3^+ \quad -\text{COO}^-$ no charge
- If pH < isoelectric point $\rightarrow -\text{NH}_3^+ \quad -\text{COOH}$ (+) charge
- If pH > isoelectric point $\rightarrow -\text{NH}_2 \quad -\text{COO}^-$ (-) charge
- Most naturally occurring colloids have negative charge

• The **isoelectric point**, is the **pH** at which a particular **molecule** or surface carries no net **electrical charge**.

Colloidal Characteristics

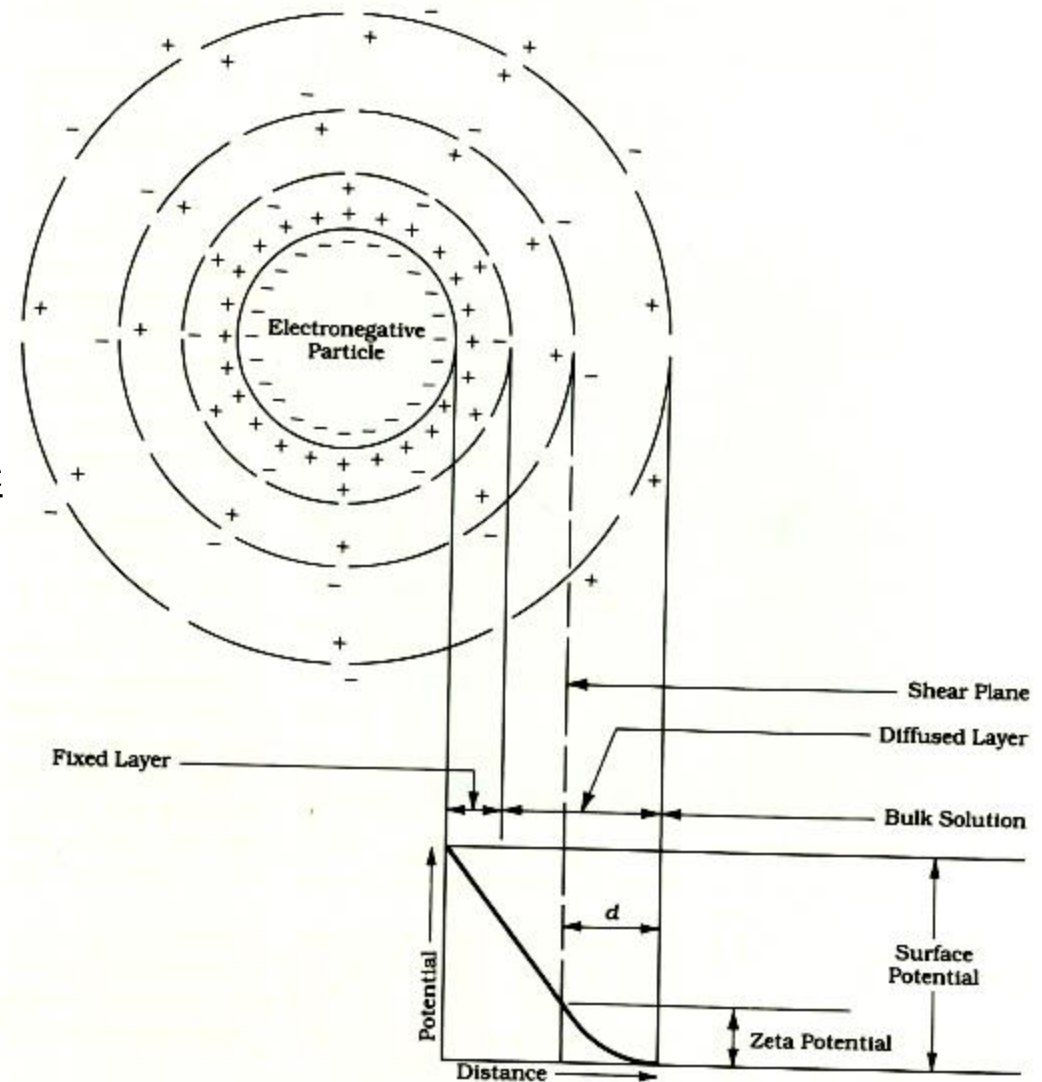
- Colloids are maintained in suspension as a result of electrostatic forces.
- Most colloids are negatively charged --- repulsive forces dominate (Electrical double layer)
- Attractive forces resulting from Van der Waals forces also act on colloids

Electrical Double Layer

Colloids however can be negatively charged

In colloidal suspensions there can be no net imbalance in the overall electrical charge

Therefore, overall electrical charge have to be counterbalanced by the counter ions in water

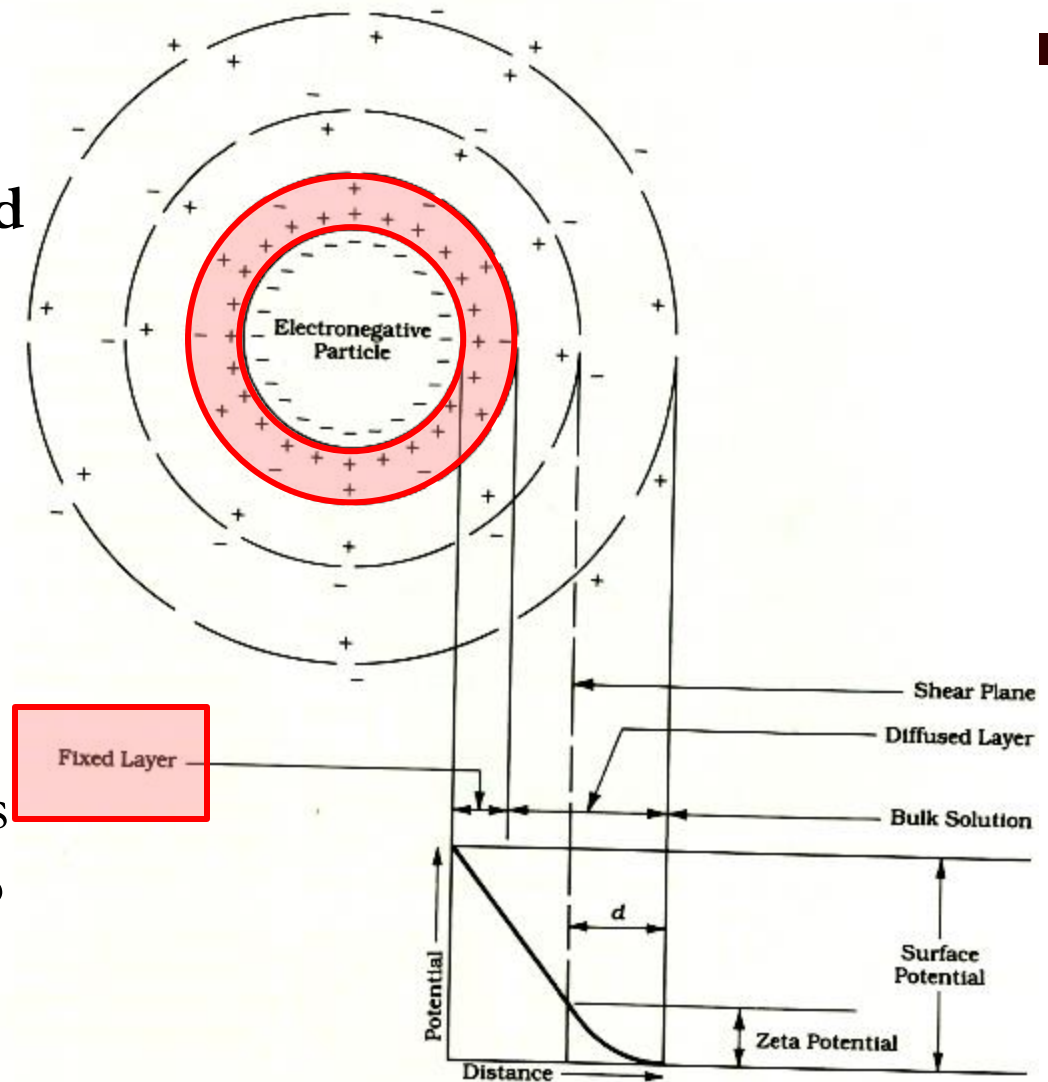


Electrical Double Layer

The compact layer of counterions is termed as **Fixed (Stern) layer**

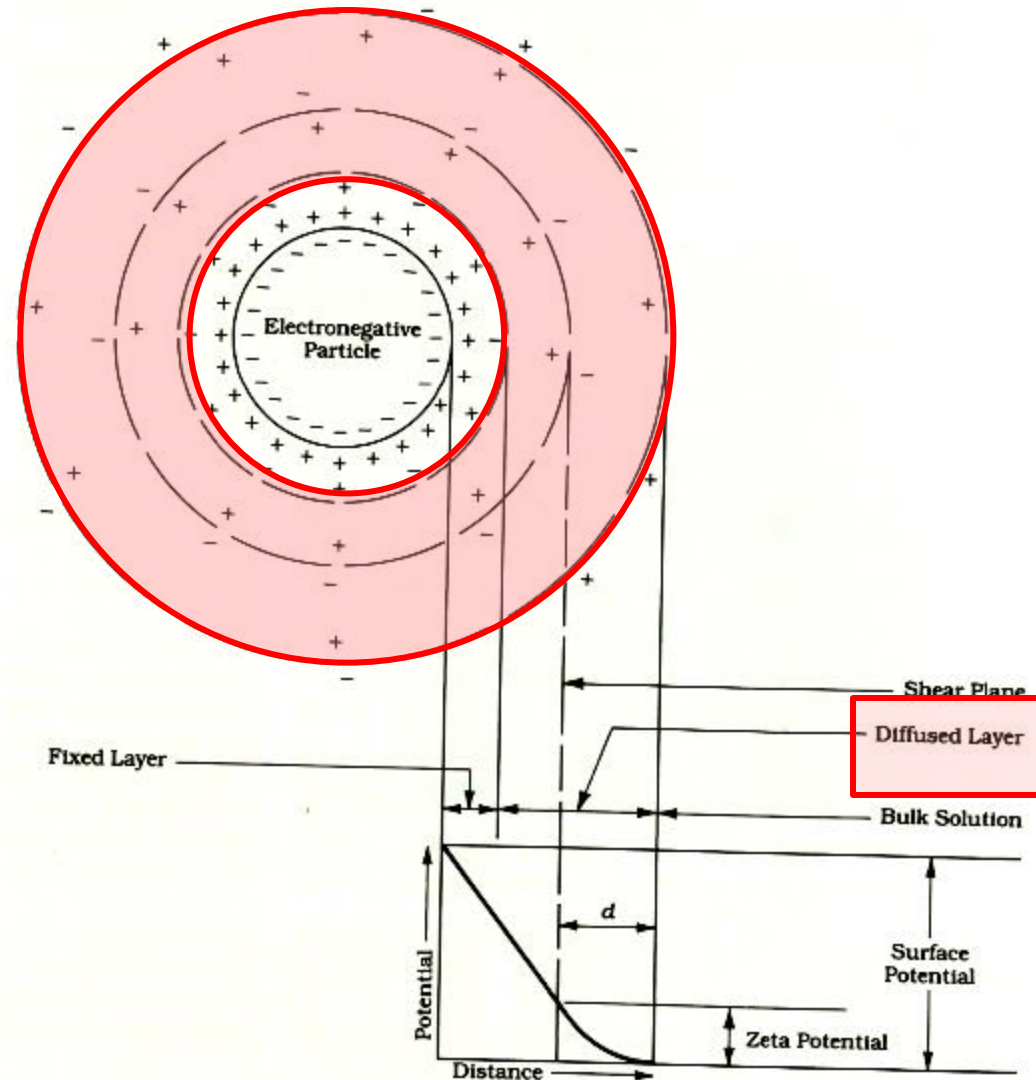
Fixed layer is attached to particle.

Negative colloidal particle attracts positively charged ions from the surrounding water to its surface



Electrical double layer

- **Diffused layer (Gouy)** is outside of the fixed layer
- Both the diffused and fixed layers contain positive and negative charged ions.
- Electrical double layer is the combination of fixed and diffused layers

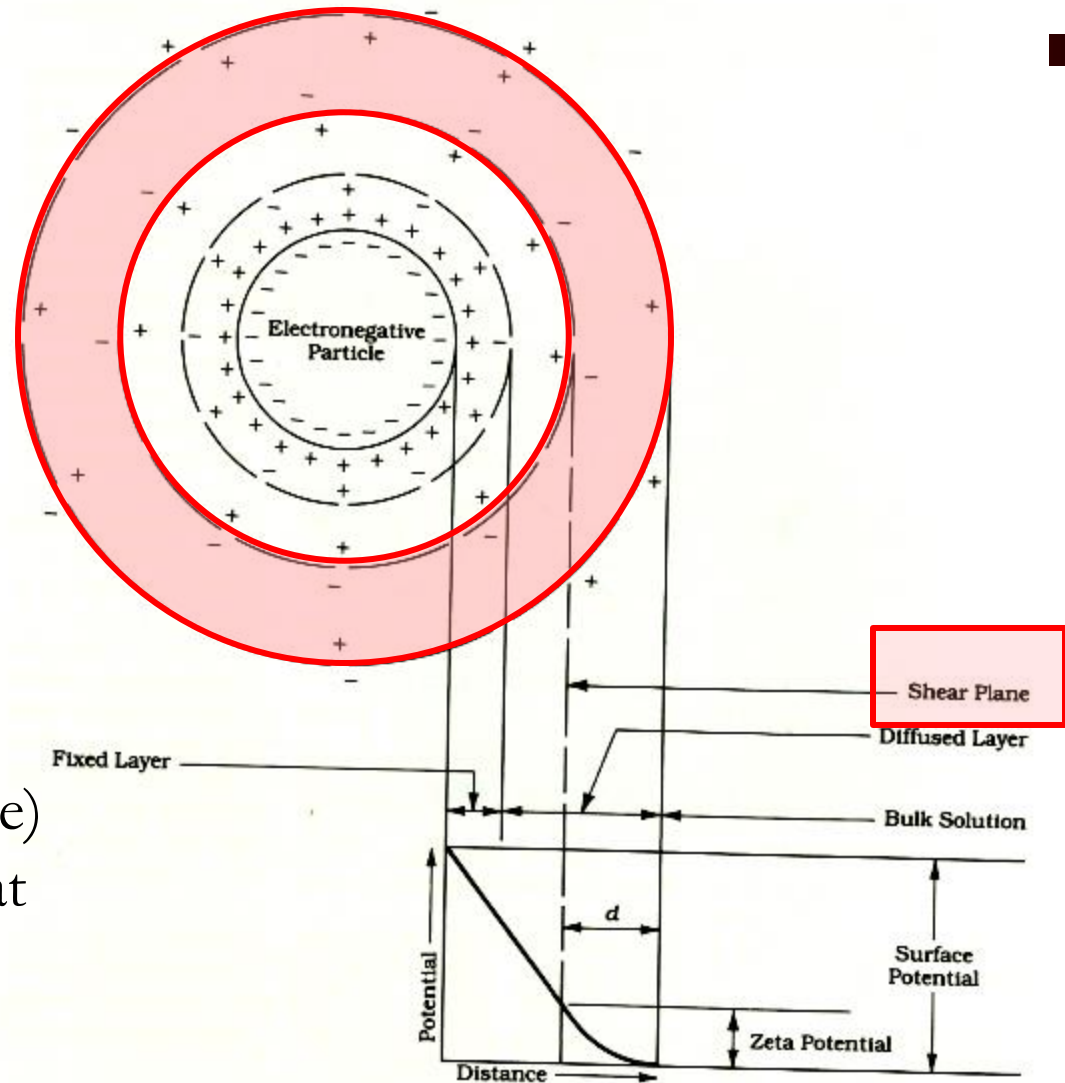


Electrical Double Layer

The concentration of counter ions is greatest at the particle surface

Concentration of counter ions decrease towards to diffusion layer

The **shear plane** (shear surface) encloses a volume of water that moves with the particle (water envelop or bound water)

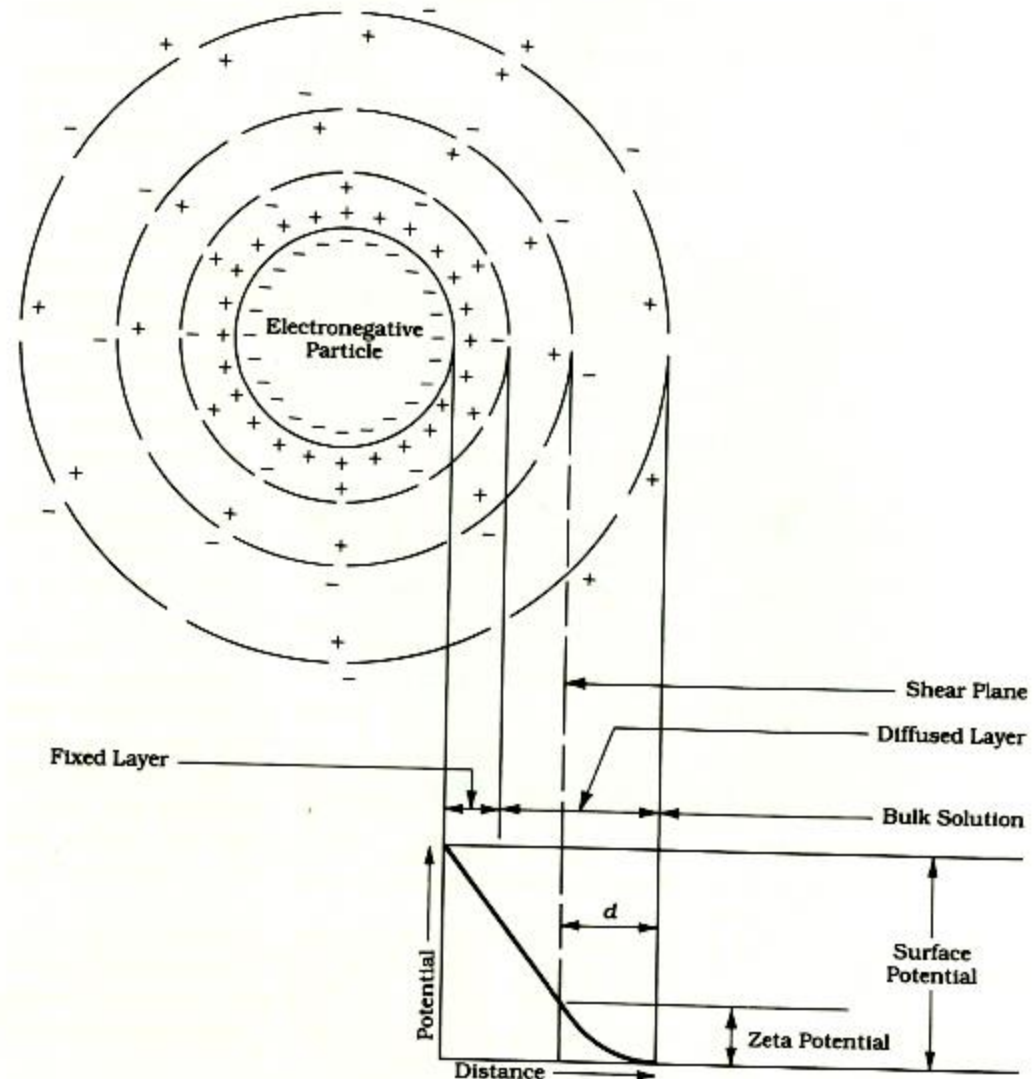


Electrical Double Layer

Zeta Potential

Zeta potential (ζ) is the electrostatic potential at the shear surface

Zeta potential (ζ) is usually related to the stability of a colloidal suspension



Electrical Double Layer

Zeta Potential

- A colloidal suspension is stable if the particles remain in suspension and do not coagulate
- The colloidal stability depends on the relative magnitude of the forces of attraction and the forces of repulsion
- The forces of attraction → Van der Waals forces which are effective only in the immediate neighborhood of the particle
- The forces of repulsion are due to the electrostatic forces of the colloidal dispersion
- The magnitude of repulsive and attractive forces are measured by **Zeta potential (ζ)**

Electrical Double Layer

Zeta Potential

$$\zeta = \frac{4\pi qd}{D}$$

- ζ : Zeta potential
- q : Charge per unit area
- d : thickness of the layer surrounding the shear surface through which the charge is effective
- D : Dielectric constant of liquid

Electrical Double Layer

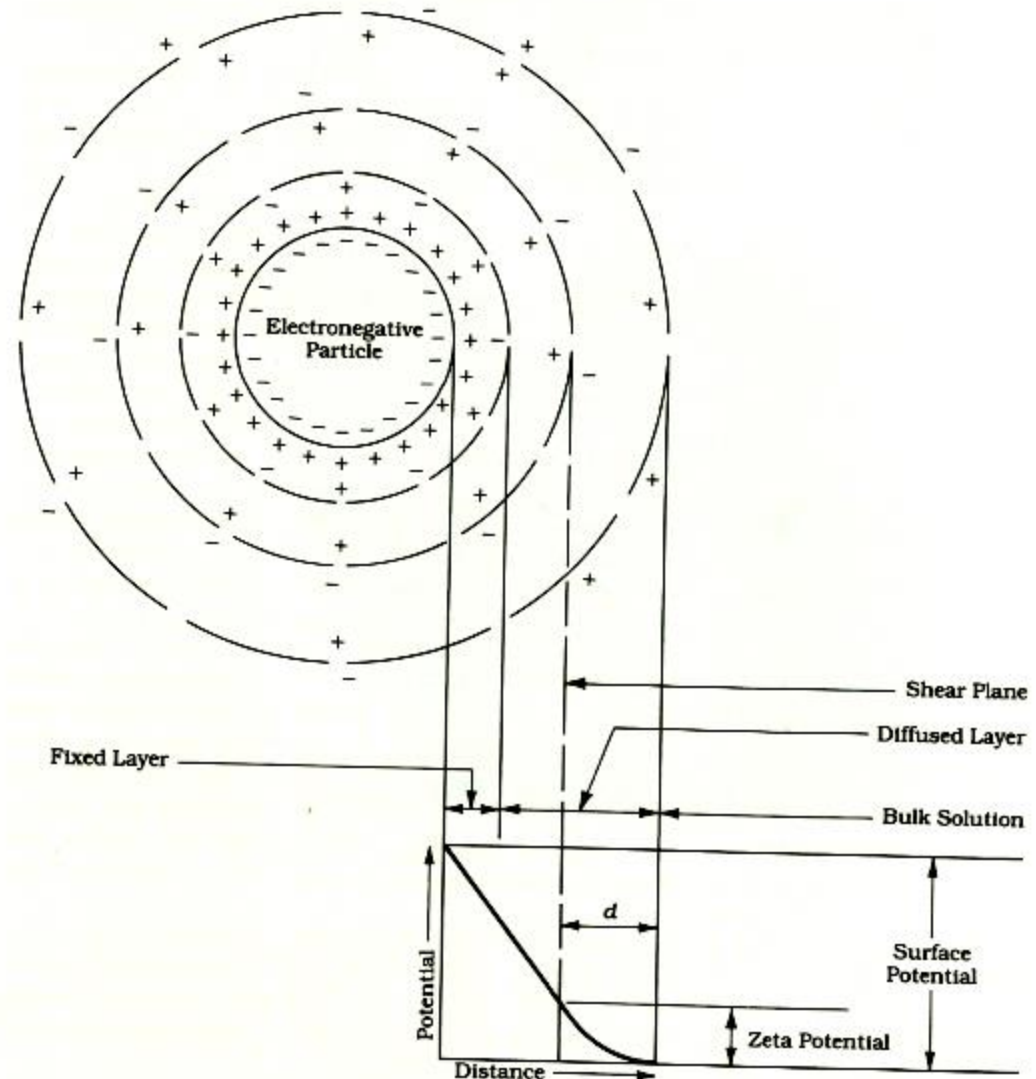
Zeta Potential

- Zeta potential measures the charge of the colloidal particle
- Zeta potential depends on the distance through which the charge is effective
- Greater the Zeta potential \rightarrow greater the repulsion forces between the colloids \rightarrow more stable colloidal suspension
- Low Zeta potential \rightarrow less stable colloidal suspension

Electrical Double Layer

Zeta Potential

- Hydrophilic colloids have a shear surface at the outer boundary of the bound water layer
- Hydrophobic colloids have shear surface near the outer boundary of the fixed layer



Forces between the Colloids of Like Charge

The net resultant force is attractive up to the distance x , beyond this point the net resultant force is repulsive.

To induce coagulation,

- ❖ Repulsive forces must be reduced
- ❖ Destablized particles should be in close proximity to enable agglomeration

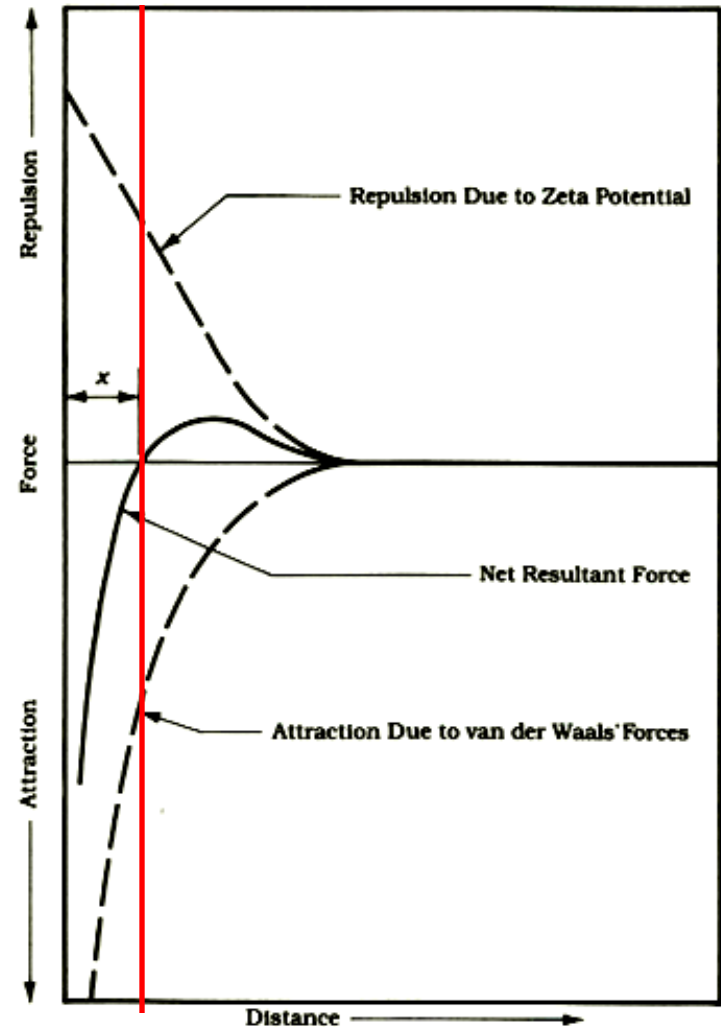


FIGURE 8.4 Colloidal Interparticulate Forces versus Distance

Coagulation of Colloids

Destabilization Mechanism

- When a coagulant added to a water or wastewater, destabilization of colloids occur and a coagulant floc is formed by the following mechanisms;
 - The reduction of zeta potential to a degree where attractive Van der Waals forces and the agitation provided cause particles to coalesce (Double layer compression)
 - The absorption and charge neutralization
 - The enmeshment of particles in the precipitate floc that is formed
 - The aggregation of particles by interparticulate bridging between reactive groups on the colloids

Coagulation of Colloids

Destabilization Mechanism

- Double layer compression
- When a coagulant salt is added to water, it dissociates and the metallic ion undergoes hydrolysis and forms positively charged hydroxometallic ion complexes (e.g. $\text{Al}_2(\text{SO}_4)_3$, $\text{Fe}_2(\text{SO}_4)_3$)
- Results in high concentrations of counter ions in the diffuse layer – which reduces the volume of the diffuse layer → Van der Waals forces dominate

Coagulation of Colloids

Destabilization Mechanism

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Coagulation of Colloids Destabilization Mechanism

- Double layer compression
- The amount of electrolyte required to achieve coagulation by double layer compression is independent of the concentration of colloids in liquid
- It is not possible to cause charge reversal on a colloid regardless of how much electrolyte is added

Coagulation of Colloids

Destabilization Mechanism

- Adsorption and Charge neutralization
- Due to large surface area of colloids, some chemical species are capable of being adsorbed onto the surface of the colloidal particle
- If the charge of the adsorbed specie is opposite to the charge of the colloids, the colloidal particle will be destabilized.

Coagulation of Colloids

Destabilization Mechanism

- Destabilization by adsorption and Charge neutralization is different than the double layer compression
- Destabilization by adsorption is stoichiometric so as the concentration of colloids increase, required dosage of coagulant increase
- Sorbable species are capable of destabilizing colloids at much lower dosages than double compression ions
- Overdosing of sorbable species cause charge reversal of the colloid → leads to restabilization of suspension
- Hydrolyzed species of Al(III) and Fe(III) can cause coagulation by adsorption

Coagulation of Colloids

Destabilization Mechanism

- Enmeshment in a Precipitate (Sweep coagulation)
- The dosages of coagulant salts used in the water / wastewater treatment are in excess of the amount required to produce positive hydroxy-metallic complexes.
- The excess complexes continue to hydrolyze until they form insoluble metallic hydroxide ($\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$)
- Colloidal particles can be enmeshed in the precipitate and settle.
- In dilute colloidal suspensions, it is advantageous to recycle small portion of the settled sludge.
- In dilute suspensions, relatively high coagulant dosage causes the restabilization of the particles → negatively charged particles become positively charged.

Coagulation of Colloids Destabilization Mechanism

- Interparticle Bridging
- Natural organic polymers (Starch, cellulose) can be used as effective coagulant agents
- Natural organic polymers have large molecular size and can be anionic, cationic, or non-ionic
- Coagulation of colloids by organic polymers occur by chemical bridging
- The tail of the polymer will extent to the bulk liquid and can be attached to another particle forming a bridge

Coagulation of Colloids

Destabilization Mechanism

- Interparticle Bridging
- Overdosing the polymer → saturate surfaces of colloids
- Intense or prolonged agitation → may destroy previously formed bridges.