



ENVE 301

Environmental Engineering Unit Operations

CHAPTER: 7

Coagulation & Flocculation

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Coagulation & Flocculation

Colloidal particles size ranging → 10^{-6} mm (1 nm) - 10^{-3} mm (1 μ m)
(in some books extends up to 10 μ m)

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

It is difficult to separate colloids from water because;

- Colloids do not settle by gravity
- They are so small particles that pass through the pores of most common filtration media.

Coagulation & Flocculation (continue)

For the removal of colloids;

- The individual colloids must aggregate and grow in size
- Coag. & flocc. are used to agglomerate colloids prior to sedimentation and rapid sand filtration

Coagulation: is the addition and rapid mixing of coagulant

- for destabilization of particles
- for initial aggregation of the destabilized particles

Flocculation: is the slow stirring or gentle agitation

- to aggregate destabilized particles
- to form rapid settling floc

Coagulation & Flocculation : Colloidal Characteristics

Colloidal Dispersions



**Solids dispersed in liquids
(sols)**

e.g., clay particles present in
surface waters



**Liquids dispersed in liquids
(emulsions)**

e.g., oil dispersed in water

Colloids have an extremely large surface area per unit volume (large specific surface area)

Because of the large specific surface area;

- they tend to adsorb water molecules and ions from surrounding water
- they develop or have an electrostatic charge relative to surrounding water

Coagulation & Flocculation : Colloidal Characteristics

Classification of colloidal solids in water acc. to their affinity for water

Hydrophilic Colloids

Have an affinity for water due to existence of water soluble groups (e.g. amino, carboxyl, sulfonic, hydroxyl etc.) on the colloidal surface

These groups promote hydration and cause a water film to collect and surround the hydrophilic colloid

Examples: proteins, soaps, synthetic detergents

Hydrophobic Colloids

Have little affinity for water

They do not have any significant water film or water of hydration

Examples: inorganic colloids (e.g., clay, metal)

Coagulation & Flocculation : Colloidal Characteristics

Electrical Charges on Colloidal Surfaces arises in three principal ways:

1) Imperfection in Crystal Structure:

Silicon atoms in crystalline material → replaced by atoms with lower valence (such as aluminium ion) giving an excess negative charge to the crystal material

→ is comparatively rare situation

→ clay particles responsible for turbidity in surface water acquire their negative charge in this manner

Coagulation & Flocculation : Colloidal Characteristics

2) Adsorption of Ions onto Particle Surface:

- Many colloidal particles acquire a charge as a result of the preferential adsorption of either positive or negative ions on their surface.
- Colloidal particles in aqueous media usually adsorb anions and acquire a negative charge.

Coagulation & Flocculation : Colloidal Characteristics

3) Ionization of Surface Sites:

many particulate surfaces —————> Contain ionogenic groups, such as hydroxyl, carboxyl groups, which dissociate in water

—————> These ionogenic groups produce a surface charge depending on the solution pH.

→ Particles may exhibit a net positive charge or particles may exhibit a net negative charge depending on pH

Coagulation & Flocculation : Colloidal Stability

Forces acting on particles in a colloidal sol.



Repulsive Forces
result from Electrical
Double Layer



Attractive Forces
result from Van der Waals
Forces of intermolecular
attraction

Interactions between these forces → contribute to the
Overall Stability of Colloidal Dispersion

Coagulation & Flocculation : Electrical Double Layer

Individual hydrophobic colloids → have an electrical charge
(usually negative)

Colloidal dispersion → does not have an electrical charge

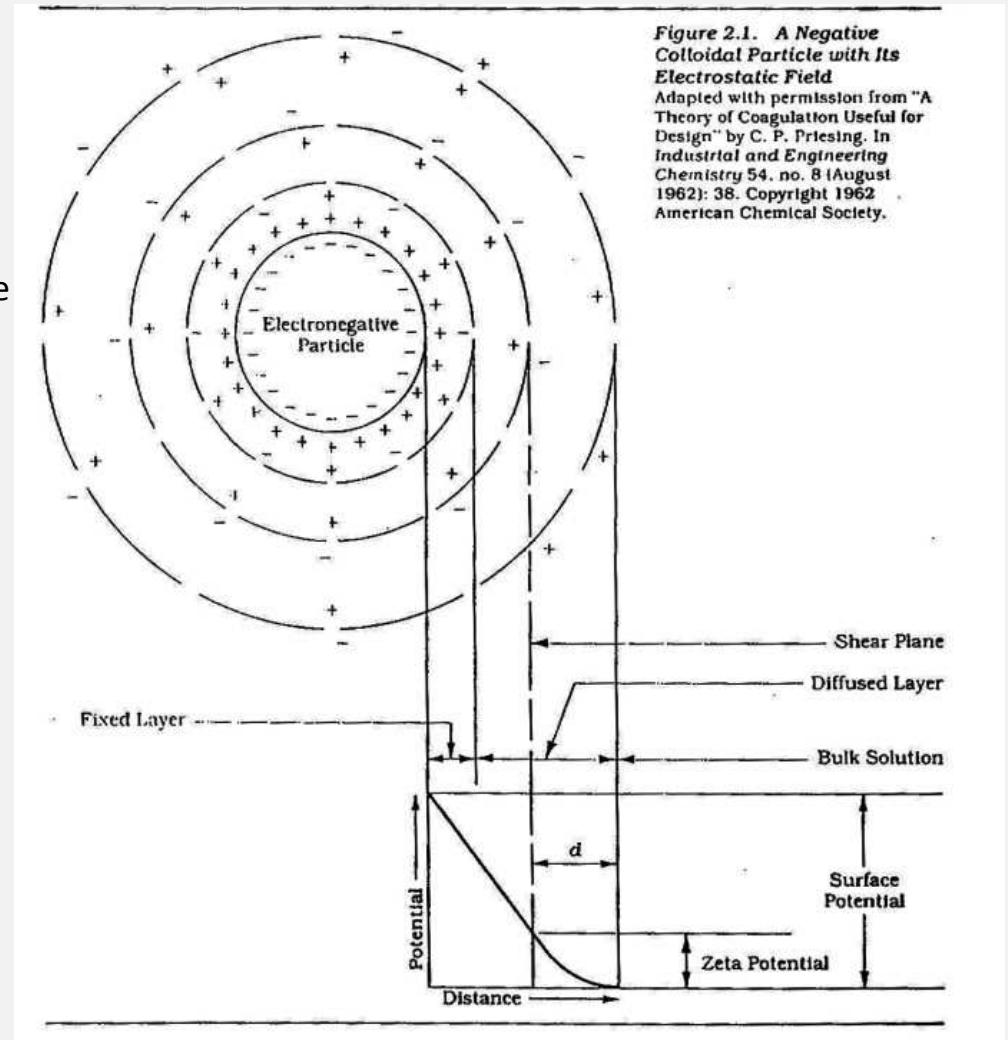
For electroneutrality to exist

the charge on the colloid must be counterbalanced by ions of opposite charge (counter ions) in the water

Therefore;

a negative colloidal particle will attract opposite charge ions (counter ions) from the surrounding water to its surface

This compact layer of counter ions → **Fixed (Stern) Layer**



Coagulation & Flocculation : Electrical Double Layer

Fixed (Stern) Layer

a negative colloidal particle will attract opposite charge ions (counter ions) from the surrounding water to its surface

Diffused (Gouy) Layer

Outside the fixed layer

electric potential decreases exponentially with increasing distance from particle

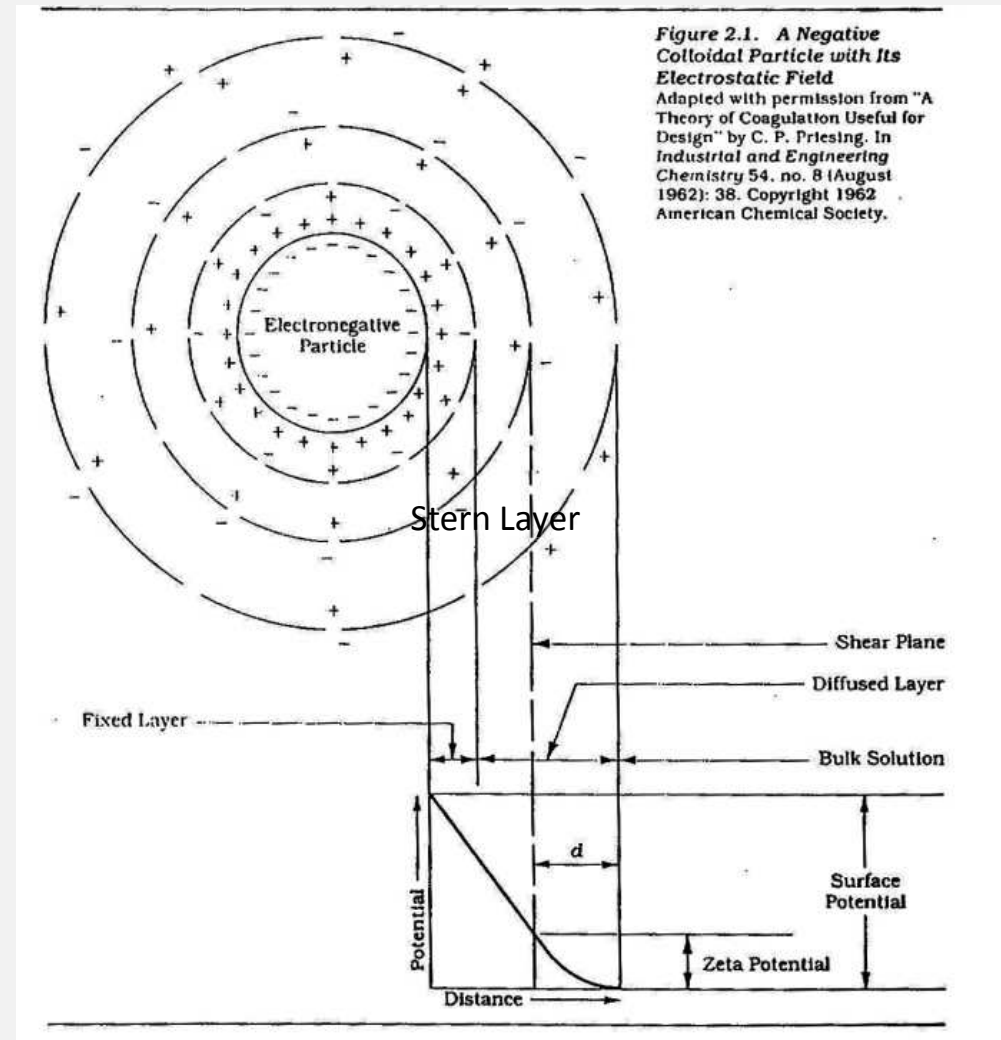
Electrical Double Layer

Stern (Fixed) Layer + Diffused (Gouy) Layer

Both layers contain positive and negative charged ions, however, there will be a much larger number of positive ions than negative ions

Shear Plane

is thought to lie in diffused layer some distance beyond Stern Layer encloses the volume of (i.e, bound water or water envelope) that moves with the particle
water beyond shear plane does not move with water



Coagulation & Flocculation : Electrical Double Layer

Electrostatic potential in shear plane

(i.e potential that exists between bulk liquid & an envelope of water that moves with particle)

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

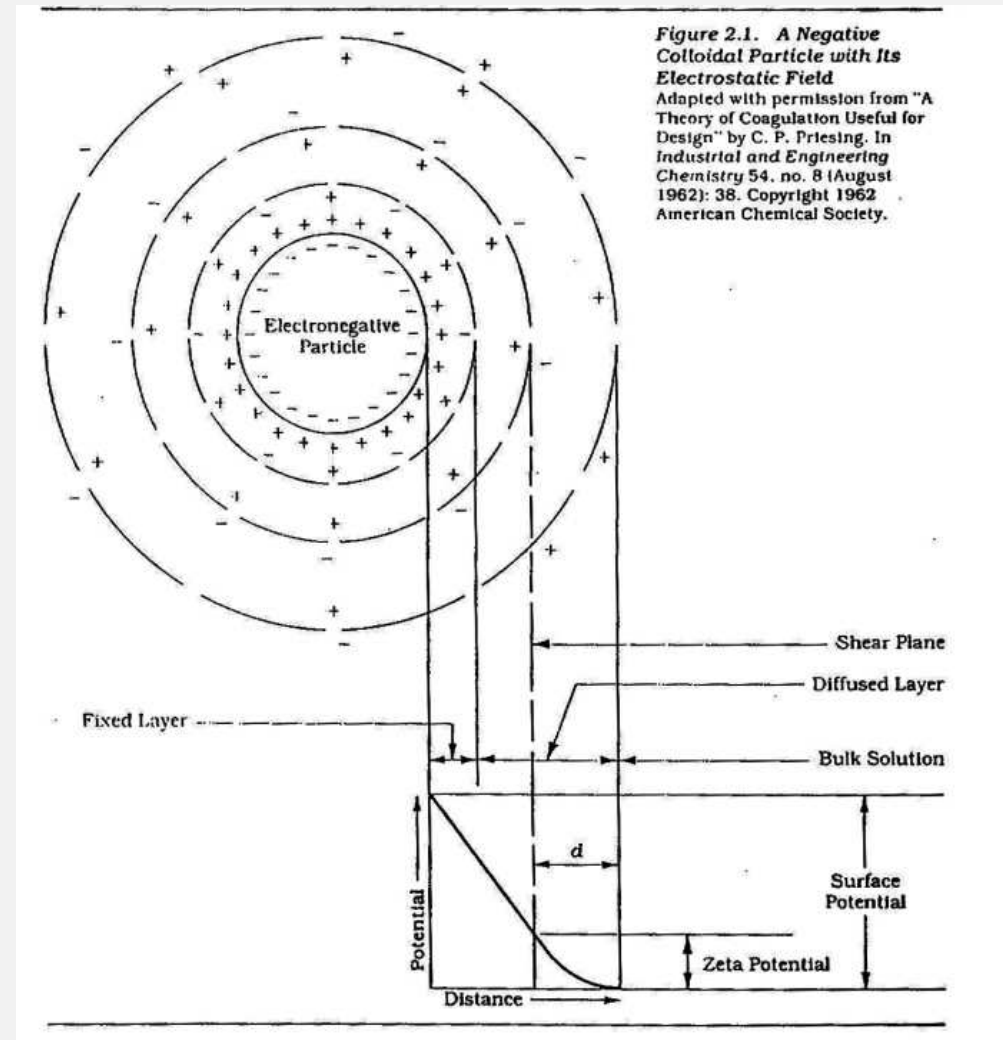
q=charge on the particle

d=thickness of the layer surrounding shear plane

D=dielectric constant of liquid

Zeta Potential

- Related to the stability of a colloidal suspension
- Greater zeta potential greater repulsion forces
- High zeta potential → stable colloidal system
Low zeta potential → less stable colloidal systems
- Only measurable potential
(@the surface of colloid can't be measured because of stern layer which is so tightly bound to colloid)
- Electrophoresis measurement
(measurement of rate of movement of particulates in an electrical field)



Coagulation & Flocculation : Electrical Double Layer

Colloidal particles in suspension → moving randomly as a result of Brownian Movement

As 2 similar charged particle approach each other as a result of Brownian Movement

Their Diffuse Counter Ion atmosphere begin to interfere

Cause particles to be repulsed

Coagulation & Flocculation :

Force Fields Between Colloids of Like Charge

When 2 colloids come in close proximity there are two forces acting on them:

1) Repulsive Forces → Caused by the electrostatic potential created by diffused counter ion atmosphere surrounding the each colloid.

Decreases roughly exponentially with increasing distance between particles

Coagulation & Flocculation :

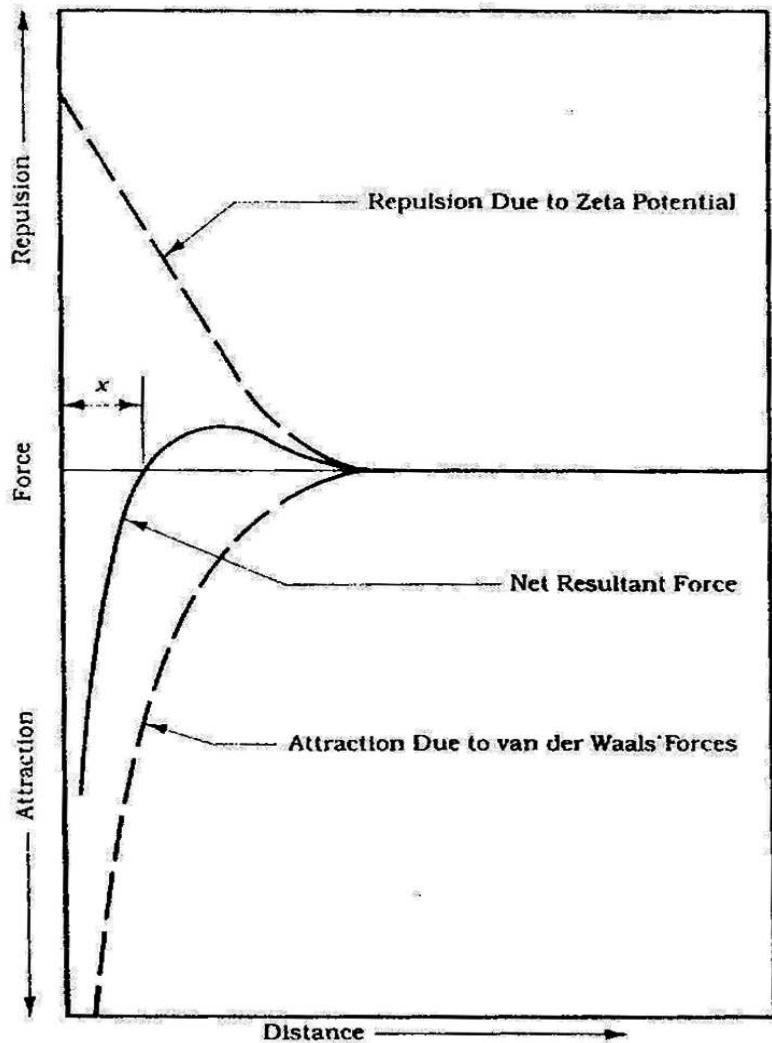
Force Fields Between Colloids of Like Charge

2) *Attractive Force* → results from van der Waals forces

Van der Waals force between two particles
is inversely proportional to the second power of
the distance separating the particles

decreases very rapidly with increasing intermolecular distance
(more rapidly than electrostatic potential)
stronger force at close distance

Colloidal Interparticulate Forces Versus Distance



- Net resultant force is attractive out to the distance x
- Beyond this point, the net resultant force is repulsive
- This net negative repulsive force at x distance from the particle imparts stability to the suspension (energy barrier)
- To induce aggregation of colloidal particles, two distinct steps must occur:
 1. the repulsion forces must be reduced (i.e., the particle must be destabilized)
 2. Contacts between destabilized particles must be provided for agglomeration to occur.

Mechanisms for Destabilization of Colloidal Dispersions

- 1) Double layer compression
- 2) Adsorption and charge neutralization
- 3) Enmeshment in a precipitate (sweep flocculation)
- 4) Adsorption and interparticle bridging

Coagulation & Flocculation (Continue)

Destabilization of Colloids

1) DOUBLE LAYER COMPRESSION

Addition of ions having a charge opposite to that of colloid



produce correspondingly high concentrations of counter ions in diffuse layer



the volume of the diffuse layer necessary to maintain electroneutrality is lowered

the thickness of diffuse layer is reduced

van der Waals force becomes predominant

net force becomes attractive

Coagulation & Flocculation : Destabilization of Colloids

- 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

EXAMPLE:

Mixing of rivers

(low in ionic strength)

with sea water

(high in ionic strength)

causes the particles in river to be destabilized by double layer compression

coagulation and settling of particles will occur (Deltas are formed at river mouths)

Coagulation & Flocculation: Destabilization of Colloids

2) ADSORPTION and CHARGE NEUTRALIZATION

Some chemical species \longrightarrow capable of being adsorbed at the surface colloidal particles

If the adsorbed species carry a charge opposite to that of colloid \longrightarrow reduction of surface potential
destabilization of colloidal particle

Coagulation & Flocculation (continue)

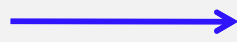
Destabilization of Colloids

It differs from destabilization by double layer compression in 3 important ways:

1) sorbable species are capable of destabilizing colloids \longrightarrow nonsorbable (double layer compressing) ions
AT MUCH LOWER DOSAGES THAN

2) Destabilization by adsorption is stoichiometric as the concentration of colloids increase \longrightarrow Required dosage of coagulant increases

3) Overdosing of sorbable species



reversal of charge on the
colloidal particle

restabilization of suspension

Hydrolyzed species of Al (III) and Fe(III) can cause coagulation by adsorption.

Coagulation & Flocculation : Destabilization of Colloids

3) ENMESHMENT IN A PRECIPITATE (Sweep-Floc Coagulation)

When a metal salt
(e.g $\text{Al}_2(\text{SO}_4)_3$ or FeCl_3)
is added to water in
concentrations
sufficiently high



precipitates of
metal hydroxides
[e.g., $\text{Al}(\text{OH})_3$,
 $\text{Fe}(\text{OH})_3$] will form



colloidal particles can
be enmeshed
(entrapped) in the
precipitates and settle
with them

Coagulation & Flocculation : Destabilization of Colloids

→ inverse relationship between the coagulant dosage and the concentrations of colloids to be removed

@low concentrations → large excess of coagulant is required to produce a large amount of precipitate that will enmesh the relatively few colloidal particles as it settles

@high concentrations → coagulation will occur at a lower chemical dosage because the colloids serve as nuclei to enhance precipitate formation

→ *It is sometimes advantageous to add turbidity to the dilute colloidal suspensions .*

Coagulation & Flocculation : Destabilization of Colloids

- **does not depend on neutralization of surface charge**
optimum coagulation do not correspond to a min. zeta potential
- **an optimum pH exist for each coagulant depending on its solubility-pH relationship**
- **the most important mechanism in water treatment**

Coagulation & Flocculation : Destabilization of Colloids

4) *INTERPARTICLE BRIDGING*

Natural organic polymers

(e.g., starch, cellulose)



effective coagulant agents

synthetic organic

polymeric compounds

They have large molecular size

They may be anionic, cationic or non-ionic

Coagulation & Flocculation : Destabilization of Colloids

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

due to

coulombic attraction → (if the polymer and particle are opposite charge)

OR

ion-exchange,

hydrogen bonding

van der Waals forces → (if the polymer and particle are similar charge)

Coagulation & Flocculation : Destabilization of Colloids

- the “tail” of the adsorbed polymer will extend out into the bulk solution and can become attached to vacant sites on the surface of another particle to form a chemical bridge
- this bridging action results in the formation of a floc particle having favorable settling characteristics

Coagulation & Flocculation : Destabilization of Colloids

- **overdosing of polymer** → saturate the surfaces of colloids
no sites are available for the
formation of polymer bridge
- **intense & prolonged agitation** → may destroy previously formed bridges