CHAPTER 1

INTRODUCTION

1.0. INTRODUCTION

1.1. Colloids: The fundamentals

A substance is said to be in the colloidal state, when it is dispersed in another medium in the form of small particles of size ranging from 10 nm-10 μm [1]. Thus, the size of the colloidal particles may be considered as an intermediate between molecular size in true solution and particles of suspension. The size spectrum of colloids is given in Figure 1.1.

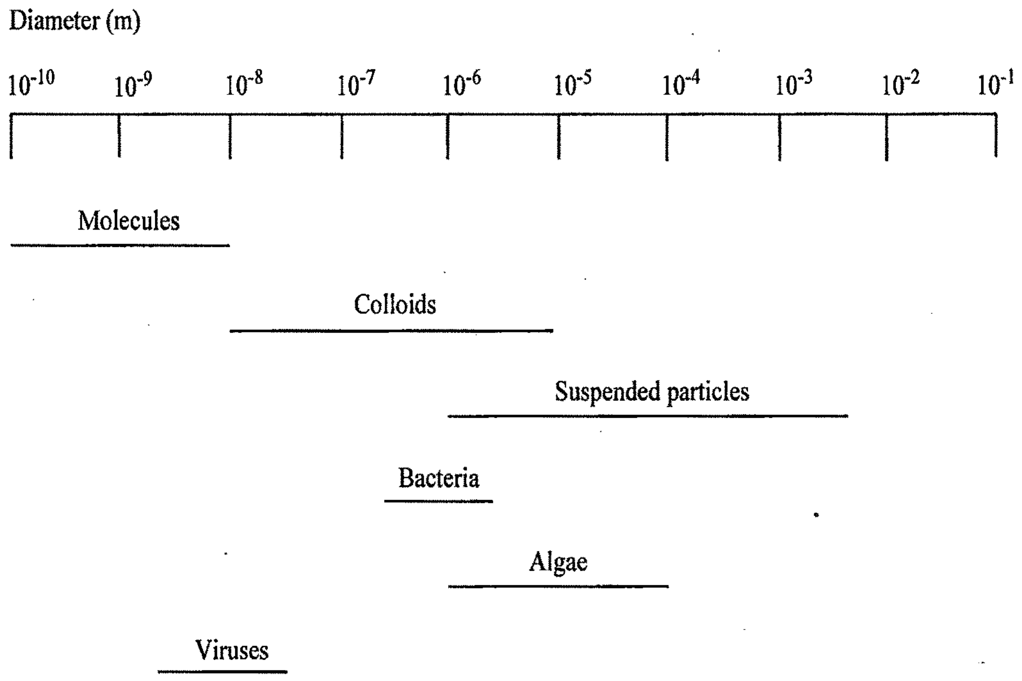


Figure 1.1. Size spectrum of particles

1.1.1. Colloidal solution

Colloidal solution is considered as a heterogeneous system consisting of a dispersed phase and dispersion medium. A dispersed phase, also known as discontinuous phase, consists of particles larger than the ordinary molecules, while a dispersion medium, also known as continuous phase, in which dispersed phase is present [2].

1.1.2. Classification of colloids

On the basis of appearance, colloids are divided into following two main categories.

(a) Sol: The systems with solids as dispersed phase and a liquid as dispersion medium are known as sols. These are named after dispersion medium. For example, when the dispersion medium is water, the system is called hydrosol or aquasol. When the dispersion medium is alcohol or benzene, the system is referred to as alcosol or benzosol.

(b) Gel: Colloids with a solid like appearance are termed as gels.

Depending on the interaction between the dispersed phase and dispersion medium, the colloids are divided into two types. They are

(i) Lyophilic or reversible colloids: When dispersed phase has a grater affinity for the dispersion medium, the colloids are termed as lyophilic or solvent loving colloids. Lyophilic colloidal systems are much stable and also known as reversible colloids, since on evaporating the dispersion medium colloidal residue can again be converted to colloidal state by addition of liquid. Example: Starch, protein and rubber.

(ii) Lyophobic or irreversible colloids: When the affinity between the dispersed phase and dispersion medium is less, the colloids are termed as lyophobic or solvent hating colloids. These systems are much less stable and are also known as irreversible colloids as the residue on evaporation cannot be readily converted into colloidal state by ordinary means. Example: Arsenic sulphide, ferric hydroxide and gold.

1.1.3. Properties of colloids

(a) Heterogeneous system: Colloidal systems, unlike true solutions, are heterogeneous in nature. They consist of two distinct phases namely dispersed phase and dispersion medium.

(b) Stability: Colloidal particles are highly stable. They tend to remain suspended in dispersion medium as long as it is destabilized by other means.

(c) Diffusibility: Colloidal particles don't readily pass through the membranes because of its large size.

(d) Colour: The colour of the colloidal suspension is very different from the colour of the substance in bulk form. The colour of the colloidal suspension depends on the size and shape of the particles.

(e) Visibility: It is not possible to view the colloidal particles with the help of powerful microscope. For example, gold sol appears to be a true solution of gold chloride in water. But the colloidal particles can be seen through a powerful ultra microscope.

(f) Surface area: The surface area of the particles in colloidal system is very high as compared to an equal mass of colloids in coarse grained size. Due to this large surface area, it shows the good adsorption capacity for contaminants.

(g) Light scattering: Colloidal particles when immersed in a fluid are able to scatter the light. This phenomenon is called Tyndall effect. The scattering pattern ie, the intensity of scattered light as a function of θ, the angle between incident and scattered light, depends on the size of the colloidal particles and on the wavelength of light.

Scattering occurs when an electromagnetic radiation interacts with the particle. If the reradiated light has the same frequency as the incident light the process is called elastic scattering. In case of inelastic scattering the incident light is degraded to thermal energy inside the particle with the less possibility of re radiation.

Light scattering theory can be categorized into two types. They are i) Rayeligh scattering ii) Mie scattering

(i) Rayleigh scattering

Rayleigh scattering is applicable to particle diameter, d< ~λ/20 and spherical particles. As the electromagnetic wave interacts with the particle, the electron orbits with in the constituents molecules of the particles are disturbed resulting in charge separation within the molecule called induced dipole moment whose magnitude is determined by the polarizability, α of the material. The oscillating induced dipole moment, according to Maxwell's theory radiate energy in all directions. This is called scattered light.

Rayleigh equation for the intensity of the scattered light (I) is

$$\frac{I}{I_0} = \frac{8\pi^4}{\lambda^4 r^2}\left(\frac{\alpha}{4\pi\varepsilon_0}\right)^2 (1 + \mathrm{Cos}^2\theta)$$

Where I_0 is the intensity of the incident light, I is the intensity of scattered light measured at distance r from the particle and α is the particle polarizability and θ is the angle between incident and scattered light.

Polarizability (α) can be written as

$$\alpha = 4\pi\varepsilon_0 . a^3(n^2 - 1)/(n^2 + 2)$$

Where n is the refractive index and a is the radius of the sphere.

So the total scattering can be shown by combining the above two equations as below

$$\frac{I_\theta}{I_0} = \frac{9\pi^2(n_1^2 - n_0^2)^2}{2\lambda^4 r^2 (n_1^2 + 2n_0^2)^2} v^2 N_p(1 + \cos^2\theta)$$

Where v is the particle volume and 1 and $\cos^2\theta$ refer to the vertically and horizontally polarized scattered light. This equation is dependence on the particle size, angle and wavelength. The intensity of scattered light increases directly with particle concentration and particle size.

(ii) Mie scattering

This theory has no size limitations and can be used for large particles ($d \sim \lambda$) also. Therefore Mie theory can be used for describing the scattering of light by spherical particles, which includes Rayleigh scattering.

(h) Electrical properties

(i) Electrophoresis

The movement of colloidal particles in electric field is known as electrophoresis. The colloidal solution is taken in a U-shaped tube and two platinum electrodes are dipped in. When the current is passed through the colloidal solution, the particles move to the oppositely charge electrode and on reaching the electrode the particles get discharged and settle down. The electrophoretic mobility is calculated by the equation given below.

$$Ue = \frac{\delta D}{4n\eta}$$

(ii) Electro osmosis

If a partition made by parchment paper or membranes between two electrodes, so that dispersion medium can pass through it excluding the colloidal particles. When the current is passed through the electrodes, then the dispersion medium would move in a direction opposite to the direction of movement of colloidal particles. This movement of dispersion medium with respect to the dispersed phase under the influence of an electric field is an electro-osmosis.

$$\xi = \frac{4\,\pi\eta K\,V}{D\,I}.(300)^2\,volts$$

Where V is the volume of liquid transported per second.

(iii) Streaming potential

The electro osmosis shows that when the dispersion medium is passed through a porous material, a potential difference is formed between the two sides. This process is called streaming potential.

(iv) Sedimentation potential

In this process, the sedimentation potential is setup when a colloidal particle is forced to move in a stable or resting liquid.

(v) Electrical Double layer

The colloidal particles present in the suspension possess the electrical double layer of opposite charge at the solid-liquid interface. This theory was first proposed by Helmholtz in 1879. Later Helmholtz theory was later modified by Guoy and Stern.

Helmholtz-Perrin theory

According to this theory, the electrical double layer is considered as a plate, one of which is connected directly to the suface of the colloid and the other is in a liquid phase. The distance between these two plates is very small. The structure of an electric double layer is given in Figure 1.2. The plus and minus sign denote the positive and negative ions of an electrical double layer. The electric potential decreases to low level as the distance X from solid surface increases.

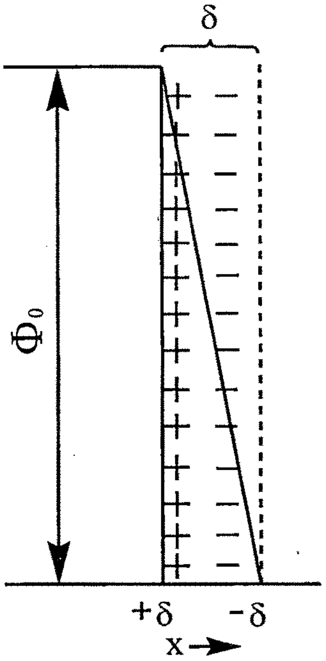


Figure 1.2. Electric double layer according to Helmholtz-Perrin

The value of the surface charge density (σ) is given by the formula

$$\sigma = \frac{\varepsilon}{4\pi\delta}\varphi_0$$

Where, σ = Dielectric constant of the medium that is present between the plates, φ_0 is the potential difference between the colloidal phase and the solution. In this theory the potential decreases as the distance X from the surface of the colloid increases. Helmholtz-Perrin theory postulates that the thickness of the double layer is very small.

Guoy-Chapman theory

This theory proposes the presence of electrical double layer with a diffuse counter ion layer. According to this theory, counter ions are not only present at the colloid surface and form a monoionic layer, but also present in the liquid phase at a certain distance away from the solid colloidal phase. The electric field of the colloidal phase attracts an oppositely charged ion towards it, and by thermal motion counter ions are present in the liquid phase. The structure of electric double layer according to Guoy and Chapman is given Figure 1.3.

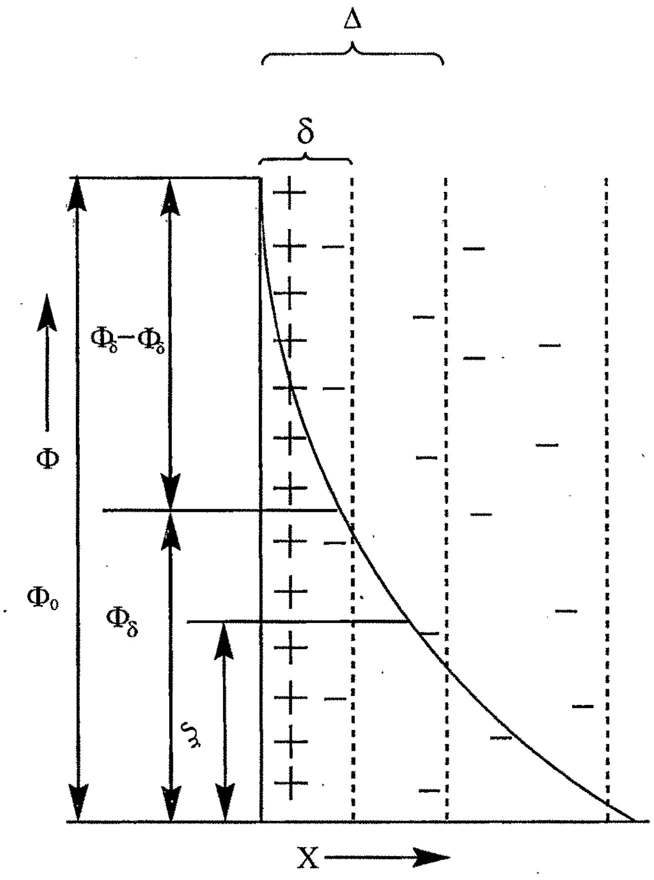


Figure 1.3. Electric double layer according to Guoy and Chapman

According to this theory, the intensity of electric field gradually decreases as the distance from the interface increases and counter ions of the double layer present in the liquid phase move farther away and get diminished. So the diffuse layer of counter ions near the surface of the colloid is formed. There exists repulsion between the ions of similar charge, present in the liquid and on the surface of the colloid and this electrostatic repulsion keeps the ions in solution.

Stern's theory

According to this theory, several layers of counter ions are attracted towards the solid phase by both electrostatic and adsorptive forces. The counter ion layer in which the potential falls sharply is called Stern layer or Helmholtz layer. The remaining counter ions form the diffuse layer. The electric double layer scheme proposed by Stern is given in Figure 1.4.

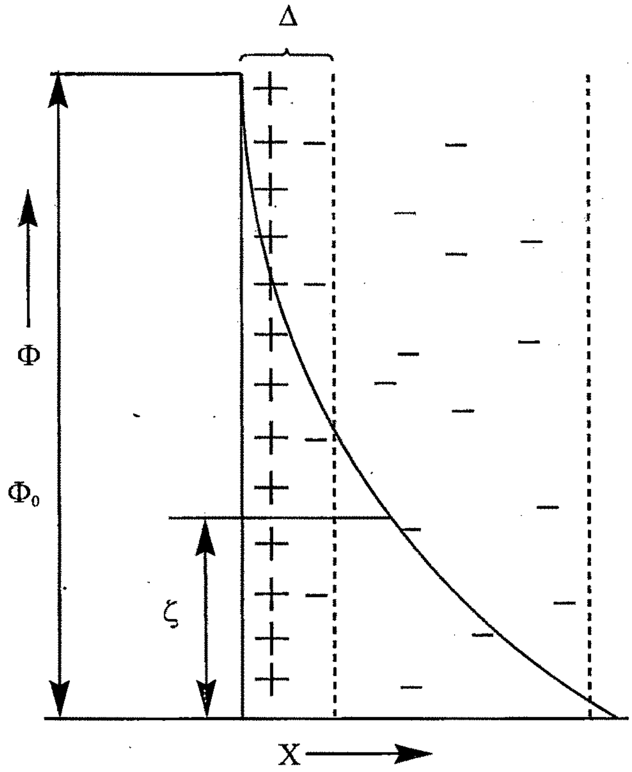


Figure 1.4. Electric double layer according to Stern and the potential drop in it

Addition of electrolytes into the colloidal suspensions results in the contraction of diffuse layer with counter ions attracted to the Stern layer. So the Zeta potential decreases to zero. According to this theory, valency of ions determines the thickness of the diffuse layer and the number of counter ions in the adsorption layer. If the valency of the counter ions is greater, the zeta potential decreases because of the thinner diffuse layer.

$$\xi = \frac{4\pi d e}{D}$$

Where D is the dielectric constant of the medium

According to modern views, a double layer of ions is formed at the interface of solid and liquid. One part of the layer is attached on the surface of the solid which is known as fixed layer, while the diffuse part is present in the liquid. While the fixed layer contains positive or negative ions, the diffuse layer consists of ions of both signs. But, the net charge of diffuse layer is equal and opposite to fixed layer. The illustration of this system is shown in Figure 1.5. Thus, the zeta potential develops because of the potential difference between oppositely charged layers.

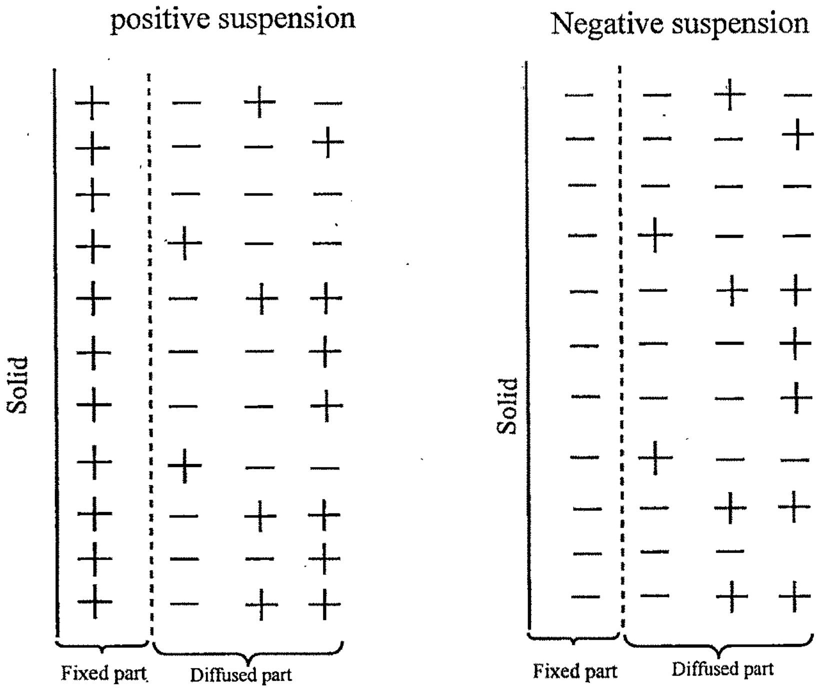


Figure 1.5. Electric double layer according to modern views.

1.2. Soils: The fundamentals

Soil is nothing but a weathered layer of earth crust and rocks which is having several living organisms and many decayed constituent products. Soils are classified based on the size of its constituents [3]. They are

Clay .... < 0.002 mm
Silt .... 0.05 – 0.002 mm
Medium sand...... 0.5 – 0.25 mm

This classification is very useful to determine the physical properties of soils such as permeability, water retention, aeration and base-exchange capacity among others. It is also useful to study the rate of siltation of rivers and also for determining the suitability of soil materials for construction purposes.

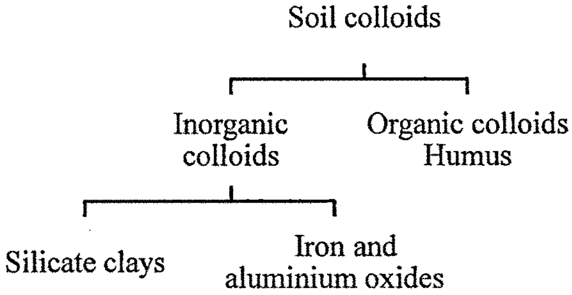
The soil constituents can be separated based on their size by techniques such as sieving, elutriation, centrifugation and sedimentation. Except the sieving method, the other three techniques are based on the constant fall velocity of particles in a suspension medium, which is influenced by the viscosity of the medium. The fall velocity of the sphere is given by Stoke's law

$$\mathbf{V = \frac{2}{9}\, g\, \frac{(d - d')}{n}\, r^2}$$

Where 'V' is the velocity of fall in cm/second, 'g' is the acceleration due to gravity, 'd' is density of particle in g/cc, 'd''is density of the fluid in g/cc, 'r' is the radius of the sphere in cm and 'n' is the absolute viscosity of the fluid in dynes-second/sq.cm.

1.2.1. Soil colloids

A variety of clay minerals, iron oxide, carbonate, silica, oxides and oxyhydroxides of Fe, Al, Mn exist as colloids in soils [4]. Soil colloids can be classified as given below:



1.2.2. Clay minerals

The inorganic fraction of soils and natural sediments consist almost entirely of silica and various silicates. The term clay is used in soil science to mean any material of particle size less than 2μm [5]. The term clay mineral refers to the specific group of silicate minerals constituents of the clay. The various clay minerals are:

Kaolinite: The term kaolin originates from the name of a Chinese hill where this product was extracted. Its structure is shown in Figure 1.6 and is a layer silicate with periodicity of stacking of 7.2 A°. The structural formula of kaolinite is

$$(OH)_4\ Al_2\ Si_2\ O_5$$

Mica: Mauguin [6] and Pauling [7] have determined the structure of micas, which consists of an octahedral sheet between two tetrahedral sheets. The Si occupies the three out of every four of the tetrahedra and the fourth one occupied by Al in tetrahedral sheet. This results in a deficit of charge for that sheet, which is filled by large ions, generally K, which occur between unit layers and increases the bond strength. The basal spacing is about 10 A°.

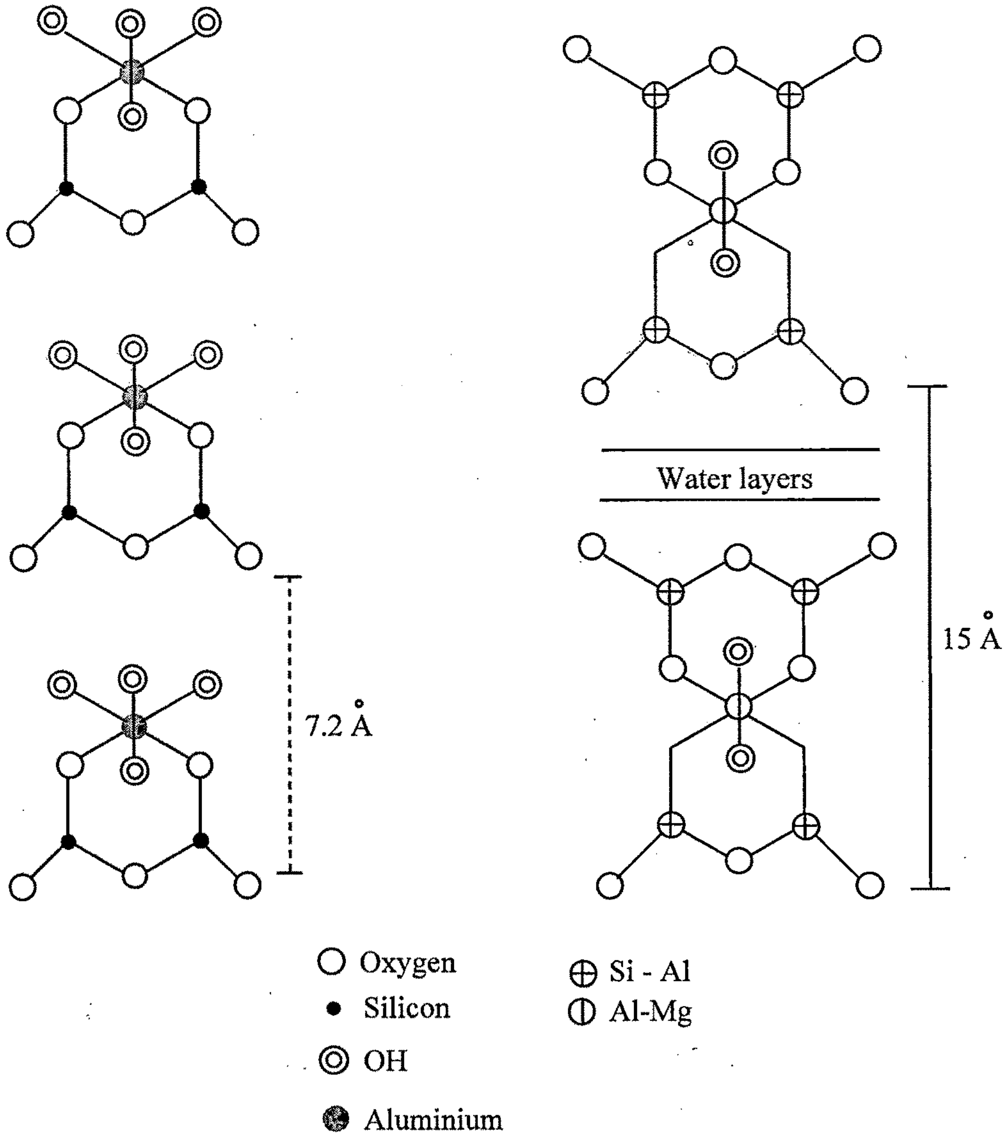


Figure 1.6. Schematic representation of the structure of the clay minerals

Montmorillonite: The montmorillonite minerals resemble mica, except the weak bond strength between the layers. Thus water molecules can enter between the unit layers, resulting in the change of stacking periodicity close to 14 A°. This property is called swelling of clays.

Iron oxides and Hydroxides: Iron and aluminium oxides and Hydroxides are present in all kinds of weathering products, in soils and in rocks rich in clay. Gaubert (1925) [8], Bohm (1928) and Goldsztaub (1935) have extensively studied about natural iron hydroxides and oxides using X-rays. Four mineral species of this group are: goethite (α FeOOH), lepidocrocite (γ FeOOH), hematite (α Fe_2O_3) and maghemite (γ Fe_2O_3).

1.2.3. Source of colloids

The number of materials for example, macromolecules of dissolved organic carbon such as humic materials, microorganisms, mineral precipitates from super saturated solution, silica, carbonates, oxides and oxyhydroxides of Fe, Al, Mn, biocolloids (including viruses, bacteria, protozoans) and weathering products exist as a colloidal particles in subsurface environments. The composition of colloidal particles is similar to that of the finest fraction of soils, but the proportions of different mineral components vary [4]. Field investigations have shown that the colloidal particles are composed of clay minerals, silica, iron and aluminium oxides & natural organic matter [9]. These colloidal particles usually occur as mixtures or aggregates in natural environmental system, which have different properties than the original components from which it comes. For example in surface soils, organic matter and clay material form complexes which have much higher stability than the corresponding clays without organic matter coatings [10, 11].

1.2.4. Precipitation of colloids

In subsurface environments, the pore water is either saturated or unsaturated with minerals of various types. Thus the possibility of precipitation never exists. However, anthropogenic activities such as ground water pumping and artificial recharge of aquifers lead to turbidity formation with changes in water chemistry. Such changes in water chemistry create the favorable conditions for the formation of precipitation. The precipitation of Fe^{3+} hydroxide colloids occurs, when the Fe^{2+} being present in dissolved form in anoxic aquifers moves into oxic aquifers. Such colloidal particles cause the increase in ground water turbidity in the aquifers [12].

1.2.5. Surface charge of colloids

The colloidal particles possess surface charge on it. The particles develop the charge by three major mechanisms. They are (a) Surface dissociation (b) Specific adsorption of ion from the solution (c) Crystal lattice defects

Crystal lattice defects are responsible for the charge observed on clay minerals in natural environments. These arise due to the isomorphic replacement of one ionic species by low ionic charge species [13]. Dissociation of ionizable surface groups gives the charge to mineral colloids. The dissociable groups are of the strong acid (Sulphate, $-O.SO_2.OH$; sulphonate, $-SO_2.OH$), weak acid (sulphite, $-O.SO.OH$; carboxyl, $-COOH$), weak base ($-NH_2$).

1.2.6. Electric charge and colloid stability

The free energy of lyophobic or irreversible colloidal systems is lowest, when the particles are condensed together into larger one [14]. Such systems can remain as individual particles only if some mechanism prevents aggregation during collision. There are two mechanisms by which this can be carried out

(a) Electrostatic stabilization: The particles can be given an electric charge (either positive or negative) and if the system contains particles of same charge they will repel each other when they come closer.

(b) Steric stabilization: Coating of some material (for example, polymer) on the surface of particles, prevents them approaching closer. This phenomenon is called steric stabilization.

1.2.7. Stability of colloids

For the colloidal particles to be transported over long distances, it must remain stable in soil solution ie without aggregation or adsorption of solid matrix, over long periods of time. Thus it is important that the conditions must be favorable for colloidal stability for transport to occur. The presence of natural organic matter coating on the surface of the colloids stabilizes it in soil pore water leads to it mobility [14, 15].

According to the DLVO (Derjaguin, Landau, Verwey and Overbeek) theory, the stability of colloidal particles in suspension is determined by van der Waals attractive forces that causes the particle aggregation and by electrostatic repulsive forces that keep the particles apart. Colloidal particles are stabilized because of the expansion of their double layers at low electrolyte concentration and ionic strength [16]. The attractive van der Waals forces are independent of changes in solution chemistry such as ionic strength and electrolyte concentration.

Total potential energy of interaction between surfaces is given by the equation

$$\mathbf{V_T = V_A + V_R}$$

Where V_A is van der Waals attraction given by the expression below

$$\mathbf{V_A = -\frac{A}{12\,\pi D^2}}$$

Where A is a constant and D is the distance between two surfaces.

The repulsive term due to the double layer interaction between identical surfaces is given by

$$\boldsymbol{V_R = \frac{64\, n^0 KTZ^2}{k} \exp(-kD)}$$

Where V_R is the van der Waals repulsion, D is the separation distance and Z is equal to tanh ($ze\psi_0/4kT$). The combination of these two equations forms the basis of the DLVO theory.

The double layer potential energy arises from the overlap of ions present in the diffuse double layer. The double layer potential energy depends on the variations in ionic strength of the solution, surface potential of the colloid and size of the colloidal particle. If the interacting particles are like charged, the potential energy will be repulsive (positive). If the particles interact with each other, the potential energy will be attractive (negative).

The potential energy diagram is shown in Figure 1.7

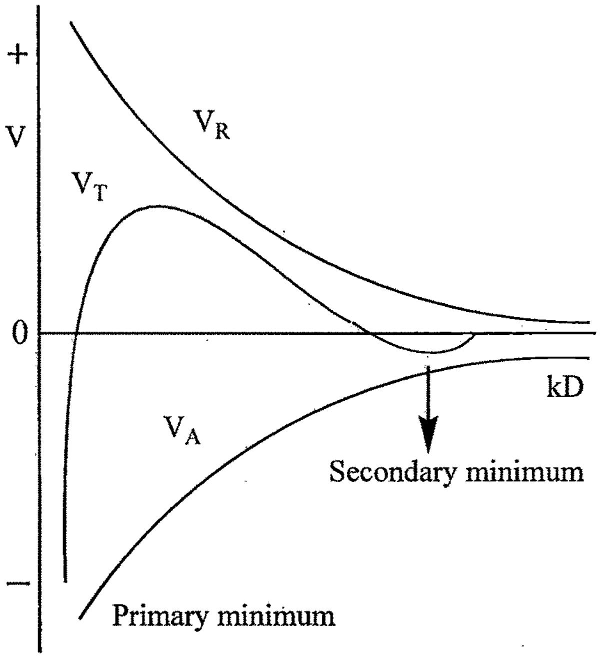


Figure 1.7. The total potential energy diagram

The van der Waals attraction dominates at both large and small separation distances. At small distances, V_A increases significantly, thus the primary minimum is observed. The secondary minimum occurs at large distances due to aggregation of colloidal particles.

1.3. The vadose zone

The vadose zone (approx. up to 100 m) is the zone that supports the life on earth and is also the zone that is least understood with very little data available on the characteristics of the soil and the dynamics of change of the subsurface. It is well known that man made activities such as use of pesticides, fertilizers, dumping of solid wastes and spillage of chemicals have caused extensive damage to the soil characteristics. These contaminants pass through the vadose zone, which is a sandwich region between the earth's surface and water table prior to entering ground water. Thus understanding the mechanisms responsible for the migration of contaminants through the vadose zone before their arrival to water table is crucial. It has been reported that the vadose zone is a significant source of colloids. These colloidal particles being smaller in size and having good adsorption capacity for the contaminants facilitate their transport to the aquifer.

1.3.1. Separation of colloids from sediments

The presence of colloidal particles in aquifers is due to the separation or mobilization of colloidal sized substances associated with sediments [17]. These are classified into two types.

(i) Detrital material: Inherited from original parent geologic material. Number of materials present as detrital materials which depends on the deposition of sediments and composition of the source sediments. Examples are layer silicates, iron and aluminium oxides

(ii) Authigenic material: Geo chemical transformation of primary minerals present in the aquifer.
The transformation of one form of mineral to other takes long period of time. Examples are Silica, alumino silicates, hydrous oxides of iron and aluminium
Earlier models of colloid transport conceptualize the vadose zone as two phase system in which contaminants partition between the immobile solid matrix and the mobile aqueous phase. But recently, it has been acknowledged that colloids in the solid phase act as a third phase and are known to be mobile in subsurface environments [18]. Thus, studying its adsorption on colloid and transport through the soil column could help in understanding its movement in natural aquifer system.

A number of studies have shown that colloidal particles are released from the soils as a result of changes in solution chemistry [19-23]. The mobilization and transport of colloids in natural porous media has been investigated for non-calcareous silt loam soil, sandy soil and aquifer sediments. The dispersion and release of colloidal particles in soils is favored by high pH, low ionic strength, low electrolyte concentration and high Na^+ saturation. The surface charge of the colloids is a function of solution pH and if the colloid and sediment matrix have the same charge, the electrostatic repulsion between them leads to the maximum colloid mobilization and maximum colloid stability. [24-28]. The effect of surfactants on the mobilization of colloids has been well documented [29]. In addition to the Na^+ content of the solution, the mobility of colloidal particles is controlled by the factors that influence the surface charge of colloids and immobile solid matrix [30].
The surface charge of the colloids is also influenced by the adsorption of high valent cations and oxyanions [31]. The pH at which charge of colloids becomes zero is

called point of zero charge (PZC). If the pH is high, the variable charge colloidal phase becomes negatively charged. If the pH of percolating solution is less than the point of zero charge of colloidal phase, the particles become positively charged [32]. There are several conditions by which colloids are released from the sediments. Dispersion of soil aggregates results in the release of colloidal particles which migrate in the downward direction [20]. The colloidal particles found in the subsurface are released from the surface of the solid porous matrix. It has been estimated that during the rainy season, concentration of these mobile colloidal particles ranges from less than 1 mg/L to a few hundred mg/L [33]. Some field observations suggest that mobilization of colloidal particles occurs by the dissolution of cementing agents such as iron oxide, carbonate and silica [4]. It has been reported that concentration of colloids released from sediment packed column exceed few hundred milligram per liter. Kaplan et al. [22] showed that effect of increasing rainfall intensity on the mobilization of colloids from undisturbed soil cores. They have drawn the conclusion that the shear stress on the macropore walls caused the greater mobilization of colloids from soil. There exist in literature a few experimental studies on the influence of rainfall intensities on the transport of colloidal particles [34, 35].

Colloidal particles are attached to larger particles or aggregated by cementing agents or electrostatic forces. Typical cementing agents that bind colloids to lager mineral grains are iron oxides, carbonates and silica. The dissolution of these cementing agents and destabilization of aggregates also leads to the release of colloids in the aquifers.

Mobilization of colloidal particles also occurs by the expansion of double layers around colloids and solid grains. At low ionic strength conditions and low electrolyte concentrations the expansion of this double layer occurs leading to the release of colloids from soil.

The mobilization of colloids occurs by the physical perturbation in soil system. An increase in flow velocity during pumping of ground water causes the colloid mobilization. Artificial recharge of ground water using bore holes leads to the hydrodynamic shear that mobilize the colloidal particles. The water flow in the vadose zone environments is often transient and occurs in response to rainfall and snow melt events. The flow transients cause the mobilization of colloids in high concentrations leading to the contaminant transport [36]. The particle advection, dispersion, and deposition are considered to be the primary mechanisms of colloids transport in natural porous media [37]. The transport of colloids in subsurface porous media and rock fractures are influenced by the size and morphology of colloidal particles, solution chemistry, ground water flow velocity etc [38].

1.3.2. Transport of colloids

The rapid transport of particles to greater depths depends on the structure of the soil, particularly on the presence of vertical continuous macropores in the soil layers [39,40]. Transport of suspended colloidal particles in soil have been reported in several experiments [41,42]. There are several studies which have described the transport of colloidal particles through the sediment packed columns [43-53]. Particle advection, dispersion and sorption are considered to be the mechanisms involved in solute transport in porous media. In addition to this, few factors such as detachment of colloids, sedimentation and sieving also influence the transport of colloids in porous media [54]. The transport of colloidal particles from the surface soil to the aquifer increases the risk of contaminant transport, thereby causing the water contamination. Thus, a quantification of transport of colloidal particles through soil assumes significance, for the estimation of leaching of contaminants [55].

Jacobsen et al. [51] have quantified the transport and mobilization of colloidal particles in undisturbed soil columns. It is reported that the total amount of colloidal particles mobilized from sediments at depth 2-22 cm is smaller than at depth 42-62 cm. The mass of the infiltrated colloids at the outflow is smaller at depth 2-22 cm than at depth 42-62 cm and the mass of colloids increases with increasing flow rate. M. Rousseau et al. [56] found that in undisturbed soil columns highest mobilization of colloidal particles was with deionized water and at highest infiltration rate. Similar studies are available on the mobilization of colloidal particles performed in undisturbed soil column [57,58] which essentially give similar observations.

The experiments involving the transport of insitu mobilized soil colloidal particles and latex colloids in packed soil columns has been reported by Grolimund et al. [44]. Nitrate has been used as a tracer in these transport experiments. They have concluded that the mobility of colloidal particles is much faster than the conservative tracer due to the size exclusion phenomena, thereby colloidal particles pass through small pores much easily in porous media. The effect of pore water velocity on particle velocity has been reported by these authors and the results showed that the colloidal particles travel about 1.45 faster than the tracer solute regardless of changes in pore water velocity.

The models describing the transport of colloids in columns have been developed by many researchers [59,60]. Lenhart and Saiers [61] developed the model that account for heterogeneity in the interaction energies and divides the colloid population into series of compartments. The authors have performed experiments on the transport of silica colloids in quartz packed sand column and results showed the increase of silica colloid release from column with reduction in NaCl concentrations. Gao et al. [46] have studied the mobilization of kaolinite colloids in sand columns and reported the slow or negligible colloid release under steady flow rate and increased colloid release at transient pore water flow. This suggests the influence of flow rate on the transport of colloids. The influence of flow transients on colloid mobilization in unsaturated media has been investigated in detail using mathematical model by Saiers and Lenhart [62] and Totsche et al. [63]. Grolimund et al. [64] reported the results of particle release from natural porous media saturated with monovalent cations. The release of colloidal particles is studied by preconditioning the soil column with high ionic strength solution followed by low ionic strength solution. In the leaching solutions, sodium was used as a major cation while varying the anionic components such as chloride, azide, malonate and phthalate.

The composition of pore water influences the release process with the decreasing salt concentration rate for particle release increases. The release of colloidal particles from soils and ground water aquifers by monovalent and divalent cations has also been studied in column experiments by Grolimund and Borkovec [65]. It was found that particle release is fastest when the medium is saturated with monovalent cations, but decreases while the solid matrix is saturated with divalent cations. They have also shown the increase in colloid release with decreasing ionic strength. The particle release rate decreased by a factor of two even with the saturation of solid matrix by 10% of calcium. The particle release from noncalcareous soil material has been studied up to 1000 pore volumes [52]. The experiments have been carried out at constant pH and in the presence of monovalent cation Na^+. Intially the soil column was preconditioned with a solution of high ionic strength, followed by low ionic strength solution under controlled pH conditions. This leads to the release of colloidal particles from soil material.

The mobility of the colloidal particles in natural porous media is also controlled by factors other than Na^+ saturation, which influence the surface charge of the colloids and the soil matrix. The pH of the solution would have influence on the surface properties of the solid matrix and colloids in oxide system [66].

1.3.3. Particle size

The influence of particle size on the transport of colloids in ground waters has been investigated thoroughly by various researchers [17]. Colloidal particles of few micron size are immobilized due to gravitational settling and straining by pores smaller than the size of colloids. Colloids of few tenths of a micrometer, are rapidly attracted towards the soil grains by van der Waals forces and become immobile. But colloids of intermediate size are considered to be highly mobile in subsurface environments, though the exact size range is not known for maximum mobility [67].

One of the possible mechanism of colloid release is shown in Figure 1.8. The circles represent amorphous iron oxyhydroxide and the plates represent clay minerals, like kaolinite. State 1a,b shows the bonds between amorphous iron oxyhydroxides and kaolinite. In States 2a, b squares represents an amorphous silica cement binding or encapsulating the clay mineral and iron oxyhydroxide constituents [68].

Chemical perturbations results in the mobilization of colloidal particles from sediments. This process occurs in several ways. (1) Dissolution of cementing agents that bind or encapsulates the colloidal fines on mineral grains (2a to 3, 2b to 4) (2) Breaking of bonds among cross bonded phases (1a to 3, 1b to 4) (3) Creation of like charge on exposed colloidal fines by alteration of surface charge of the variably charged constituents eg., iron and aluminium oxides and kaolinite edges through the change in pH of the solution (3 to 4) (4) Enhancement of electrostatic repulsion between like charged colloids by lowering ionic strength of the solution.

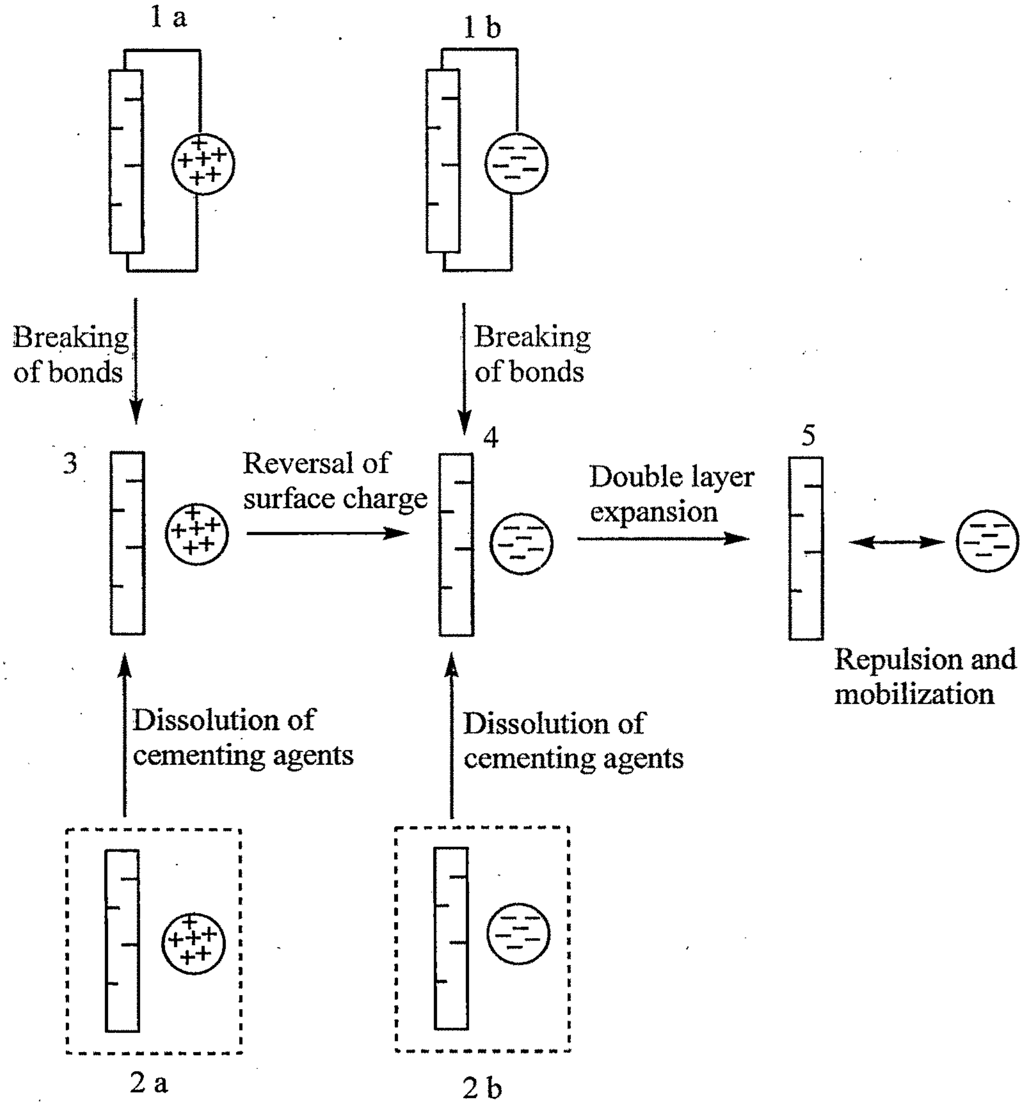


Figure 1.8. Schematic diagram of possible mechanism of colloid mobilization.

Ryan and Gschwend [69] suggested that under anoxic conditions, colloids were mobilized due to the dissolution of ferric oxyhydroxide coatings which cemented the colloidal particles to aquifer solids. However, laboratory results suggested that electrostatic interactions dominate the binding of clay colloids to large grain surfaces and dissolution of iron oxyhydroxide is unimportant to mobilize colloids from sediments [23].

Bunn et al. [48], have shown that for colloid release the pH_{pzc} of the influent solution should be higher than the pH_{pzc} of the ferric oxyhydroxide coatings that binds clay colloids to larger mineral grains. If the pH of the solution is less than the point of zero charge of ferric oxyhydroxide, it becomes positively charged and leads to the electrostatic attraction of negatively charged clay colloids. Ferric oxyhydroxide coatings become negatively charged if the pH of the solution exceeds their pH_{pzc}, resulting in electrostatic repulsion and subsequent release of colloids. These iron oxyhydroxides sometimes occurs as discrete goethite crystals in sediments.

1.3.4. Association of contaminant with colloids

The colloidal particles possess large surface area because of small size [70]. Colloidal particles can adsorb variety of contaminants such as hydrophobic organic and ionic contaminants, radionuclides etc. Inorganic mineral colloids in natural aquifer system adsorb radionuclides and toxic metals through ion exchange and surface complexation reactions [71].

The colloid-contaminant association must be strong enough for the contaminant transport to occur, as there is a possibility of desorption during their transport in soil pores. The species adsorbed on the colloids such as alkali earth cations and weak acid anions and hydroxides of Fe^{3+} and humic substances form surface complexes, leading to their greater stability.

1.3.5. Colloid associated contaminant transport

Ground water in many locations on earth is heavily polluted by man-made activities such as use of pesticides, dumping of chemical wastes, spillage of chemicals and discharge of industrial effluents into the water bodies. These pesticides and chemical wastes pass through the soil layers to the aquifers. The strongly sorbing contaminants have traditionally been regarded as immobile, but the idea of colloids being involved in contaminant transport gave rise to the three-phase model of contaminant transport i.e. mobile liquid phase, mobile colloidal phase and the immobile solid phase highlighting the role of colloids on contaminant transport in natural subsurface environments.

For the colloid-facilitated transport to occur colloids must be generated initially and be present in higher concentrations. The colloidal particles then should adsorb the contaminants strongly without desorption. After the adsorption of contaminants it should move through the soil layers to the aquifer. The schematic representation of contaminant transport is given in Figure 1.9.

The variety of contaminants is adsorbed strongly on the colloids and they can be classified into two broad types. 1) Organic contaminants 2) Inorganic contaminants

1.3.6. Inorganic contaminants

Radionuclide elements such as Cs, Pu and Am are considered to be susceptible to colloid facilitated transport in the subsurface environments [72]. These radionuclides are adsorbed strongly on the colloids by various mechanisms. Sorption of Cs on the phyllosilicate minerals is high than other minerals. For example, it is sorbed strongly on expansible layer silicates such as smectite, vermiculite and nonexpansible micas such as biotite and muscovite [73,74]. But the Cs sorption onto quartz, calcite is low due to their low ion exchange capacity [75]. Cs is adsorbed on the colloids by ion exchange process. The experimental investigations involving the transport of Cesium (Cs) by colloids in sediment packed column has been reported by Zhuang et al. [76]. The authors have used synthesized colloids for the transport studies and demonstrated the participation of colloids on the transport of Cs radionuclide in the column. Several field studies have also reported the colloid facilitated transport of radionuclides in the subsurface system. Few studies have been carried out on the transport of Cs in the presence and absence of colloidal particles in laboratory level. Noell et al. [77] investigated the role of silica colloidal particles on Cs transport in glass bead packed columns. The role of inorganic colloids on the transport of radionuclides with a specific emphasis on bentonite colloids has been reviewed [78]. It has been reported that the bentonite colloids influences the transport of Am and Pu in laboratory column, proving the role of colloids on radionuclide transport.

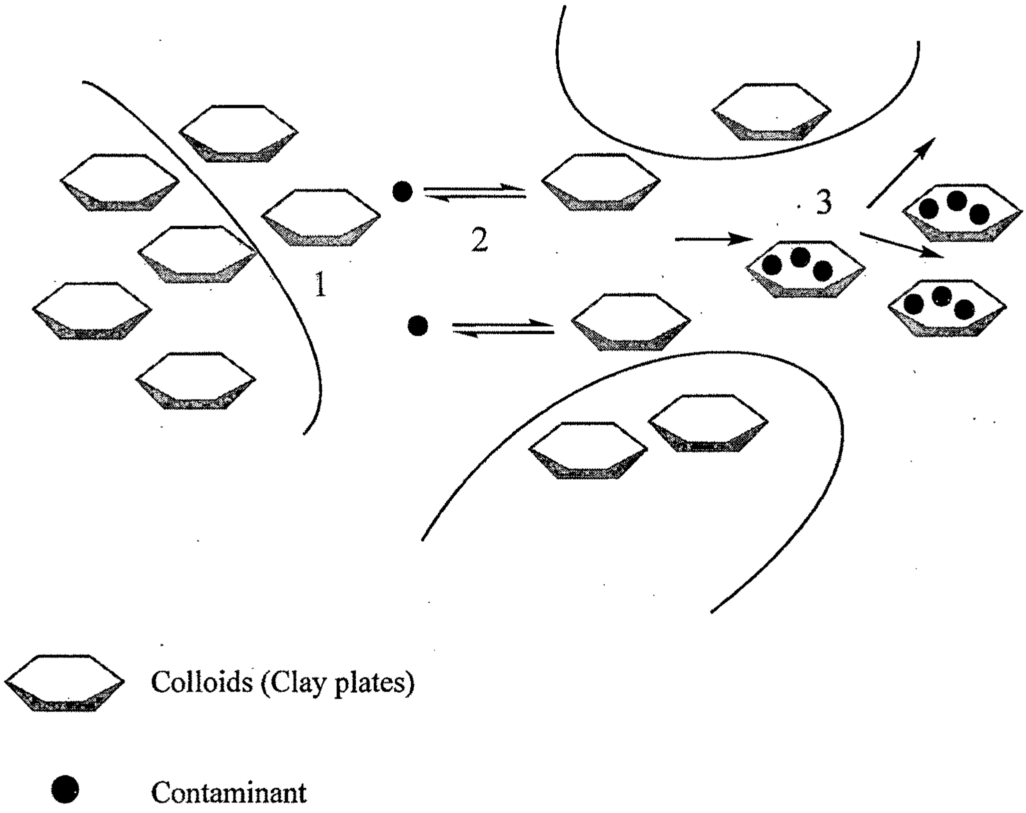


Figure 1.9. Three criteria for colloid facilitated contaminant transport (1) Colloid must be generated (2) Colloids must adsorb the contaminants (3) Transported through the porous media

Ions of transition metals as well as organic compounds are adsorbed strongly on the sediment matrix and thus considered to be immobile. But, when the colloidal particles are released from the contaminated sediment, the released colloids are also contaminated and carry it to longer depths and greater distances proving the role of colloids on contaminant transport [79]. When the monovalent cations saturated soil is infiltrated with the low ionic strength water, colloidal release occurs. The colloid release is due to the decrease in the salinity of water after the change in normality front. The colloid facilitated transport of Pb as a model contaminant has been investigated in laboratory column experiments with sodium and calcium as major cations. It has been shown that colloid release could be inhibited by infiltrating the sediment column with concentrated divalent cation, Ca^{2+} solution, thus preventing the contaminant transport [79].

The investigations into the ability of biosolid colloids on the transport of copper, lead and zinc performed in undisturbed soil monoliths, have demonstrated their role as a potential contaminant carrier and the risk of ground water contamination by dumped biosolid wastes. The enhanced mobility of colloids and contaminants with decreasing pH and colloid size and increased soil macroporosity has been well reported [80]. The role of colloids on the transport of Ni(II) and phenanthrene hydrophobic organic compound has been studied in sand packed columns with influent solutions of different pH and ionic strength [81]. The authors have also justified the selection of Ni(II) and phenanthrene, with the explanation of their strong sorption to organic matter and mineral surfaces. Puls and Powell [82] have studied the stability and transport of Fe_2O_3 colloids at different experimental parameters in terms of pH, ionic strength, particle concentration and size and concluded the stability of iron oxide colloids on its transport. They have also shown that the colloid associated arsenate travels 21 times faster than the dissolve arsenate, proving the implications of colloids on the transport of contaminants. Sen et al. [83] have conducted column experiments to investigate the mobilization of kaolin colloids and Ni(II) metal ion through the kaolin mixed sand bed.

A variety of experimental evidences are available on the adsorption of heavy metal ions onto the soil components. Some studies have demonstrated the transport of ionic and nonionic contaminants through soil columns by dissolved organic carbon and dissolved organic matter, among others. Sen et al. [84] have investigated the adsorption of Cu(II) and Ni(II) metal ions on iron oxide, kaolin and sand material. In this study they have proved that the adsorption of Cu(II) and Ni(II) occurs preferentially on the colloidal materials and adsorption is favored at high pH. Solution pH, ionic strength and complexation influences the sorption of adsorbate [85, 86].

Sen et al. (87) have noted that most of the three phase models that have been reported so far have assumed equilibrium interactions between the colloidal particles and the contaminant in the dissolved phase. These models predict a reduction of the effective retardation arising out of sorption onto the solid matrix depending on the concentration of the colloidal fines and the partition coefficient for contaminant sorption on the colloidal fines. These investigators developed a one-dimensional three phase transport model based on equilibrium adsorption of contaminant species and on colloidal induced release, migration and capture of colloidal fines. The overall contaminant balance on the solid matrix, aqueous phase, captured colloids and free colloids yields the expression

$$\frac{\partial \rho_m X_m}{\partial t} + \emptyset \frac{\partial C_c}{\partial t} + \emptyset \frac{\partial X_f C_f}{\partial t} + \frac{\partial \sigma_1 X_f}{\partial t} + \frac{\partial \sigma_2 X_f}{\partial t}$$
$$= \emptyset \mathrm{D_c} \frac{\partial^2 \mathrm{C_c}}{\partial \mathrm{x}^2} - \mathrm{q} \frac{\partial \mathrm{C_c}}{\partial \mathrm{x}} + \emptyset \mathrm{D} \frac{\partial^2 \mathrm{X_f C_f}}{\partial \mathrm{x}^2} - \mathrm{q} \frac{\partial \mathrm{X_f C_f}}{\partial \mathrm{x}}$$

Where, ρ_m is the bulk density of the solid matrix, X_m the mass fraction of contaminant on solid matrix, X_f the mass fraction of contaminant on colloids, C_c the contaminant concentration in aqueous phase (kg/m^3) and D_c is the dispersion coefficient for dissolved contaminant (m^2/s).

Presence of colloids has been shown to enhance or retard the extent of contamination depending critically on the system parameters such as concentration of suspended fines at the inlet (C_{f0}), initial concentration of fines on release sites (σ_{10}) and colloid release rate constant (α). The utility of the various models of contaminant transport is restricted due to the inability to get precise estimate of these parameters.

Surface coordination reaction is an important factor on the adsorption of cations and anions on the surfaces of colloids. This coordination is possible by the exchange of H^+ and OH^- by metal ions and anions respectively [88].

1.3.7. Organic contaminants

The soil organic matter content, biological activity influences the presence of organic contaminants in the subsurface environments. The transport of these organic contaminants becomes possible only if they adsorb strongly to colloids irrespective of their type. The experimental investigations involving the verical transport of DDT and paraquat pesticides in soil column have been conducted by Vinten et al [89]. The transport of 50 % of paraquat by Li- montmorillonite suspension to a depth of 12 cm has been reported in this study.

Batch experiments were conducted to study the sorption of pyrene to water-Dispersible colloids at two different concentrations of K^+ and Ca^{2+}. The sorption was found to be higher with K^+ than Ca^{2+}. The addition of Ca^{2+} condenses the humic substances, which reduce the sorption capacity because of non diffusion of pyrene into the interior of the soil organic matter [90]. It has been reported that colloids had high adsorption capacity for pyrene, than soil. In contrast to this effect, the sorption of pyrene increased with the addition of K^+ as it increases the available sorption sites on colloids.

Herbert et al. [91] have studied the interactions between pyrene and fractions of water soluble organic carbon, humic acid and fluvic acid. Nelson et al. [92] confirmed the ability of dissolved organic carbon on the adsorption properties of plutonium in natural waters. Hydrophobic organic compounds have been observed to migrate farther distances and its presence in the environment is based on their partitioning with colloidal particles in the natural environment. The experimental investigations into the transport of phenanthrene in porous media have been carried out with dissolved organic macromolecules (DOM) as colloids by Magee et al. [93]. The authors reported that DOM derived from soil itself increased the transport of phenanthrene in sand columns, proving the influence of DOM on the transport of contaminants. The transport of cadmium and nonionic contaminant (hexacholorobiphenyl) by dissolved organic carbon (DOC) in columns were investigated by Dunnivant et al. [94]. The contaminant mobility was found to be increased with increasing DOC concentration. Few researchers have attempted to study the transport of organic contaminants with polystyrene latex as model colloids through the porous media. The molecular weight of humic substances in the subsurface environments typically vary from $<10^4$ to $>10^5$. The low molecular weight components of dissolved organic carbon are considered to be highly mobile [95,96].

Only few field studies are available on the colloid facilitated transport of contaminants. Um and papelis have studied the transport of Pb(II) at the Nevada test site [97]. Schafer et al. [98] reported the transport of U, Th, Eu by natural colloids at the grimsel test site. Transport of U, Pu, Am and Sr at grimsel test site have been reported by Mori et al [78].

1.3.8. Heavy metal contamination

The environmental pollution and its impact on human beings and livestock is one among the much discussed topics today. An extensive industrialization and ever increasing urbanization has led to the environmental pollution worldwide. The untreated industrial effluents and sewage water are being discharged into the river causing the water pollution and sediment contamination [99,100]. These untreated sweage and industrial effluents are considered to be the major sources of heavy metals contamination of aqueous environment [101]. It is well known that the river sediments are the potential sources of contaminants in aquatic systems and hence widely used as a indicators of environmental pollution [102-104]. Of these, the heavy metals constitute the specific group of contaminants and deserve special attention as it is not degraded by natural processes [105]. Heavy metals in sediments occur in different geochemical forms which possess distinct mobility, toxicity and persistence and accumulative in nature [106,107]. Both natural and anthropogenic activities are responsible for the heavy metal contamination of river sediments. Runoff from river banks is the natural source contribution of heavy metals while the discharge of untreated industrial effluents, sewage from households, mining activities and fossil fuel burning are the anthropogenic sources of pollution [108,109].

The source of heavy metal contamination is given in Figure 1.10.

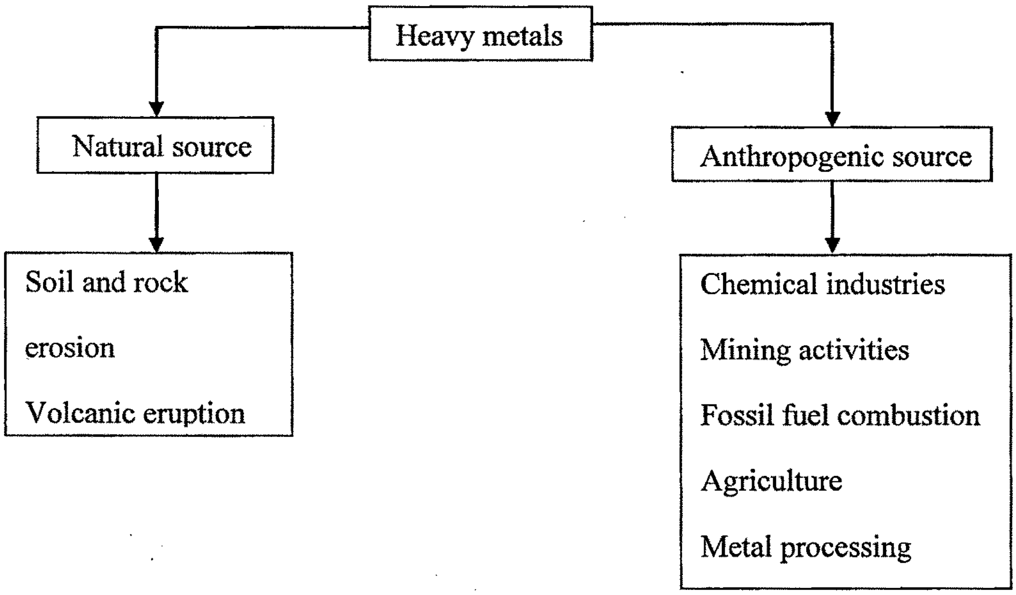


Figure 1.10. Source of heavy metal contamination

Many investigations dealing with the heavy metal contamination of sediments rely on total metal concentrations, but the comprehensive study on the speciation of heavy metals within different particle size classes of sediments would give an insight into the processes influencing the presence of heavy metals in sediments. Heavy metals, polycyclic aromatic hydrocarbons, radionuclides are partially of anthropogenic origin which are physorbed or chemisorbed on the finer fraction of the sediments [110]. These heavy metals are introduced into the environment as inorganic complexes or hydrated ions, which are adsorbed on the surface of the sediment particles through the weak physical and chemical bonds. The heavy metals present in the sediment may find their way to aquifer, thus posing a risk to aquatic life and ecosystems. The accumulation of heavy metals in sediments provides a record of the history of pollution [111]. These accumulated metals in sediments can also become mobile again under different environmental conditions and enter the food chain by means of benthos organisms.

About one third of the population in the world relies on the ground water for drinking and domestic purposes. Thus the presence of heavy metals in ground water needs to be well studied. The contamination of soil and water poses a risk to human health as it enters the food cycle by various means [112]. The presence of heavy metals in river sediments and ground water has been extensively studied across the globe [113-119]. Although number of studies involving the heavy metal contamination of sediments and water are available separately, comprehensive studies involving contamination of sediments, river surface water and ground water at different locations is less. Such investigations could lead to better understanding of source of heavy metal, its accumulative trend in sediments and finally its flow to the ground water.

Rapid industrialization and urbanization are responsible for the introduction of ionic contaminants in the environment. Metals exist in the soil as either free metal ions or in various soluble complexes with organic or inorganic ligands or associated with inorganic or organic colloids. Chromium and its compounds originate in the environment mainly from anthropogenic sources [120]. Chromium and its compounds are useful in common life and is widely used in electroplating, tanning and anodizing industries, ferrous and nonferrous alloys, in refractories and chemicals among others [121]. The most stable oxidation states of chromium in the environment are Cr(III) and Cr(VI), which are present in various forms in soil and aquifer system [122]. Of these Cr(III) is not transported over great distances because of its low solubility and is an important bioelement and plays an exceptional role in metabolic processes. Hexavalent chromium is of particular concern because of its toxicity, carcinogenicity and high mobility in soil and aquatic system [123]. Hexavalent chromium present in the soil is adsorbed mainly to mineral constituents.

1.3.9. Chemistry of chromium

Hexavalent chromium exists in solution as monomeric ions $H_2CrO_4^0$, $HCrO_4^-$ (bichromate) and CrO_4^{2-}(chromate) or as the dimeric ion $Cr_2O_7^{2-}$ (bichromate) [124,125]. The relative concentration of each of these depends on the pH and the total concentration of Cr(VI). At the pH>6.5, CrO_4^{2-} dominates, while at the pH<6.5, $HCrO_4^-$ dominates when the Cr(VI) concentrations are <30mM [126].

Trivalent chromium exists as Cr^{3+} below pH 3.5. With increase in pH, hydrolysis of Cr^{3+} gives more thermodynamically stable form such as $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3^0$ and $Cr(OH)^{4-}$ and as precipitates such as $Cr(OH)_3$ and $Fe,Cr(OH)_3$ at pH ranges found in the environment. The solution becomes green at higher concentrations of Cr(III) [127].

Toxicity of Hexavalent Chromium

It has been reported that Prolonged exposure to Cr(VI) compounds leads to variety of health related problems. Inhalation and continous expsosure to skin of Cr(VI) causes asthma and skin related diseases and cancer.

Reduction of Cr(VI)

Cr(VI) is a strong oxidant and is reduced in the presence of aqueous Fe(II), reduced sulfur, ferrous iron minerals and soil organic matter [126]. Minerals that contain significant amount of ferrous iron such as Pyrite (FeS_2), Biotite (black mica) and magnetite (Fe_3O_4) among others reduce the hexavalent chromium in the natural environments. It has been reported that photo reduction is another possible pathway of Cr(VI) reduction.

Bichromate reduction in the presence of soil organic matter is as follows

$$2Cr_2O_7^{2-} + 3C + 16\,H^+ \longrightarrow 4\,Cr^{3+} + 3CO_2 + 8H_2O$$

The reduction of Cr(VI) by ferrous iron is given below

$$HCrO_4^- + Fe^{2+} + 7H^+ \longrightarrow Cr^{3+} + Fe^{3+} + 4\ H_2O$$

Oxidation of Cr(III)

In natural environments, Cr(III) is oxidized to Cr(VI) by manganese dioxide present in soil [130]. The dissolved oxygen plays a minor role in the oxidation Cr(III) in natural conditions. But this transformation of Cr(III) to Cr(VI) requires longer time.

$$CrOH^{2+} + 1.5\ MnO_2 \longrightarrow HCrO_4^- + 1.5\ Mn^{2+}$$

1.4. Organic colloids

Organic matter in soils can be divided into humic and non humic substances [129]. Humic substances are brown to black polyelectrolytes, formed through plant degradation by biological and chemical processes [130] Non humic substances are organic compounds like carbohydrates, protein, waxes etc. Humic acids are divided into three fractions, on the basis of their aqueous solubility 1) Humic acid fraction (soluble at pH $\geq$ 6.0) 2) Fulvic acid fraction (soluble at all pHs) and 3) Humin (insoluble at all pHs) [131].

Earlier studies described that the humic substances comprised of randomly coiled macromolecules and had elongated shapes in basic or low ionic strength solutions, but at acidic or high ionic strength conditions, it had coil shape [131]. According to new studies of humic substances that suggest that, many small and chemically different organic molecules are connected by hydrogen bonding and hydrophobic interactions [132,133].

It has been well observed that the humic substances are capable of binding the organic contaminants, heavy metals, metal ions [134-139] and subsequent transport through natural aquifers to the ground water. The molecular weight, size, elemental composition of humic substances varies depending on the origin. It has variety of functional groups in their structure like carboxylic, phenolic hydroxy, ether, quinone, hydroxyquinone etc. Although it possess variety of functional groups in their structure carboxylic groups are responsible for the binding of metal ions in the natural aquifer. Humic materials possess higher cation exchange capacity and water holding capacity.

Water solubility of organic contaminants are the most important physical properties for the transport of these to natural aquifers. A large number of studies are available on the water solubility enhancement and stability of organic contaminants and pesticides by dissolved or particulate natural organic matter [140]. Chin et al. [141] have studied the binding of pyrene to aqueous humic materials and commercial substances. They have found the strong correlation between the molecular weight and aromaticity of humic substances to pyrene binding coefficient. It has observed that the aliphaticity of humic materials plays the important role on the adsorption of polycyclic aromatic compounds [142]. Organic carbon in the humic fraction causes the enhanced sorption of organic contaminants [143].

Properties of humic acids depend on the intramolecular and intermolecular interactions between humic molecules [144]. A very few studies are available on the determination of particle size distribution of humic materials using Dynamic light scattering and Small angle neutron scattering. Humic acids and fluvic acids form fractal aggregates in aqueous solution. Humic substances have wide range of molecular weight from few thousand to few hundred thousands. Hirata [145] has studied the molecular weight distributions of humic acid and fluvic acid derived from marine sediments. A wide range of techniques have been used to measure the molecular weight distribution of humic acids and fluvic acids. High performance size exclusion chromatography has been used for the weight average and number average distribution of humic acids.

1.5. AIM OF THE THESIS

A number of studies have referred to the concept of mobile colloids acting as carriers of strongly adsorbing contaminants through vadose zone environment to aquifer. Studies on laboratory model column experiments have revealed the importance of physical and chemical factors on the mobilization and transport of commercially available colloids. So far, the transport of contaminants has been demonstrated with laboratory column studies with only few contaminants without much emphasize on adsorption. However, the available information about the mobilization and transport of natural colloids isolated from soil in soil column and the effect of chemical parameters such as ionic strength, pH, flow rate and adsorption is insufficient to predict the risk of colloid and colloid associated transport of contaminants.

Thus an attempt has been made in this study to investigate the physical and chemical properties of colloids such as size, shape, element content, electrical conductivity and adsorption. The size distribution and electrical conductivity of colloidal particles isolated from number of soil samples, collected at different depth intervals from type section of river would be determined. The studies on the adsorption of organic dyes such as alizarin red and methylene blue and metal ions such as Pb(II), Ni(II), Cu(II) and Cr (VI) on soil colloids would be presented. The amount of release of colloids from soil, packed in a column, with distilled water would be measured as it reflect the susceptibility of soil to release colloids in response to water flow. The uniform water flow rate would be maintained throughout the colloid release experiments.

This study also seeks to investigate the effect of changes in solution chemistry such as ionic strength and pH on the transport of alizarin red in soil packed laboratory column. To mimic the transport of contaminants in natural environments, when the contaminants being spilled, the transport of chromium in mixed bed of different length scales would be conducted and the changes in breakthrough curve would be studied. The mass balance of transport experiments would be calculated as it gives information on the mass of contaminant in the outlet and mass remained inside the column.

The presence of heavy metals in river sediments and ground water has been extensively studied across the globe. Although number of studies involving the heavy metal contamination of sediments and water are available separately, comprehensive studies involving contamination of sediments, river surface water and ground water at different locations is less. Such investigations could lead to better understanding of source of heavy metal, its accumulative trend in sediments and finally its flow to the ground water. The main objective of this work is to study the influence of anthropogenic activities on the heavy metals in river sediments, river water samples and ground water collected from nearby wells along the river.

The investigations into the removal of alizarin red and methylene blue dyes and Cr(VI) from aqueous solution would be carried out with humic acid isolated from soil, as an adsorbent.